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Membrane Hydrophilization: Towards Low Fouling Polymeric Membranes

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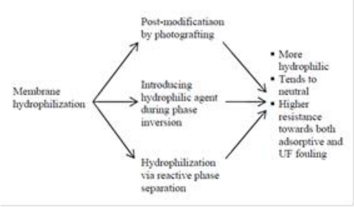
Graphical abstract



Abstract

In this work, hydrophilization strategies to manufacture low fouling membranes, which include (i) post-modification performed by photo-graft copolymerization of hydrophilic monomers onto a commercial polyethersulfone (PES) UF membrane, (ii) hydrophilization via blend polymer membrane with hydrophilic additive during phase separation (NIPS) and (iii) reactive PS method performed by UV-irradiating the proto-membrane before coagulation, are presented. The results suggest that all hydrophilization methods resulted in membranes having lower contact angles indicating more hydrophilic. Furthermore, the membranes demonstrated higher resistances towards adsorptive and ultrafiltration fouling. Consequently, higher permeate fluxes were resulted from hydrophilized membranes than without hydrophilization.

Keywords: Hydrophilization; low fouling membranes; ultrafiltration; microfiltration; fouling

■1.0 INTRODUCTION

Membrane processes using porous polymeric membrane (ultrafiltration (UF) and microfiltration (MF)) have become promising separation process in a wide range of applications including water and wastewater treatments, dairy, biotechnological and pharmaceutical industries, food and beverage processing, and medical applications[1–4]. MF and UF have replaced not only the conventional separation techniques but they have also successfully been utilized to solve mass separation problems. Along with those increasing demands, concentration polarization and fouling – causing significant loss of performance with respect to flux and often selectivity – are still two severe problems during their applications. Concentration polarization can facilitate membrane fouling by altering interactions among solvent, solute and membrane. Eventually, fouling not only prevents a more widespread commercial applicability of UF and MF but also shorten the membrane life due to chemical cleaning.

Since fouling significantly worsens MF and UF membranes performance, efforts to overcome this problem have drawn more and more attention in the membrane research. Those efforts in principle include feed pretreatment, advanced membrane and module design manufacturing, and process condition optimization. In general, previous works can be summarized as follows: feed pretreatments and process conditions have been remarkably engineered to achieve better control of membrane fouling, but in most cases, the permeate fluxes are determined by the membrane itself.

As MF and UF are now well established technique for separation, they are supported by large scale production of membrane materials. Polymeric membranes prepared by non-solvent-induced phase separation (NIPS) are still dominating commercially available UF and MF membranes. Due to their mechanical strength, thermal and chemical stability as well as excellence film forming properties polyethersulfone (PES) is one of the most used polymers for the preparation of MF and UF membranes[5]. Nevertheless, the hydrophobicity of those materials can cause more severe fouling problem. High flux UF membranes made from polysulfone (PSf) or polyethersulfone (PES) are easily fouled by solute/macromolecules in the feed. Therefore, the preparation of low-fouling membranes is strongly needed.

Three different approaches including (i) membrane polymer modification (pre-modification), (ii) blending of the membrane polymer with a modifying agent (additive), and (iii) surface modification after membrane preparation (post-modification) have been proposed to modify the PS and PES MF/UF membranes[6]. Because the first approach can involve significant changes in composition of the casting or spinning solution, membrane structure formed during the phase separation and, consequently, membrane properties can be quite different from the unmodified reference material. An important example for polymer modification before membrane formation is sulfonation or carboxylation, e.g., of PSf or PES, to obtain a more hydrophilic ultrafiltration membrane from a very stable membrane polymer[7]. In this paper, preparation of low fouling porous polymeric membranes via membrane surface modification and modified of phase separation are described.

■2.0 EXPERIMENTAL

2.1 Materials

Commercial PES UF membrane with a nominal molecular weight cut-off (NMWCO) of 50 kg/mol obtained from Mycrodyn-Nadir, Germany, was used as the base membrane for modification. In addition, a PES membrane from Microdyn-Nadir with NMWCO of 10 kg/mol (P010F) was also used for performance comparison. Poly(ethylene glycol) methacrylate (PEGMA 400, the number indicating PEG molar mass in g/mol) from Polysciences Inc., Warrington, USA was used as the hydrophilic monomer. Myoglobin from horse skeletal muscle (95-100% purity), was purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. Commercial PES (Ultrason E 6020 P) donated by BASF (Ludwigshafen, Germany) was used and dried at 120 ^{o}C for at least 4 h before use. N-methyl-2-pyrrolidone (NMP) was purchased from Merck (Hohenbrunn, Germany). Polyvinylpyrrolidone (PVP) (MW ~10.000 g/mol) was purchased from Serva Feinbiochemica GmbH&Co (Heidelberg, Germany). Polyethylene glycol (PEG) (MW ~ 10000 g/mol), potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$) were purchased from Fluka Chemie AG (Buchs, Germany). Pluronic F127 (Plu) (MW ~ 12600 g/mol) was purchased from BASF (Mount Olive, NJ, US). Bovine serum albumin (BSA) was purchased from ICN Biomedicals, Inc. (California, US). Triethylenglycol (TEG), PEG 100 and PEG 200 (the number indicating molar mass in kg/mol) were purchased from Arcos (Geel, Belgium). Polyethylene glycols (PEG 1.5, PEG 6, PEG 10 and PEG 35) were from Fluka Chemica GmbH. Myoglobin solution (in phosphate buffer pH 7) was pre-filtered through a 0.45 μm microfilter (Sartorius, Germany) to remove undissolved material. Potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$) were purchased from Fluka Chemie AG (Buchs, Germany).

2.2 Method

2.2.1 Membrane Modification

The method and experimental set-up used for modification have already been described in detail[8,9]. Briefly, a UVA Print system (Hoenle AG, Gräfelfing, Germany) equipped with a high–pressure mercury lamp, emitting wavelengths >300 nm and providing homogenous illumination of up to 100 cm^2 area with an intensity of 35 ± 5 mW/cm^2, was used. PES membrane samples were immersed into monomer solutions in a petri dish. A second smaller glass Petri dish was used to cover the membranes and also as another deep-UV filter. The samples were then subjected to UV irradiation for various time periods. Thereafter, the membranes were taken out, immediately rinsed with water and then washed with excess of water to remove any unreacted monomer or physically adsorbed polymer.

2.2.2 Membrane Preparation by Phase Separation

PES with certain concentration was dissolved in NMP with stirring until the homogenous solution was obtained. Different additive with similar molar mass (PVP, PEG or amphiphilic triblock copolymer Plu; 10 wt%) was added to the polymer solution. The relatively high concentration of additive was used to see significant effects on resulting membrane. Polymer solution without an additive was also prepared for control experiments. The homogenous polymer solution was left without stirring until no bubbles were. The polymer solution was cast with a thickness of 200 □m using a steel casting knife on a glass substrate. Thereafter, the proto-membrane was solidified in a coagulation bath containing water (20 ^{o}C ± 1) for 1 h. The resulting membranes were washed and soaked in the water for 24 h before drying. Detailed membrane preparation used can be found in previous publication[10].

In general, preparation MF membrane was similar with UF membranes and has been described in detailed[11]. Nevertheless, in MF membrane preparation, before immersing in coagulation bath, the proto membranes were subjected to humid air (RH = 50-60%) for 1 min. In addition, significant amount of a non-solvent triethylenglycol (TEG) was added into polymer solution. Polymer solution without an additive was also prepared for control experiments. It should be noted that ~0 in exposure means that no additional exposure time was applied, i.e., the substrate with the cast film was not passed through the humidifier box before it had been completely immersed in the coagulation bath.

2.2.3 Membrane Hydrophilization by Reactive Phase Separation

PES was dissolved in N-methyl-2-pyrrolidone, and polymeric additive was added to the polymer solution. The polymer solution was cast on a glass substrate and subjected to UV light (8 W, 366 nm) powered with 12 V AC, Switzerland. Thereby, it was expected that the hydrophilic polymer additive will covalently be attached to the membrane matrix polymer in a single process. Thereafter, the proto-membrane was solidified in a coagulation bath containing water for 1 h. The resulting membranes were washed and soaked in the water for at least 24 h before drying.

2.2.4 Performance Evaluation

Relative flux reduction and adsorptive fouling resistance (see Eqs. (1) and (2)) were used to evaluate the performance of modified membranes and then finally to select those which show a significantly better performance than the original membranes. Ultrafiltration experiments at a constant trans-membrane pressure were conducted using a solution model. The permeate flux profile over time of filtration was investigated. The UF performance was expressed in term of permeate flux to initial water flux ratio. It is defined that a fouling resistance value of 1 means that no adsorptive fouling occurs. The ideal functionalized membrane should have a high fouling resistance as well as a high hydraulic permeability.

$$\mathrm{RFR} = \frac{J_{am} - J_{ads}}{J_{am}} \qquad (1)$$

$$R_f = 1 - \mathrm{RFR} \qquad (2)$$

where J_{am} and J_{ads} are water flux of modified membrane before and after exposing to the protein solution test, respectively. In RFR calculation for unmodified membrane, initial water flux (J_o) was used instead of J_{am}.

■3.0 RESULTS AND DISCUSSION

3.1 Low Fouling UF Membranes by Photo-Graft Surface Modification

First of all, it is important to mention that all modified membranes presented in Figure 1 had lower lower contact angle than unmodified base membrane indicating more hydrophilic.

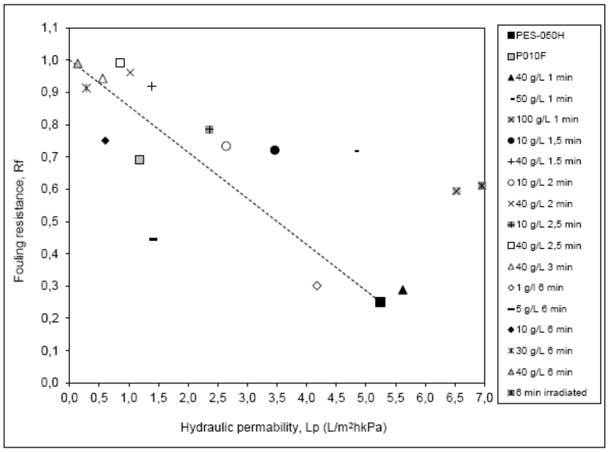


Figure 1 Hydraulic permeability–fouling resistance analysis of UV-irradiated and PEGMA–modified membranes. Membrane fouling resistance was evaluated using BSA (1 g/L, pH 7.2, 2.5 h exposure). PES-050H and P010F are 50 and 10 kg/mol unmodified membranes, respectively

Figure 1 suggests that all modified membranes display a trade-off relationship between fouling resistance and membrane permeability, i.e. membranes with higher fouling resistance had lower hydraulic permeability. Further, no membrane would fully meet this ideal criterion with respect to adsorptive protein fouling. However, when compared with a simple "trade-off curve" – assuming that the fouling resistance of the investigated PES UF membrane would approach a value of 1 if the flux would be reduced to zero (by reducing the pore size) –, the additional effects of the modification (e.g., by shielding the porous surface towards adsorption) may be separately discussed. It should be noted that the unmodified PES UF membrane with a lower cut–off (10 kg/mole) from the same company (and presumably the same manufacturing process) had indeed a higher fouling resistance at lower permeability as compared to the base membrane used for the modification, but the value was well below the simple "trade-off" curve. Membranes with medium fouling resistance (0.6–0.7) and high or moderate flux can be obtained from modification using UV irradiation of ≤ 1 min. Membranes with high fouling resistance (~1) and low (but potentially still acceptable) flux can be obtained from modification using medium UV irradiation times (1-3 min). Surprisingly, all membranes functionalized with long UV times (>3 min) had a performance below the "trade-off curve".

Modified membranes presented in Figure 1 with improved adsorptive fouling resistance were selected and compared with the unmodified membrane with respect to UF flux and observed protein rejection. As obviously seen in Table 1, a flux versus rejection "trade-off" was also observed during UF for the series of different membranes. Membranes with high flux yielded lower rejection and membranes with high rejection had lower flux. The unmodified base membrane (50 kg/mol) had a relatively high flux, but the lowest rejection and the lowest UF flux ratio (indicating that this membrane had the highest fouling tendency). With the exception of the modified membrane #1, all modified membranes yielded lower flux than the unmodified membrane (#0), and all membranes (#1–5) had higher rejection than the unmodified membrane. Furthermore, the rejection increased systematically with decreasing flux. Interestingly, all hydrophilized membranes also had higher UF flux ratio than unmodified base membranes. Nevertheless, only modified membranes prepared using UV irradiation time more than 1 min had higher flux ratio than 10 kg/mol unmodified membrane.

Table 1 Filtrate flux, solute rejection and flux ratio during ultrafiltration^{a} of modified membrane obtained from the first batch modification

No	Membrane	Flux (L/m^{2}h)^{b}	Rejection (%)	Flux ratio^{c}
#0	Unmodified 50 kg/mol	138	56	0.21
#1	100^{d} g/L, 1 min (~8^{f})	142	62	0.24
#2	50^{d} g/L, 1 min (~33^{f})	135	59	0.22
#3	40^{d} g/L, 1.5 min (~38^{f})	112	71	0.65
#4	40^{d} g/L, 3 min (~40^{f})	70	80	0.73
#5	40^{d} g/L, 6 min (~170^{f})	29	96	0.92
#6	Unmodified 10 kg/mol	58	91	0.52

^{a}Filtration was performed at a constant pressure of 100 kPa up to ~ 10 mL of permeate (from 60 mL of sample) was collected.
^{b}Permeate flux; ^{c}UF flux ratio is the ratio between filtrate flux and the initial water flux.
^{d}Monomer concentration used for modification, ^{f}Degree of grafting (μg/cm^2).

3.2 Low Fouling UF Membranes by Introducing Hydrophilic Agent during NIPS

The performance of three macromolecular additives (polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG) and poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (Pluronic®, Plu)) as modifier agent was compared. Adsorptive fouling experiments showed that all membranes prepared with the addition of hydrophilic agent show a better performance than the membrane prepared without hydrophilic agent (detailed data can be found in our previous publication[10]). Membrane prepared with addition of PEG showed the highest resistant towards adsorptive fouling. However, it should be kept in mind that adsorptive fouling is also influenced by the barrier pore size, and the highest flux reductions were found for matching pores and solute sizes[12] but considering that the pore size distributions were different but still in the same range, the hydrophobicity of PES seemed to have an additional impact on RFR. This suggests that blending of hydrophilic macromolecular additive with polymer membrane could indeed significantly increase the hydrophilicity of the resulting membrane. PES-PEG membrane showed the lowest RFR among the membranes prepared with an additive. This result can be explained by the highest hydrophilicity of this membrane (contact angle data are not presented).

Ultrafiltration experiments using BSA (0.1 g/L in phosphate buffer) demonstrated that the presence of hydrophilic macromolecular additive increased the normalized flux indicating higher resistance towards fouling (Figure 2). The membrane prepared without an additive had permeate flux of only ~30% relative to the initial water flux, whereas the PES-Plu membrane had the highest permeate flux (more than 70%). Of course, the highest initial flux of the membrane without an additive also contributed to the lowest normalized flux but the effect of hydrophilic modifier was quite clear. Interestingly, at the beginning of filtration PES-PEG membrane had higher normalized flux than PES-Plu membrane but further decrease with filtration time was more significant. The possible reason for this phenomenon would be the stability of the additive in the matrix polymer membrane. Rejection data show that the PES membrane prepared without an additive had the highest protein rejection while all membranes prepared with an additive showed similar protein rejection. In general, performance test showed that the membrane prepared with addition of Pluronic as modifier agent showed the best performance, i.e., the lowest flux decline and similar rejection could be obtained.

3.3 Low Fouling MF Membranes by Introducing Hydrophilic Agent in a Combination of VIPS and NIPS Method

Preparation of UF membranes using different additives (cf. Section 3.2) suggests that Pluronic should be selected as hydrophilic agent for manufacturing low fouling membranes. In this section Pluronic was used as modifier agent for preparing MF membranes. To obtain high flux, the membranes were prepared via a combination of VIPS (vapor induced phase separation) and NIPS (non-solvent induced phase separation) methods[11]. The membrane performance was investigated with respect to static adsorptive fouling and microfiltration. The amount of BSA bound to the membrane was determined by gravimetric method. The results are presented in Figure 3.

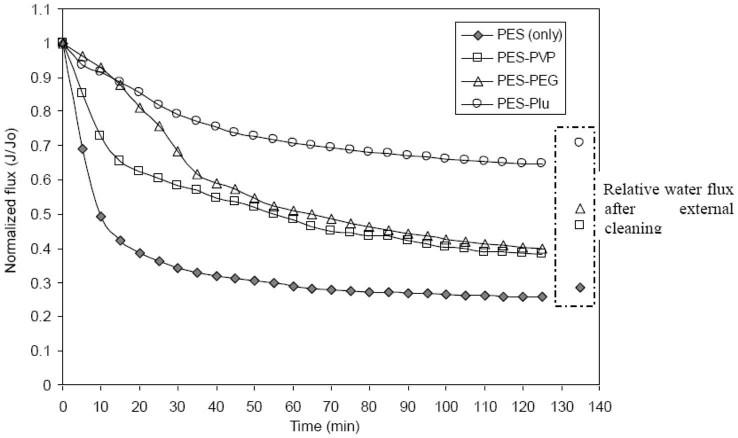


Figure 2 Normalized flux during ultrafiltration of BSA solutions (0.1 g/L in phosphate buffer pH 7) at a trans-membrane pressure of 300 kPa. Water fluxes after external cleaning with water, relative to initial water flux are also included

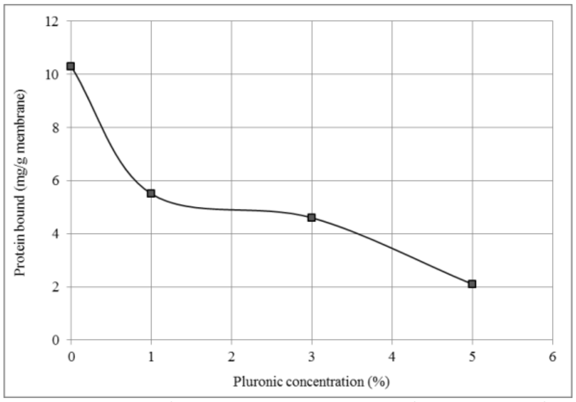


Figure 3 Amount of protein bound to the membranes (weight of protein relative to weight of membrane) after incubation in 1 g/l BSA solution (pH 5)

As expected, the addition of Pluronic decreased the amount of protein adsorbed by the membrane decreased with increasing Pluronic content. These results indicate that addition of Pluronic increases the membrane resistance towards adsorptive fouling. To investigate microfiltration performance, dead-end stirred filtration was performed with constant trans-membrane pressure (0.2 bar). The results are presented in terms of permeate flux relative to initial water flux (Figure 4). It is observed that all membranes showed similar behavior, i.e., permeate flux dropped rapidly in the beginning of filtration. Indeed, the presence of Pluronic additive increased the relative flux indicating that higher resistance towards fouling has been obtained. It is also clearly observed that as the Pluronic content was increased the permeate flux increased.

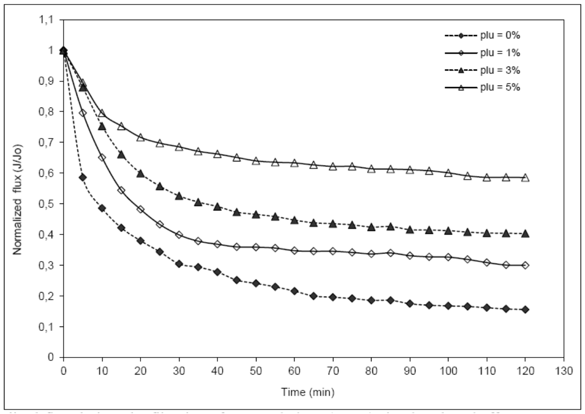


Figure 4 Normalized flux during ultrafiltration of BSA solutions (0.1 g/L in phosphate buffer 0.05 M, pH 5) at a trans-membrane pressure of 20 kPa.

3.4 Membrane Hydrophilization via Reactive Phase separation

In this work, to increase the stability of modifier agent (PVP) in membrane matrix, the proto-membrane after casting was exposed to the UV irradiation. In this method, membrane contact angle was decreased by both the addition of PVP and UV irradiation[13]. All membranes prepared with addition of PVP have lower contact angle than the membranes prepared without PVP. Further, for the membrane prepared with PVP, the effect of UV irradiation on membrane hydrophilization was also observed. As the UV irradiation was increased the membrane CA decreased (data not shown).

As also shown by modified membranes prepared in the previous sections, addition of hydrophilic agent (PVP) could increase the resistance towards adsorptive fouling using BSA. Furthermore, the UV irradiation increased the fouling resistance for both PES and PES-PVP membranes. Figure 5 shows that ultrafiltration membranes prepared with addition of hydrophilic modifier had higher resistance towards ultrafiltration fouling than without additive. Interestingly, PES-PVP membrane with UV irradiation had higher flux for long term application even though it had lower flux in the beginning of filtration. This results may indicate that the stability of PVP in membrane matrix is more stable.

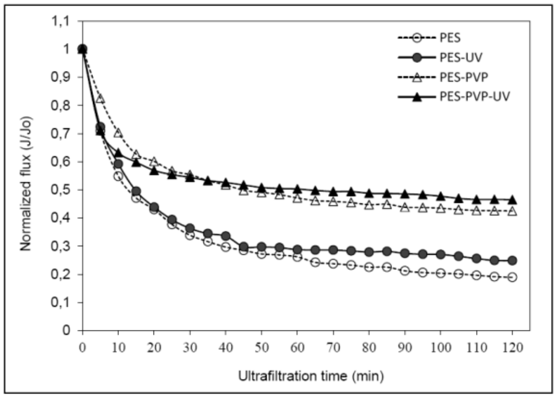


Figure 5 Normalized flux behavior during ultrafiltration of BSA solutions (0.1 g/L in phosphate buffer 0.05 M, pH 5) at a trans-membrane pressure of 300 kPa

■4.0 CONCLUSION

Three different approaches for preparing low fouling porous polymer membranes have been described. Highly protein-resistant thin-layer hydrogel composite membranes could be prepared by photograft copolymerization of neutral hydrophilic monomers (PEGMA and SPE) onto PES UF membranes. All composite membranes showed much higher adsorptive and ultrafiltration fouling resistances than the unmodified PES UF membrane. Second method for preparing low fouling porous polymer membrane is by engineering of phase separation methods. The performance of three macromolecular additive were compared. Performance evaluation via investigation of adsorptive fouling and ultrafiltration using BSA suggests that PES–PEG membrane showed the lowest RFR after static adsorption followed by PES–Plu. Ultrafiltration experiments demonstrated that the antifouling effects of PES–Plu were the most efficient at similar protein rejection: permeate flux during ultrafiltration using the PES–Plu was much higher than using the PES–PEG and the PES–PVP membranes, and more than 70% of the initial water flux could be recovered after UF just by external cleaning with water. This startegy has also been applied for the preparation of low fouling microfiltration membranes. Overall, performance test and stability study suggest that the membrane prepared with the addition of Pluronic as modifier agent showed the best performance as well as the best stability; therefore, it should be considered as additive in practical applications. The use of pluronic for preparing MF membranes showed the same effect, i.e. the fouling resistance of the polymer membrane could significantly be reduced. Integration of UV irradiation into phase separation method seems to be promising method to increase modification stability during hydrophilization using blending method.

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