Surface Modification of Polyethersulfone Hollow-Fiber Membranes by γ-Ray Irradiation†

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SYNOPSIS

The fouling of ultrafiltration membrane is often caused by gel formation on the membrane surface. This gel layer arises due to concentration polarization or macromolecular adsorption on the membrane surface. The gel layer affects both the hydraulic permeability and the rejection properties of the membrane. In this report, the adsorption of porcine albumin and the concentration polarization effect on modified and unmodified polyethersulfone (PES) hollow-fiber membrane is studied. PES ultrafiltration hollow-fiber membranes were modified by the grafting of polyethylene glycol (PEG) polymer on the internal surface using γ-ray irradiation method. The modified hollow fibers were less susceptible to fouling than were the unmodified fiber. The performance of both modified and unmodified hollow fibers was tested as a function of feed flow rates and protein concentrations. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Ultrafiltration of a protein-containing solution is limited by the fouling of the membrane surface and its pores, resulting in a gradual decline in permeate flux. This phenomenon is especially prominent with hydrophobic polysulfone membranes, and it has been shown to be directly related to the amount of protein adsorbed.[1-3] The membrane performance depends strongly on properties of feed solution, such as the nature and concentration of the protein and its interaction with the membrane material.

Hydrophilic membranes such as cellulose acetate, poly(vinyl alcohol), and polyacrylonitrile membranes have superior characteristics of less absorption of solutes and lower molecular weight cutoff compared to hydrophobic membranes. The hydrophilic membranes, however, do not usually have thermal stability and are susceptible to chemical and bacteriological agents, whereas the hydrophobic membranes, i.e., polysulfone and polyimide, have thermal stability and some chemical resistance.

Surface modification of hydrophobic membranes that introduce hydrophilic segments only on their surface may be a better idea to present both advantages of hydrophilic and hydrophobic membranes. The original characteristics of mechanical strength and thermal stability are retained, because only the surface is modified.[4,5] There are many routes for surface modification, and sulfonation is one of the most common surface reaction reagents. The degree of sulfonation can be controlled by the reaction time. Graft polymerization provides another method of surface modification and can give several functional groups.[6-10]

The grafting technique is commonly used to modify the properties of polymers. Most of the work done in this field has been in the textile, paper, and rubber industries. However, with the rapid development of membrane technology, a number of workers[11-14] have used the technique to modify the properties of the existing membranes or the polymer before casting into membranes.

We will discuss in this article the performance of both modified and unmodified hollow fibers in ultrafiltration of porcine albumin. We will also compare the experimental flux for different feed flow rates and feed concentrations.

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EXPERIMENTAL

Material

Polyethersulfone (PES) 200P and 600P, supplied by Imperial Chemical Industries, was used as a membrane material. Polyvinylpyrrolidone (PVP), supplied by Sigma Chemical Co., was used as an additive. *N*-Methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc), supplied by BDH, was used as the solvent. Poly(ethylene glycol)s (PEG) of different molecular weights supplied by A. G. Fluka were used as the reference solutes to test the performance of the hollow-fiber membranes. They were also used as monomers in the grafting process.

Porcine albumin was chosen for this study for the following reasons:

1. Most of the fouling studies have been done on other types of proteins (e.g., bovine serum albumin, ovalbumin, myoglobin, etc.). However, there is a lack of literature data on porcine albumin's fouling characteristics.
2. To evaluate the ultrafiltration process as an alternative process for isolation and purification of this protein fraction, which has gained a particular interest in several applications.

The porcine albumin sample solutions were initially supplied by Agriculture Canada, then by Sigma Chemical Co., and were used as feed solutions in fouling experiments.

Preparation of Hollow Fibers

Hollow fibers were made by the wet–dry spinning process. Liu et al.[15] described the spinning system in detail. Table I summarizes our spinning conditions. The hollow-fiber membranes spun under these conditions were inner-skinned hollow fibers. They were 0.70–1.10 mm in diameter. The average nominal molecular weight cutoff (MWCO) estimated from PEG retention tests ranged from 6000 to 12,000 Daltons.

Membrane Surface Modification

The hollow fibers were cut into desired lengths and immersed in water with nitrogen gas bubbling through for 16 h. An aqueous solution of PEG in a syringe was deoxygenated by passing N_2 gas through the solution. The deoxygenated polymer solution was injected into the bore side of the fiber against a stream of N_2 gas. The fibers were drawn into wet glass tubes sealed with a rubber stopper and placed in a gamma cell and irradiated at a rate of 0.7 Mrad/h for 0.5–2 h. After the γ-ray irradiation, the hollow fibers were flushed with distilled water to remove the excess of polymer solution.

A special code was given to each unmodified and modified hollow-fiber membrane to indicate the casting solution composition and grafting condition. For example, the code HF22 means unmodified hollow fibers spun from a 22 wt % polymer solution. The HF22-1-10K code means the same hollow fiber grafted with 10K PEG polymer for 1 h.

Table I Hollow Fiber Spinning Conditions

	Hollow Fiber Code		
	HF22	HF23	HF35
Composition of casting solution (wt %)			
Polyethersulfone (200P)	22	—	—
Polyethersulfone (600P)	—	23	25
Polyvinylpyrrolidone	8.8	—	—
N-Methyl-2-pyrrolidinone	—	77	75
N,N-Dimethylacetamide	69.2	—	—
Other spinning conditions			
Extrusion pressure (kPag)	17.2	27.6	68.9
Air gap (cm)	60	60	60
Internal bath composition (wt %)	100% water	20% NMP, 80% water	100% water
Internal bath flow (mL/s)	6.9	19.3	6.9
External water bath temperature (°C)	25	25	25

Ultrafiltration Experiments

Hollow fibers were tested in bundles of one to three fibers, each 28 cm long. Fibers were potted at both ends with epoxy resin and mounted in a test module. Figure 1 shows the testing system, which was a closed-loop circulation system. The operating pressure and the feed flow velocity were controlled, unless specified, at 137.9 kPa and 1.95 m/s, respectively. The feed solution was supplied to the bore side of the hollow fiber, and the permeate was collected from the shell side. The PEG solute concentration in the feed solution was kept at 200 ppm. The concentrations of the feed and permeate solutions were determined with a Shimadzu Total Carbon Analyzer Model TOC-5000. The solute separation, f, was calculated by the following equation:

$$f = \left\{ \frac{C_{\text{feed}} - C_{\text{permeate}}}{C_{\text{feed}}} \right\}$$

The pure water permeation rate (PWP) and the product rate (PR) for each solute were also obtained.

Adsorption Amount of Porcine Albumin

A 28 cm hollow fiber with epoxy resin at both ends was dried and weighed. The hollow fiber was mounted in a test module and 50 ppm porcine albumin solution was circulated through the bore side at a velocity of 1.95 m/s and at a pressure of 137.9 kPa for 1 h. It is assumed that a dynamic sorption equilibrium was attained during this period. The circulation of the solution was stopped and the solution was left in the hollow fiber for 1 h before the bore side of the hollow fiber was gently washed with distilled water to remove the unsorbed porcine albumin. The hollow fiber was then dried and weighed with an electric balance. The difference in weight before and after the adsorption experiment was recorded as the adsorbed amount.

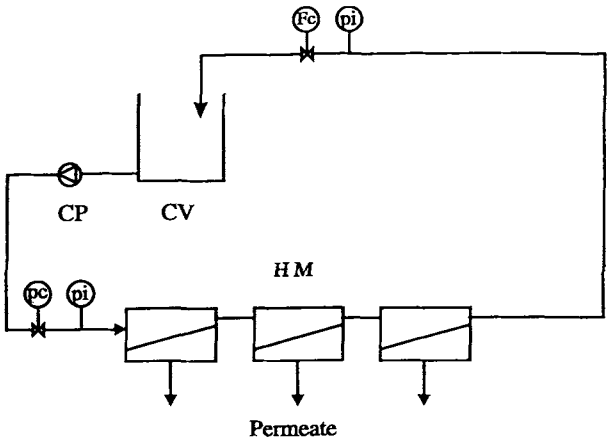

Figure 1 Flow diagram of experimental setup. CV: circulation vessel; CP: circulation pump; pc: pressure control valve; pi: pressure indicator; HM: hollow-fiber modules; Fc: flow control valve.

Fouling Experiments

Ultrafiltration experiments were carried out with both modified and unmodified hollow-fiber membranes using porcine albumin solution as feed. Three sets of experiments were conducted.

In the first set of experiments, a 50 ppm porcine albumin solution was used in the ultrafiltration experiment conducted at the feed flow rate of 1.95 m/s and at the operating pressure of 137.9 kPa for 3 h. The permeation rate was measured and recorded every half-hour. On the second day, the ultrafiltration experiment was resumed and continued under the same operating conditions as on the first day for 6 h. The permeation rate was measured every hour. On the third day, the porcine albumin concentration was changed from 50 to 500 ppm and the ultrafiltration experiment was conducted for 7 h. On the fourth day, the feed porcine albumin concentration was kept at 500 ppm and the system was operated for 4 h. After the ultrafiltration was terminated, the system was flushed with distilled water for 1 h to prevent protein decay in the system each day. At the end of the fourth day's experiment, ultrafiltration was carried out with a feed PEG 6000 solution of 200 ppm and pure water permeation rate (PWP), product rate (PR), and solute separation, f, were measured.

In the second set of experiments, hollow-fiber membranes were tested using 500 ppm porcine albumin solution as feed. The system was operated for 3.5 h on the first and second day of the ultrafiltration experiment and the permeation rate was recorded every half-hour. After the termination of the ultrafiltration experiment, the system was flushed with distilled water for 2 h each day. At the end of the second day's experiment, PWP, PR, and separation data of 200 ppm PEG 6000 were measured.

In the third set of experiments, hollow-fiber membranes were tested at a higher feed flow rate of 4.85 m/s to investigate the effect of the turbulence to the fouling resistance. Porcine albumin was used again as feed. On the first and second day, ultrafiltration was conducted using 50 ppm porcine albumin solution as feed for 2.5 h. On the third day, the feed porcine albumin concentration was changed from

50 to 100 ppm. The system was operated for 3 h at the same operating conditions as before. On the fourth day, the feed concentration was kept at 100 ppm and the system was operated for 5.5 h. On the fifth day, the feed porcine albumin concentration was changed from 100 to 500 ppm. The system was operated for 5 h. At the end of each day, the system was flushed with distilled water for 1 h to prevent protein decay in the system. At the end of the fifth day, the PWP, PR, and separation data were measured using PEG 6000 solution of 200 ppm. After each set of experiments, an enzyme solution (10 mL of trypsin dissolved in 4 L of pure water) was circulated over the membrane surface for 20 min, which was followed by a similar circulation of distilled water.

RESULTS AND DISCUSSION

Comparison of Adsorbed Amount of Porcine Albumin

Table II summarizes the results of the protein-adsorption experiments. The weight of hollow fibers increased after the adsorption experiment when the fibers were not modified by PEG grafting. When the fibers were modified, the weight of the fiber decreased after the adsorption experiment. This is probably because the drying of the hollow fiber before the adsorption experiment was not completed. The experimental results clearly indicate that the adsorption on the unmodified hollow fiber is much stronger than the adsorption on the modified one.

Surface Modification of the Hollow Fiber

Table III shows some of the performance data of modified and unmodified hollow-fiber membranes. HF23a and HF23b are results of experiments using different pieces of hollow fibers prepared under the same conditions. Results of HF22 and HF23 hollow fibers indicate that both the PWP and the solute separation decreased with grafting. The hollow fiber HF25, with the largest pore size (i.e., lowest solute separation) and the lowest porosity (i.e., lowest PWP) among the hollow fibers studied, showed a decrease in PWP but a significant increase in the PEG solute separation by grafting.

Table II Comparison of the Dry Weight of Modified and Unmodified Hollow Fibers Before and After Protein Adsorption

Membrane Sample	Dry Weight (g)
HF25 (before protein adsorption)	0.0306
HF25 (after protein adsorption)	0.0318
HF23 (before protein adsorption)	0.0319
HF23 (after protein adsorption)	0.0324
HF25-1-10K (before protein adsorption)	0.0340
HF25-1-10K (after protein adsorption)	0.0330

The results of the first set of ultrafiltration experiments are given in Figure 2. HF22 without grafting and HF23-100K-1 hollow fibers were compared. Note that PWP data of HF22 and HF23 hollow fibers are almost the same before grafting (see Table III). Therefore, any difference in product rate (PR) observed between the above two hollow fibers reflects the effect of the grafting and the presence of porcine albumin in the feed solution. The solute separation of porcine albumin was nearly equal to 100% for both hollow fibers. The permeation rate data of the HF22 hollow fiber without grafting is featured by the steep decline in the initial 3 h followed by a rather slow decline. On the third day when the albumin concentration in the feed was increased to 500 ppm, the permeation rate kept decreasing slowly.

The initial permeation rate for the grafted hollow fibers (HF23-100K-1) was significantly lower than that of HF22, probably due to the effect of irradiation. However, the permeation rate was extremely stable and after 2.5 h of operation the permeation rate of grafted hollow fibers became higher than that of hollow fibers without grafting. When the feed albumin concentration was increased to 500 ppm, the permeability of both HF22 and HF23-100K-1 hollow fibers became close to each other.

Apparently, the flux is decreased by γ-ray irradiation. Table IV indicates that the decrease in PWP was caused by the γ-ray irradiation alone, without grafting of the PEG polymer.

As described in the earlier part, there are three stages in the fouling of unmodified HF22 hollow fiber. The first one is a steep decline of the permeation rate in the very beginning of the ultrafiltration experiment. The second stage is a gradual decrease in the permeation rate that follows the initial steep decline. The third one is the continuation of decline that occurs when the albumin concentration is increased to 500 ppm. It is believed that the first stage is related to the albumin adsorption directly to the membrane surface. This adsorption equilibrium is attained very fast and an albumin monolayer formation is completed. During the second stage, a kinetic adsorption takes place, leading to the forma-

Table III Performance Data of Modified and Unmodified Hollow Fibers

Membrane Type	PWP (g/cm^2 h)	Solution Separation (%)		
		PEG-3000	PEG-6000	PEG-9000
HF22	6.64	90.08	97.75	98.72
HF25	1.02	9.37	21.25	74.38
HF23a	6.11	23.40	56.42	83.05
HF23b	6.34	19.37	57.09	80.38
HF22-1-10K	4.67	75.63	90.77	94.64
HF25-1-10K	0.40	54.82	64.29	96.32
HF23-1-10K	2.99	13.01	41.95	78.10
HF23-1-100K	3.63	14.00	35.42	76.54

tion of a multimolecular layer. This stage is much slower due to its kinetic nature and depends on the amount of adsorbed albumin in the first stage. The third step that occurs only when albumin concentration is increased to 500 ppm is related to the formation of a thick gel layer and its denaturation. Our adsorption experiment shows clearly that the grafting by γ-ray irradiation reduced the amount of adsorbed albumin significantly. This is reflected in the absence of an initial steep decline of the permeation rate for HF23-100K-1 modified hollow fiber. As well, the decline of the permeation rate in the second stage was suppressed since albumin adsorption was weak in the first stage. On the other hand, the gel formation in the third stage does not depend on the history of the formation of adsorption layer, and HF22, unmodified, and HF23-100K-1, modified, hollow fibers were fouled equally in the third stage. The above description of the fouling process is in accordance with that of Suki et al.[16]

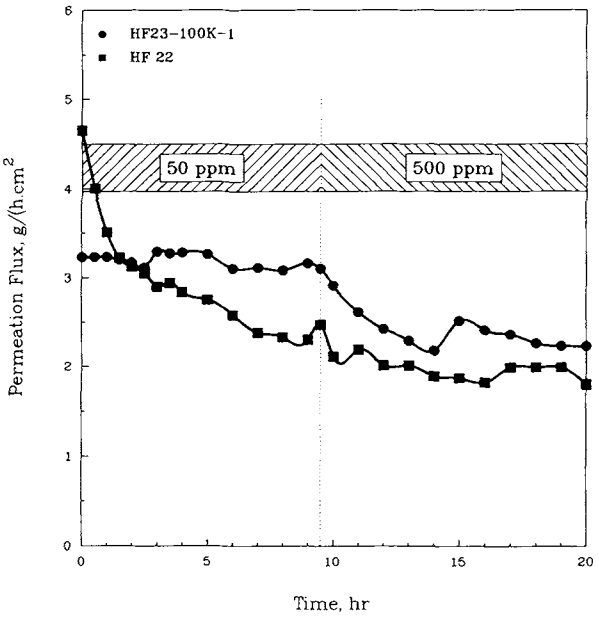

Figure 2 Permeation flux for modified hollow-fiber HF23-100K-1 and unmodified hollow-fiber HF22 during ultrafiltration of porcine albumin solution; ΔP = 137.9 kPa, U = 1.95 m/s.

Influence of Feed Flow Rate

Classically, in pressure-driven membrane processes, fouling is minimized by a tangential flow, which reduces concentration polarization and limits the thickness of the gel layer formed on the membrane surface. The amount of protein deposited on the membrane surface appears to be reduced less at higher feed flow rates, so that the higher the velocity, the more the protein deposited and the higher the permeation flux.

Figure 3 shows the permeation rate as a function of time for HF23 and HF23-100K-1 during ultrafiltration of the 50 ppm porcine albumin solution at different feed flow rates. It indicates also that the permeation rate of unmodified HF23 hollow-fiber membranes was maintained at a high level when the feed velocity was high, whereas the permeation rate decreased significantly when the feed velocity was low. In contrast, the permeation velocity of HF23-100K-1 showed practically no change over the entire

Table IV Influence of γ-Ray Irradiation on the Water Permeability of Hollow Fiber

Membrane Type	PWP (g/cm^2 h)[a]
HF23	5.90
HF23 (after irradiation)	3.87
HF23-1-10K	3.75

[a] Surface area = 16.17 cm^2; feed velocity = 1.95 m/s; feed pressure = 137.9 kPag.

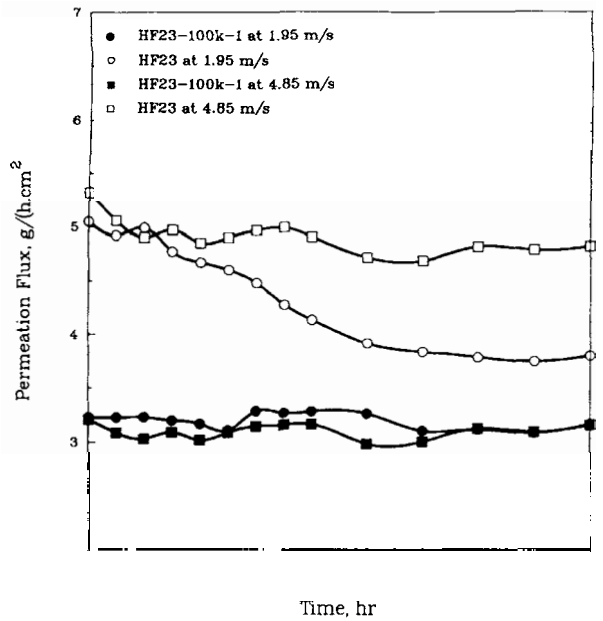

Figure 3 Permeation flux for modified HF23-100k-1 and unmodified HF23 during ultrafiltration of porcine albumin solution at different feed flow rates; C_0 = 50 ppm; ΔP = 137.9 kPa.

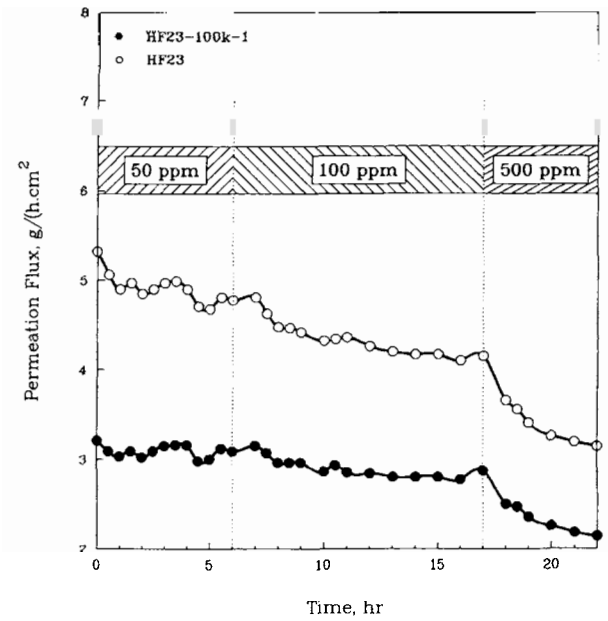

Figure 4 Effect of concentration on the flux for modified HF23-100k-1 and unmodified HF23 at steady state; ΔP = 137.9 kPa; U = 4.85 m/s.

period of the ultrafiltration experiment. This figure indicates also that the PEG surface treatment significantly reduced the albumin deposition onto the membrane surface. As a result, practically no fouling was observed after the modification of the membrane surface even when the feed velocity was low.

Influence of Porcine Albumin Concentration

Experimental data presented in Figure 4 have been obtained by successive increases from 50–500 ppm in the feed concentration. Ultrafiltration was continued until a steady state was reached, which was indicated by an achievement of a constant permeation rate. Then, the experiment was stopped and the whole ultrafiltration unit was flushed with water. Referring to Figure 4, the flushing was performed at 2.5, 6, 10, and 16 h, respectively, as it is noticed by small increase in the product permeation rate. The experimental data show that the pattern of the permeation rate decline was very similar with and without grafting. The data also indicate that the higher the feed concentration, the lower the permeation rate.

Figure 5 shows the PWP data measured at the end of the day after ultrafiltration of albumin solutions of 50 and 500 ppm. At the end of the day, hollow fibers were flushed with distilled water after the ultrafiltration experiment and the PWP was measured.

Figure 5 indicates that at feed velocity of 1.95 m/s the fouling of HF23 unmodified hollow fiber was

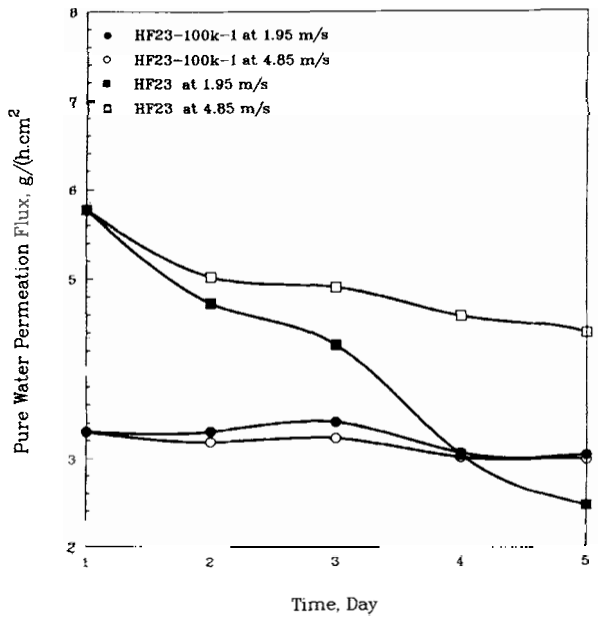

Figure 5 Comparison of PWP for modified HF23-100K-1 and unmodified HF23 after protein test; ΔP = 137.9 kPa; U = 1.95 m/s.

permanent, and after 5 days of ultrafiltration experiment, the PWP went down to about 50% of the initial value. In contrast, HF23-100K-1 showed practically no fouling, and at the end of the experiment, the PWP of HF23-100K-1 hollow fiber surpassed that of unmodified HF23 hollow fiber. Figure 5 also shows that at feed velocity of 4.85 m/s the fouling was reduced substantially for the unmodified HF23 hollow fiber. As a result, the PWP of HF23 hollow fiber was maintained higher than that of HF23-100K-1 hollow fiber. The data in Figures 3 and 5 show clearly that both feed velocity and the hollow-fiber grafting affect the degree of fouling.

CONCLUSIONS

1. The modification of the internal surface of PES hollow fiber decreases the adsorption of porcine albumin onto the hollow-fiber surface.
2. The surface modification decreases the fouling of hollow fibers that occurs during ultrafiltration of porcine albumin solutions. The effect of the surface modification is more obvious when the porcine albumin solution concentration is low.
3. The surface modification is more effective when the pore size of the porous PES membrane is larger.
4. The increase in the feed flow velocity decreases the fouling, particularly when the hollow-fiber surface is unmodified.

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