Surface Modification of Poly(ether sulfone) Ultrafiltration Membranes by Low-Temperature Plasma-Induced Graft Polymerization

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ABSTRACT: Low-temperature helium plasma treatment followed by grafting of *N*-vinyl-2-pyrrolidone (NVP) onto poly(ether sulfone) (PES) ultrafiltration (UF) membranes was used to modify commercial PES membranes. Helium plasma treatment alone and post-NVP grafting substantially increased the surface hydrophilicity compared with the unmodified virgin PES membranes. The degree of modification was adjusted by plasma treatment time and polymerization conditions (temperature, NVP concentration, and graft density). The NVP-grafted PES surfaces were characterized by Fourier transform infrared attenuated total reflection spectroscopy and electron spectroscopy for chemical analysis. Plasma treatment roughened the membrane as measured by atomic-force microscopy. Also, using a filtration protocol to simulate protein fouling and cleaning potential, the surface modified membranes were notably less susceptible to BSA fouling than the virgin PES membrane or a commercial low-protein binding PES membrane. In addition, the modified membranes were easier to clean and required little caustic to recover permeation flux. The absolute and relative permeation flux values were quite similar for the plasma-treated and NVP-grafted membranes and notably higher than the virgin membrane. The main difference being the expected long-term instability of the plasma treated as compared with the NVP-grafted membranes. These results provide a foundation for using low-temperature plasma-induced grafting on PES with a variety of other molecules, including other hydrophilic monomers besides NVP, charged or hydrophobic molecules, binding domains, and biologically active molecules such as enzymes and ribozymes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1699–1711, 1999

Key words: surface modification; polymeric ultrafiltration membranes; low temperature plasma; graft polymerization; poly(ether sulfone); protein fouling

INTRODUCTION

For conventional applications of ultrafiltration (UF), one persistent problem causing performance decline has been "membrane fouling." A well-known example of this phenomenon occurs during filtration of biological solutions where proteins deposit and adsorb onto and within the porous membrane.[1] To extend the potential of UF, much research has been done on new materials and membrane formation methods that have led to membranes with reduced fouling. In addition to new materials and structures, a less expensive approach is the development of surface modification techniques that transform the surface chemistry of current commercial polymer membranes without significantly affecting their bulk properties.

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Adsorption and permeation properties of porous membranes can be changed by the addition of polymeric layers onto their active surfaces.[2] Various investigations[2–4] have shown that adsorbed hydrophilic polymers on the membrane surface alleviates protein fouling during UF and microfiltration (MF). However, grafted polymer layers that are chemically bound to the surface are expected to provide a much more stable and long-lasting surface. Heterogeneous polymer grafting or graft polymerization could be attractive alternatives because they combine *in situ* layer formation and attachment.

Plasma-induced polymerization is one of the techniques that has been successfully used for modifying polymeric membrane surface chemistry.[5–9] Because plasma techniques (including deposition, grafting, and polymerization) are extremely surface selective, they have been used to create new surface chemistries to enhance the culturing of cells on surfaces and to modify protein and cell interactions, thereby enhancing the biocompatibility of the surfaces.[10,11] Simple treatment with an inert gas such as nitrogen or oxygen plasma, followed by exposure to air, can create peroxides that are suitable reactive sites for subsequent monomer grafting and polymerization. The capability of plasma to alter the physical and chemical properties of polymeric surfaces without affecting the bulk properties (especially mechanical properties) of the base material is advantageous for the design and development of surface-modified polymer membranes. Because modification by low-temperature plasma treatment is usually confined to the top several tens of nanometers, it is not expected to effect the bulk polymer properties.[12] With plasma treatment, specific surface chemistries can be created for reducing protein–surface attractive interactions, thereby minimizing protein adsorption and, hence, membrane fouling. An important limitation of plasma treatment is its temporal instability such as the gradual loss of surface chemical properties with time.[13] This has been explained by Langmuir[13] and Yasuda et al.[14] to be due to short-range surfaces forces and restructuring as a result of chain and polar group reorientation in the surface region. One method to reduce this loss of surface properties is to graft and polymerize monomers onto a plasma-treated film/membrane to attempt to "lock in" a desired surface chemistry. Although the grafted polymer could also reverse its orientation at the interface, the larger and more bulky these grafted molecules are, the more unlikely reorientation will occur.[16,17] Thus, an important reason for extending plasma treatment with post-grafting of monomers and subsequent polymerization is the possible reduction of surface restructuring. Both plasma treatment and polymerization conditions could then be used to adjust the degree of the modification.[7]

Variation of the membrane permeability by grafted polymer layers have been reported for polyacrylonitrile (PAN) and polysulfone (PSU) ultrafiltration membranes,[7] for straight-pore polycarbonate membranes,[18] and for poly(vinylidene fluoride) MF membranes.[19] In one of the few reports on plasma modification of UF membranes with asymmetric pore structure, monomers such as 2-hydroxy-ethyl-methacrylate (HEMA), acrylic acid, and methacrylic acid were grafted polymerized onto poly(acrylonitrile) and poly(sulfone) membranes after excitation with helium and helium/water plasma.[7] It was observed that the amount of grafted polymer influenced the water permeation rate. After static protein adsorption, the HEMA-grafted PAN membrane showed significantly reduced fouling and improved protein UF performance. However, a tradeoff between reduced fouling (from increased hydrophilicity) and reduced permeation rates (from pore narrowing) existed.

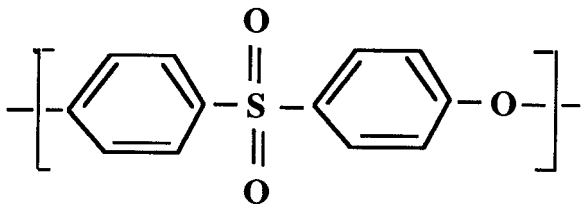
The goal of this study was to evaluate low-temperature helium plasma-induced grafting of *N*-vinyl-2-pyrrolidone (NVP) for modifying poly(ether sulfone) (PES) membranes under varying conditions. Specifically, we studied the modification of a 10-kDa commercial PES membrane using both plasma treatment and plasma-induced graft polymerization. Then, using a well-defined filtration protocol with DI water and protein solution, the membranes were characterized with respect to their disposition toward fouling and their "cleanability" by water flushing and caustic rinsing on both sides of the membrane. Poly(ether sulfone) UF membranes were chosen because they are widely used commercially, and little is known about their low-temperature plasma-induced modification properties. Their thermal stability and resistance to many organic solvents make them attractive for many applications. Like poly(sulfone), it is likely that the hydrophobic character of PES is related to the intensity of protein fouling, possibly due to protein adsorption, denaturation, and aggregation at the membrane–solution interface.[20] Because of the paucity of data, the chemical processes induced by low-temperature plasma excitation of PES are not known in detail. NVP was chosen because it is a well-known Lewis base (electron pair donor), and

hence, a hydrophilic monomer, and has been used commercially for years by membrane companies as a comonomer to impart flexibility and hydrophilicity.[21] After presenting the experimental methods, the membrane characterization and filtration results are discussed and summarized.

EXPERIMENTAL

Membranes

The PES ultrafiltration membranes used in this study were from Millipore Corp. (Lot No. 042897 AGC 2A). The chemical structure of PES is:



The nominal molecular weight cutoff of the membranes were 10 kDa, and the glass transition temperature, T_g, of the polymer was 230°C. Because drying can irreversibly damage the membranes' permeation fluxes, they were not dried before use.

Chemicals

Water was purified from tap water by reverse osmosis, UV irradiation, activated carbon treatment, and passed through a 0.1-μm pore-size membrane. The other solvents included ethanol (99.9%), and octane (99+%); the monomer NVP was purchased from Aldrich Chemical Co. (Milwaukee, WI). The inhibitor with NVP was removed by vacuum distillation before use. Sodium chloride and potassium chloride, purchased from Mallinckrodt Specialty Chemical Co. (Paris, Kentucky), were of analytical grade purity. Sodium phosphates, purchased from Sigma Chemical Co. (St. Louis, MO), were of reagent grade purity. Helium and nitrogen gas, received from Matheson Co. (Secaucus, NJ), were of ultrahigh purity.

Bovine Serum Albumin

Bovine serum albumin (BSA, initial fractionation by heat shock, purity > 98%, Lot #10H0262) was obtained from Sigma Chemical Co. (St. Louis, MO). Its isoelectric point was 4.9, and molecular weight was 66.5 kDa. All protein solutions were prepared in phosphate-buffered saline (PBS, see below) solution and filtered with a 0.22-μm Nylon filter before use.

Plasma

The plasma reactor and the helium plasma treatment procedures have been described in detail elsewhere.[6] Membrane samples were fixed in the center of a tubular reaction chamber. The whole system was evacuated for at least 30 min (for a final system pressure of ca. 0.050 Torr). After sufficient purging with helium, the gas pressure was set to 0.20 Torr by adjusting the helium gas flow rate. Plasma was created using a power supply (RF5S) with matching network (AM5 and AM-NPS-2A, 13.67 MHz; all made by RF Plasma Products, Inc., Marlton, NJ), connected with a copper coil surrounding the reaction chamber. After plasma treatment, the vacuum was immediately broken with air for subsequent formation of peroxides.

Plasma-Induced Graft Polymerization

The plasma induced graft polymerization of membranes closely followed earlier work in this group described by Ulbricht et al.[7] in detail. NVP solutions in DI water [0.5–10% (wt)] in a glass cylinder sealed with a ground joint was deaerated and adjusted to 50°C (±0.5°C). Preweighed plasma-treated samples were placed into the monomer solutions and kept there for the reaction time under continuous deaeration with nitrogen bubbling through a silicate frit. The reaction was interrupted by immersing the membrane samples in a large excess of water. Then, the samples were extracted with water for at least 16 h at 50°C. The samples were stored in water for subsequent characterization by UF. To determine the amount of graft polymer gravimetrically, the samples were dried after step-wise solvent exchange using water/ethanol mixtures with increasing ethanol content (up to 50%) and sonication for 4 min.

Contact Angle Measurements

Captive-bubble contact angle measurements were used to characterize the polarity or energy of membrane surfaces. Air/water/membrane interfaces were formed by immersing small membrane panels in a glass observation cell containing DI water and releasing an air bubble beneath the membrane surface with a curved syringe. A camera (SIT66, Dage-MTI, Michigan City, IN) fitted with a video screen, provided a magnified image

of the bubble, which was then recorded and used to measure the contact angles. The values for the contact angles were averaged over five different air bubbles. To measure advancing and receding angles, the air bubbles were inflated and deflated with air, and the respective contact angles were measured. The advancing edge of the captive air bubble explored a PES/water interface with exposed hydrophilic groups (after treatment and grafting), and the receding edge explored an air/PES interface with submerged hydrophilic groups. The glass chamber, the syringe, and the needle were washed with an acid solution and rinsed carefully with water before use. Reproducibility of the measurements was better than $\pm 2°$.

Atomic-Force Microscopy

Atomic force microscopy (AFM) provided topographical images by scanning a silicon nitride tip or stylus attached to a cantilever over the membrane surface, while maintaining a constant force between the tip and the sample. The deflection of the tip and cantilever was measured optically by a reflected laser beam off the back face of the cantilever (AFM, Auto Probe CP, Park Scientific, Sunnyvale, CA). Typical forces between the probing tip and the sample varied from 10^{-11} to 10^{-6} *N*. Motions from micrometers to a few tenths of an angstrom were measured by the deflection sensor. In the contact mode, ionic repulsion forces allowed the surface topography to be traced with a high resolution. Key advantages of the AFM technique are its ability to image nonconducting materials such as membranes directly in air or liquid without special sample preparation.

Other Analytical Methods and Equipment

FTIR/ATR spectra were recorded using a model 1800 FTIR (Perkin-Elmer Corp.), equipped with an ATR unit (germanium or KRS 5 crystal, 45 degree, Perkin-Elmer Corp. CT). 400 scans with a nominal resolution of 4 cm^{-1} were routinely taken. UV/Vis spectra were recorded with a spectrophotometer (UV 2000, Hitachi Instruments, Danbury, CT).

The electron spectroscopy for chemical analysis (ESCA or XPS) spectra for the membrane samples were obtained with a Multi Technique System 5500 (Perkin-Elmer Corp., Norwalk, CT) using a Mg Kα source (No. 04-548) at 200 W and 15 kV. The takeoff angle was 60°, nominal resolutions were 0.8 and 0.125 eV for the survey and the high-resolution scans, respectively. Static charging of the polymer film (insulator) was not considered, because (1) the measurements were not used to determine chemical state, and (2) the component peaks were extremely close to the reference state.[12]

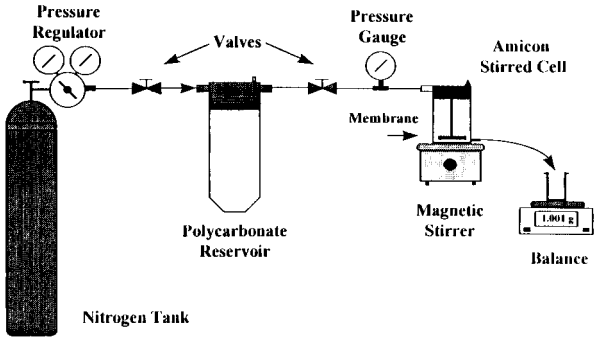


Figure 1 Flow sheet for the dead-end stirred cell filtration system.

Protein Ultrafiltration

Protein solutions were prepared by carefully dissolving BSA powder in a phosphate-buffer solution (pH 6.9) at room temperature. No stirring was used during the dissolution of the protein. The phosphate buffer solution (8.1 m*M* Na_2HPO_4, 1.9 m*M* NaH_2PO_4, 2.7 m*M* KCI, and 128 m*M* NaCl) was prepared by dissolving preweighed quantities of the salts in the desired volume of DI water. The protein solution was filtered with a 0.22 μm Nylon filter (Gelman Sciences, Ann Arbor, MI) prior to use. To avoid bacterial contamination, protein solutions were stored at 4°C and used within 48 h of preparation. The concentration of the BSA was measured with a UV spectrophotometer at 280 nm (UV 2000).

A flow sheet of the filtration apparatus used in this study included a membrane test cell, nitrogen pressure to the feed reservoir, permeate collection reservoir, and pressure gauges (Fig. 1). The ultrafiltration experiments were conducted in a dead-ended stirred cell (Model 8050, Amicon Div., Millipore Corp., MA) with an active membrane area of 12.57 cm^2. All experiments were conducted at room temperature (23 $\pm$ 2°C).

The filtration protocol, which was similar but not identical to that reported earlier,[22] is shown schematically in Figure 2. In a typical run, the stirred cell and solution reservoir were initially filled with DI water, and the membrane was precompacted for 30 min during the filtration of DI water at a transmembrane pressure (TMP) of 172 kPa (25 psi). Then, the TMP was dropped to 34.4

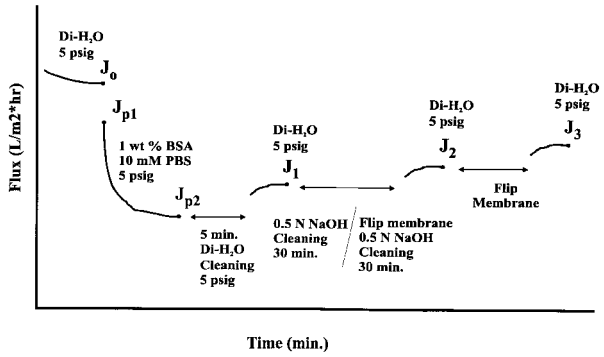


Figure 2 Schematic of filtration protocol: (1) as a precompaction step, DI water was passed through the membrane for 30 min at a transmembrane pressure (TMP) of 25 psig; (2) The TMP was lowered to 5 psig and the flux (J_0) noted when the difference between consecutive measurements was less than 2%; (3) BSA solution of ca. 1 wt % was filtered at TMP of 5 psig and until 10 mL of permeate was collected (J_{p1} and $J_{p2} = J_p$ at the start and end, respectively); (4) the cell was rinsed with DI–H_2O three times for 1 min each, and the DI–H_2O flux was measured (J_1); (5) 0.5 *N* NaOH was filtered for 30 min at TMP of 1–2 psig and the membrane was turned over and a second 30-min caustic run was undertaken, followed by a DI water run at 5 psig (J_2); and (6) the membrane was turned over to its original orientation and the DI–H_2O flux was again measured at TMP of 5 psig (J_3).

kPa (5 psig) and the DI-water flux (J_0) was measured every 5 min until the flux remained constant for at least two successive readings (usually after 15 min). Next, the ultrafiltration experiments were performed with ca. 10–12 g/L BSA solution at 34.4 kPa until 10 mL of permeate were collected. The values of the permeate flux at the start (J_{p1}) and at the end (J_{p2}) of the protein solution run were recorded. After this exposure to protein solution flux, the membrane was briefly rinsed with DI water to remove BSA before the pure water flux (J_1) was measured again at a TMP of 34.4 kPa. Due to irreversible BSA fouling, J_1 was typically lower than J_0, with the magnitude of the difference dependent on the degree of fouling.

To determine how much of the original water flux could be recovered by cleaning both sides of the membrane with NaOH solution, the cell was emptied, filled with 0.5 *N* NaOH solution, and stirred for 30 min while maintaining a low transmembrane pressure of ca. 6.88–13.76 kPa (1–2 psi). After rinsing with DI water, the membrane was removed and placed upside down in the cell and the cell was re-filled with 0.5 *N* NaOH solution. After stirring for 30 min while maintaining a TMP of 6.88–13.76 kPa, the cell was emptied and rinsed with DI water before the pure water flux at 34.4 kPa was determined (J_2). Note that J_2 was the pure water flux with the membrane inverted. After the cell was emptied and rinsed with DI water, the membrane was flipped back to its original orientation and the DI water flux (J_3) was measured. The expected error for measuring the permeate flux was ca. ± 2.0 L/m^{2}h.

To evaluate the antifouling properties of the modified membranes and to compare them with the unmodified membranes, besides the absolute values of the fluxes, three ratios were used: (1) J_{p2}/J_0: this ratio provided a direct measure of the membrane's tendency toward fouling by the BSA solution; (2) J_1/J_0: this ratio measured the ability to clean the membrane by flushing with water after exposure to the BSA solution; and (3) J_3/J_0: this ratio measured the extent of flux recovery by cleaning both sides of the membrane with 0.5 *N* NaOH solution. Generally, this ratio was less than 1. The higher this ratio, the more effective the caustic rinsing.

The larger the values of these three ratios compared to the unmodified membrane, the better the modified membrane.

RESULTS AND DISCUSSION

Effects of Plasma Treatment on PES Membranes

After plasma treatment and subsequent exposure to air, peroxides are formed on the membrane surface that can greatly change the membrane surface's wettability.[7] Table I shows the values of the static, advancing, and receding contact angles after different times of plasma treatment. The large value of the contact angles of the virgin PES membrane confirms its strong hydrophobic character. As can be seen from the large decrease in the values of the static and receding contact angles after plasma treatment, the modified membrane surfaces were considerably more hydrophilic compared with the virgin PES membrane. However, changes in the values of the contact angles with the plasma treatment time range were not very significant. The differences between values of the advancing and receding contact angles, or hysteresis as it is often called, increased considerably after plasma treatment but remained invariant with plasma treatment time. The large observed hysteresis could be the result of several factors such as increased surface roughness, increased heterogeneity, reorientation

Table I Air–Water Contact Angles Measured by the Captive Bubble Technique for Virgin and Plasma-Treated PES 10-kDa Membranes[a]

Contact Angle	Virgin PES θ (°)	He Plasma-Treated (0.2 Torr, 25 W) PES θ (°)			
		10 s	30 s	60 s	90 s
Static, θ_s	67 ± 1	24 ± 2	28 ± 2	25 ± 1	28 ± 2
Advancing, θ_a	93 ± 1	75 ± 2	76 ± 1	78 ± 1	83 ± 1
Receding, θ_r	59 ± 1	22 ± 2	23 ± 2	28 ± 2	26 ± 2
$\theta_a - \theta_r$	34 ± 2	53 ± 4	53 ± 3	50 ± 3	57 ± 3
Pure water flux, J_0 (L/m^2h)	58.2 ± 8.6	64.0 ± 11.7	55.3 ± 10.3	63.6 ± 14.6	61.1 ± 12.9

[a] For the plasma treatment, plasma power 25 W, initial system pressure 0.2 Torr, plasma time was 10, 30, 60, and 90 s, respectively. After plasma treatment, the membrane samples were exposed to air for 10 min prior to storage in DI water for further measurements. Each value was an average of at least four measurements.

of surface molecules, solubility of the surface region (and the effect on T_g), and the interfacial energy between the solid and solvent.[23] Here, the likely causes for the large increase in observed hysteresis was the increase in roughness (see AFM results below) and molecular reorientation of oxygen (O_{1s}) containing species (see ESCA results below). However, when stored under water

Table II ESCA Data for Virgin, Plasma-Treated, and NVP-Grafted PES UF Membranes

		Component Peaks					
	Total (%)	E (eV)	%	E (eV)	%	E (eV)	%
Carbon (C_{1s})							
Theoretical	72.0						
Virgin	76.0	286.4	70.5	287.7	29.5		
He 30 s	71.1	286.2	65.7	287.6	34.3		
He 60 s	62.7	286.4	73.7	287.9	26.3		
NVP grafted (2%)	65.1	286.4	60.2	288.2	33.7	290.4	6.0
NVP grafted (5%)	62.6	286.6	53.1	288.2	35.8	289.9	11.1
Nitrogen (N_{1s})							
Theoretical	0.0						
Virgin	0.0						
He 30 s	1.4						
He 60 s	13.6						
NVP grafted (2%)	4.9	401.4	83.2	402.9	16.8		
NVP grafted (5%)	5.6	401.4	85.5	402.5	14.6		
Oxygen (O_{1s})							
Theoretical	20.0						
Virgin	19.1	533.1	65.2	534.6	34.8		
He 30 s	22.7	532.9	71.7	534.6	28.3		
He 60 s	19.7	532.9	73.8	534.6	26.2		
NVP grafted (2%)	27.0	533.6	100.0				
NVP grafted (5%)	28.5	533.8	100.0				
Sulfur (S_{2p})							
Theoretical	8.0						
Virgin	4.9	169.9	75.4	171.2	24.6		
He 30 s	4.8	169.5	77.4	170.8	22.6		
He 60 s	4.1	169.6	82.7	171.0	17.3		
NVP grafted (2%)	3.0	169.6	80.0	170.8	20.0		
NVP grafted (5%)	3.2	169.8	81.9	171.3	18.1		

for 3 weeks after He plasma treatment (results not shown), the surfaces were quite stable, i.e., static contact angles changed very little during this period, $\Delta\theta_s \pm 2°$.

One of the adverse effects of plasma treatment on polymeric membranes is surface etching.[24] Sufficient etching can increase pore size, leading to higher pure water fluxes and lower rejections for solutes. In this work, the effects of plasma treatment on pure water flux were investigated. The plasma conditions were as follows: vacuum pressure 0.2 Torr, plasma power 25 W, and plasma treatment times 10, 30, 60, and 90 s. For all the filtration measurements, the membrane was precompacted at 25 psig for 30 min. Then, the pressure was reduced to 5 psig to measure the pure water flux. The flux results before and after plasma treatment are listed in the last row of Table I. It can be seen from the results that the plasma treatment, at least under the present conditions, did not have a significant effect on the pure water flux. Thus, the adverse effect of etching was relatively small. It should be noted that, similar to industrial experience (Robert van Reis, private communication), the pure water flux for different pieces of the same virgin membrane exhibited large variations, i.e., from ca. 45 to higher than 70 L/m^{2}h. This large variation makes it difficult to determine the influence of plasma treatment time on flux.

The elemental composition of the top layer of a polymer sample (a few nanometers thick) can be retrieved from ESCA survey scans and information about the binding state of elements from high resolution spectra via chemical shift. Surface compositions by ESCA of PES UF membranes before and after He plasma treatment are summarized in Table II, and the ESCA spectra of carbon (C_{1s}) core level signal in the membrane surface region are shown in Figure 3. The C/O/S core level values for the virgin PES membrane were in reasonably good agreement with the theoretically predicted values (Table II). However, some sulfur seems to have been displaced by carbon in the surface region. Significant changes were observed due to plasma treatment. After a 30-s exposure, 22.7% oxygen was detected, while the carbon content decreased. Interestingly, for a 1 min He plasma treatment, a large increase in the nitrogen content and a strong decrease in the carbon content (from 72 to 62.7%) were observed. These results are similar to those for the helium plasma-treated poly(sulfone).[7]

Table III shows the surface roughness information obtained with AFM for virgin, plasma-treated, and NVP-grafted membranes. Clearly, plasma treatment significantly increased the roughness of the membrane surface, and subsequent NVP grafting possibly rendered the surface more smooth. As mentioned above, the increase in roughness could be partially responsible for the increased hysteresis ($\theta_a - \theta_r$) observed in Table I.

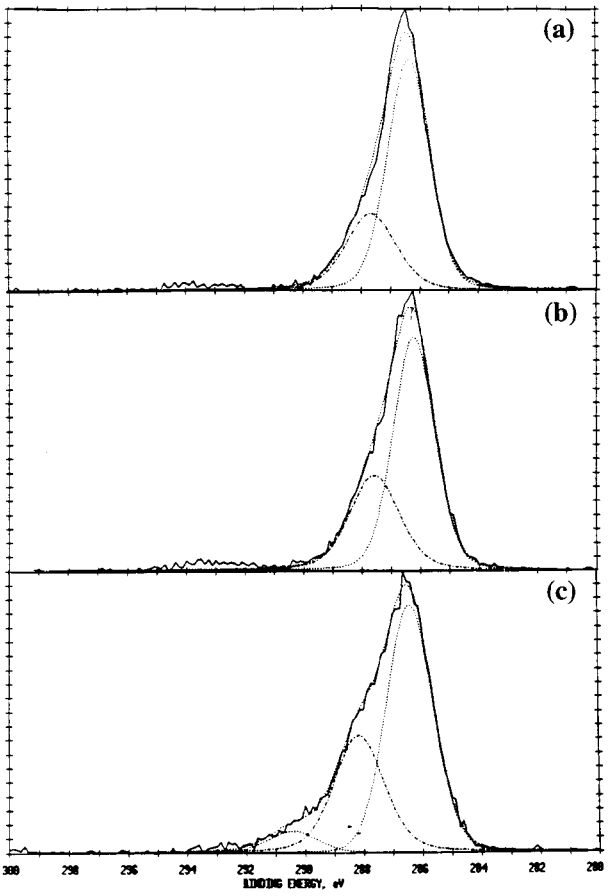


Figure 3 High resolution ESCA carbon (C1s) core level spectra of the surface of a PES membrane: (a) for the virgin membrane, (b) after 30 s of helium plasma treatment (0.05 Torr, 25 W), and (c) after similar plasma treatment and subsequent grafting of NVP from a 5 wt % solution. The smooth dashed and doted lines are calculated best-fit contributions of different carbon-binding states to the measured spectra assuming Gaussian peaks. The takeoff angle was 60°.

The filtration results for the unmodified 10-kDa UF membrane and membranes that were plasma treated without subsequent NVP grafting are shown in Table IV. The pure water flux values (J_0) were 25% higher and the flux ratios after protein fouling (J_{p2}/J_0) were 73% higher at equivalent or higher retentions (R) after plasma treatment. Also, cleaning the membrane after protein fouling with water (J_1/J_0, i.e. reversible

Table III AFM Results for the Virgin, Plasma-Treated, and NVP-Grafted 10-kDa PES Membrane Surfaces

	Average Roughness[a] (Angstrom)	Mean Height[b] (Angstrom)	Root-Mean-Square Roughness[c] (Angstrom)	A_{3D}/A_{2D}[d]
Virgin PES	8.2	49	11	1.00
Plasma treated[e]	28	164	39	1.16
NVP grafted[f]	22	137	29	1.08

[a] Average deviation of the height data from the average of the data.
[b] Average height within the selected height profile.
[c] Standard deviation of the height data from the average of the data.
[d] Ratio of three-dimensional, actual surface area to two-dimensional, projected area for the scanned sample.
[e] He plasma conditions: 0.2 Torr, 25 W, 30 s.
[f] Plasma conditions the same as (e), NVP grafting conditions: 5 (wt) % NVP in deionized water, graft polymerization at 50°C for 1 h.

fouling) and with caustic (J_3/J_0, i.e., irreversible fouling) was more effective for the plasma-treated membranes. The difference between the water and caustic ratios [$(J_1 - J_3/J_0$], which is proportional to the amount of irreversible fouling removed by the caustic, was 34% higher for the untreated membrane. These results support the contention that the plasma treatment has hydrophilized the membranes, resulting in higher filtration performance (water and protein solution fluxes) with less total and irreversible fouling. Unfortunately, the BSA feed concentration was 20% lower for the plasma-treated membranes compared with the untreated ones. In spite of this, the results look most promising, because at such high protein concentrations, the sensitivity of permeation flux on protein concentration is thought to be weak. One word of caution is, however, appropriate. Plasma treatment alone is susceptible to surface restructuring, and will need to be "stabilized" by grafting as is presented below.[17]

Plasma-Induced Graft Polymerization

Earlier research with polyacrilonitrile and poly(sulfone) membranes[7] showed that, using He plasma treatment followed by exposure to air, peroxide species (about 10 nmol/cm^2) were created, which could subsequently decompose. We have tried to determine the peroxide concentrations by the 2,2-diphenyl 1-picryl hydrazyl hydrate (DPPH) assay[25] without success because the PES membrane was not stable in benzene at the required reaction conditions. From plasma activation results with polyethylene, polystyrene, and poly(ether ether ketone) results,[26] we infer that the plasma-induced graft polymerization proceeds according to Scheme 1.

The graft polymerization steps in Scheme 1 should be initiated by thermolysis of peroxides at elevated temperature. In this work, the *N*-vinyl-2-pyrrolidone monomer was selected because of its excellent potential for radical polymerization. To remove homopolymer from the pores or adsorbed onto the membrane surface, membrane samples were extracted exhaustively with DI water at 50°C after grafting. Significant graft polymer formation was only observed after plasma treatment. In control experiments, PES membranes without plasma treatment exhibited very small weight increases after immersion in NVP solutions under the same grafting conditions.

The graft yield dependency on NVP concentration in the grafting solution was nearly linear in the range studied (Fig. 4). This is reasonable because, at the relatively low NVP concentrations used here, the monomer was mostly consumed by chain growth. Plasma excitation conditions such as "oxidation" time and grafting temperature and time were kept constant for the various samples.

Effort has been made to determine NVP graft density on membrane surfaces under different grafting conditions. To obtain reproducible gravimetric results, NVP-grafted membrane samples were extracted with 20 and 50% ethanol aqueous solutions consecutively at 50°C for 1 h and sonicated for 4 min before drying in vacuum. Table V lists the graft densities as well as the pure water fluxes as a function of plasma treatment time. Each value in the table represents the average of at least three data points. The NVP graft density reached a maximum at a plasma treatment time of 60 s, and then decreased significantly. The pure water flux, on the other hand, remained relatively constant for the range of treatment times tested. The large relative errors in pure water fluxes could be due to the increase in roughness of the treated membranes (Table III) or the inherent variability mentioned above. The constancy of the

Table IV Comparison of the Filtration Performance for Virgin and Surface-Modified 10-kDa PES Membranes[a]

Experiment	J_0 L/m^{2}h	J_{p1}/J_0	J_{p2}/J_0	J_1/J_0	J_3/J_0	[BSA] g/L	R (%)	J_s,[b] (g/m^2-h)	Plasma Conditions
PES–Virgin	51.6	0.462	0.370	0.481	0.665	11.4	98.7	3.18	
PES–Virgin	61.1	0.468	0.260	0.380	0.547	11.7	99.9	0.26	
PES–plasma treated	70.1	0.705	0.524	0.625	n/a	9.8	99.6	1.69	30 s, 0.2 Torr, 25 W
PES–plasma treated	71.2	0.838	0.566	0.698	0.722	9.4	99.9	0.47	60 s, 0.2 Torr, 25 W
PES–NVP grafted[c]	70.6	0.621	0.534	0.721	0.712	12.5	99.9	0.51	30 s, 0.2 Torr, 25 W
PES–NVP grafted	82.9	0.767	0.524	0.672	0.679	10.3	99.9	0.55	120 s, 0.2 Torr, 25 W
PES–NVP grafted	64.3	0.627	0.586	0.694	0.635	10.2	99.8	0.80	30 s, 0.2 Torr, 25 W
PES–NVP grafted	64.4	0.823	0.593	0.669	0.699	10.8	99.8	0.99	180 s, 0.2 Torr, 25 W
CLPBPES[d]	128	0.407	0.345	0.453	0.655	12.1	99.8	1.16	
CLPBPES[d]	121	0.375	0.268	0.341	0.557	11.5	99.6	1.79	

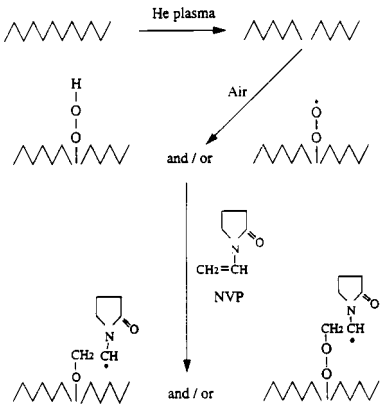
[a] J_0, J_1, and J_3 are defined in the filtration protocol; J_{p1} and J_{p2} are the permeate flux at the start and the end of BSA solution filtration, respectively.
[b] $J_s = [\text{BSA}]_1 (1 - R) J_{p\text{avg}}$ (g/m^2-h) where $J_{p\text{avg}} = (J_{p1} + J_{p2})/2$.
[c] Grafting conditions: NVP concentration 5% (wt), grafting at 50°C for 1 h.
[d] Commercial low protein-binding PES UF membrane.

fluxes may also be due to competing phenomena: ablation and grafting of NVP (pore narrowing) causing an increase and a decrease in flux, respectively.

Surface Characterization of NVP-Grafted PES Membranes

The captive bubble contact angles for air–water–membrane systems are tabulated for the virgin and the NVP-grafted PES membranes in Table VI. Contact angles were measured on both sides of the bubble surface for at least five bubbles at different places on each sample. Therefore, each reported value is an average of at least 10 independent measurements. The values of the contact angles for the NVP-grafted PES membranes were all substantially lower, and hence, the surfaces were more hydrophilic than the untreated PES and the commercial hydrophilic PES membrane. The effect of treatment time on the values of the contact angles seemed to be small, although the values do appear to have risen slightly when the treatment time was increased from 30 to 60 s. The large increase in the difference in the values of the advancing and receding contact angles (hysteresis) on treatment was likely due to the significant increase in surface roughness (Table III), molecular reorientation of the grafted polymer, and a solubility effect on the T_g (as described below, NVP could act as a solvent reducing the T_g below 230°C, facilitating molecular reorientation[27]).

Comparison of the values of the contact angle data for plasma-treated and postgrafted membranes in Tables I and VI show that grafting of



Scheme 1 Plasma-induced grafting of a PES membrane with NVP.

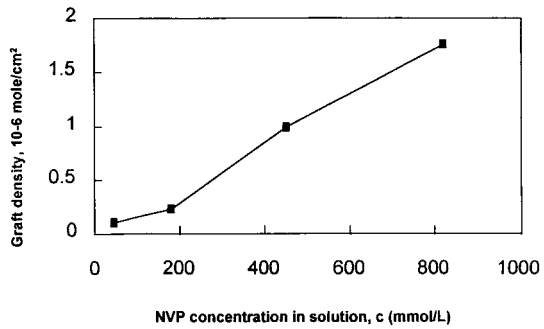


Figure 4 Graft density as a function of NVP monomer concentration.

Table V Pure Water Flux and Graft Density of *N*-Vinyl Pyrolidone on PES Membranes[a]

Plasma Treatment Time[b] (s)	Pure Water Flux (L/m^2h)	NVP Graft Density ($\mu mol/cm^2$)
10	85.6 ± 19.2	0.64 ± 0.18
30	77.6 ± 17.9	0.69 ± 0.29
60	74.4 ± 14.0	1.27 ± 0.40
90	82.4 ± 15.7	0.42 ± 0.13

[a] NVP grafting conditions: 5% (wt) NVP in deionized water; graft polymerization carried out at 50°C for 1 h. Each value is an average of at least three measurement results.
[b] Plasma conditions: power 25 W; initial pressure: 0.2 Torr.

NVP to PES results in marginally lower values of the contact angles. As discussed above, plasma treatment is susceptible to surface reorientation and can be "stabilized" by grafting (hydrophilic) polymer onto the PES membranes.[16,17]

Fourier Transform Infrared Spectroscopy (FTIR) used in the Attenuated Total Reflection (ATR) mode was conducted on the unmodified and modified membranes to confirm that NVP was grafted on the surface. The penetration depth of this method has been estimated to be of the order of 1 μm. Modified membranes were extracted for 20 h in DI water at 50°C to remove any homopolymer in the pores or adsorbed on the membrane surface. The results are displayed in Figure 5. The appearance of the absorbence peak at $\gamma(C = O) \approx 1670\ cm^{-1}$ representing the amide I carbonyl group of the NVP five-member ring confirmed that NVP had been grafted onto the membrane surface. The relative intensity of the bands depended on the amount of graft polymer, which was determined gravimetrically (Fig. 4). All other peaks were similar, confirming that the PES composition was otherwise unchanged by the plasma treatment and subsequent NVP grafting. Also, from a comparison of the spectra of both the outer membrane surfaces (not shown), only the plasma-exposed active membrane surface and not the support layer was modified by the graft polymer.

Comparing the ESCA results for the NVP grafted membranes with the virgin PES membrane in Table II, both carbon (C_{1s}) and sulfur (S_{2p}) contents were reduced, while the detected nitrogen (N_{1s}) and oxygen (O_{1s}) levels were increased. This was because NVP contained oxygen and nitrogen (Scheme 1). Thus, the ESCA data (especially the large increase in nitrogen) confirmed the existence and contribution of the graft copolymer to the surface composition of the modified PES membranes. The presence of PES in the surface region (due to the presence of sulfur) also suggests that the grafted polymer did not fully cover the membrane surface. It is important to realize that the sampling or penetration depths for these processes were different. They varied from < 1 nm for contact angle measurements, 6–7 nm for ESCA ($3\lambda \sin \alpha$, where $\alpha = 60°$ and $\lambda = 2.5$ nm for C1s photoelectrons produced by the Mg Kα X-ray in an organic matrix[13]), and of the order of 1 μm for ATR/IR. The ESCA and ATR/IR evidence, that the surface region comprised of both substrate polymer (PES) and grafted poly-

Table VI Air/Water Contact Angle Measurement Results for Virgin and NVP-Grafted PES 10-kDa Membranes[a]

Contact Angle, θ	Virgin PES Membrane, θ (°)	Commercial Low Protein-Binding PES Membrane, θ (°)	NVP-Grafted PES, θ (°) Plasma Treatment Time		
			30 s	60 s	90 s
θ_s, static	67 ± 1	54 ± 1	27 ± 2	33 ± 1	29 ± 2
θ_a, advancing	93 ± 1	86 ± 1	76 ± 1	80 ± 1	81 ± 1
θ_r, receding	59 ± 1	45 ± 1	25 ± 2	26 ± 2	27 ± 2
$(\theta_a - \theta_s)$	34 ± 2	41 ± 2	51 ± 3	54 ± 3	54 ± 3

[a] For all plasma experiments reported in this table: the plasma power 25 W, initial pressure 0.2 Torr. The NVP concentration was 5% (vol) in deionized water. Grafting was carried out at 50°C for 1 h.

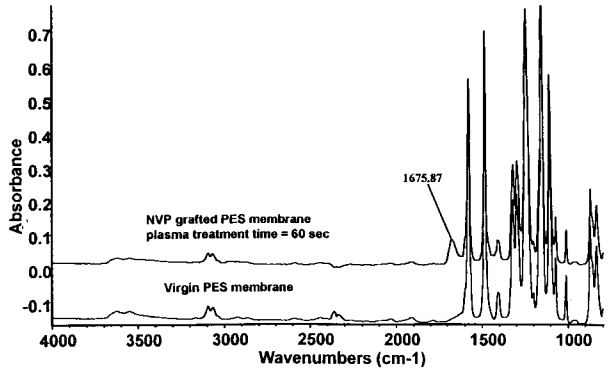


Figure 5 FTIR-ATR spectra for (a) virgin PES 10-kDa membrane, and (b) plasma-treated membrane (0.2 Torr, 25 W, 60 s) with subsequent NVP grafting. The peak at 2360 cm^{-1} is assigned to carbon dioxide.

mer (NVP), together with the supporting contact angle results suggest the following qualitative picture of the grafted interface region. In the hydrated state, the grafted hydrophilic polymer partially penetrated the surface similar to that proposed by Loh et al.,[17,27] using angle-resolved ESCA. Much lower contact angle values and higher sulfur contents by ESCA would have been observed if the surface was completely covered with the NVP polymer.[17]

Filtration of BSA Solutions Using NVP-Grafted PES Membranes

Table IV shows the filtration results for the unmodified, the plasma-treated, and the plasma-treated/NVP-grafted PES 10-kDa membranes (all the PES membranes were from the same lot number). The pure water flux values (J_0) and the flux ratios (J_{p2}/J_0) after protein fouling were in all cases higher at equivalent or higher retentions (R) when comparing the untreated (virgin PES membrane) with the plasma-treated/NVP-grafted membranes. Also, cleaning the membrane after protein fouling with water (J_1/J_0, i.e., reversible fouling) and with caustic (J_3/J_0, i.e., irreversible fouling) was more effective for the plasma-treated/NVP-grafted PES 10-kDa membranes compared with the untreated membranes. The difference between the water and caustic ratios [$(J_1 - J_3)/J_0$], which is proportional to the amount of irreversible fouling removed by the caustic, was consistently higher for the untreated membrane. Actually, this difference was very small or close to zero for the grafted membranes, suggesting that for these membranes (1) irreversible fouling was essentially absent, and (2) the use of caustic could be obviated. The latter is of commercial interest, because frequent cleaning with water rather than with caustic may be possible with these membranes saving chemical and disposal costs. Because these membranes are known to have a small fraction of pores larger than the nominal molecular weight cutoff of 10 kDa, it is not surprising that some BSA is able to pass the membranes (i.e., $J_s > 0$).

Once again, these filtration results, together with contact angle measurements, support the claim that plasma treatment and subsequent NVP grafting has hydrophilized the membranes, resulting in higher filtration performance (water and protein solution fluxes) with less total and irreversible fouling. Again, the BSA feed concentration was about 11% lower for three of the grafted membranes compared with the untreated ones. In one case, however, the BSA feed concentration (12.5 g/L) was 8% higher than that for the two untreated membranes and, despite this, the favorable trends described above were again observed.

In comparing the results for the grafted membranes with those for the plasma-treated (no grafting) membranes, one notes that the flux values and ratios were quite similar. Recall the contact angle results (Tables I and II) were also similar, the main difference being the expected long-term instability of the plasma-treated (no grafting) compared with the NVP-grafted membranes.[13–17]

Table IV shows the filtration results in the last two rows for a commercial low protein-binding PES UF membrane. This membrane exhibits double the water fluxes of the unmodified PES membrane, a higher solute leakage flux (J_s), and slightly lower BSA retention compared to the grafted membranes. All this suggests that the commercial membrane has a more open pore structure (higher porosity), and/or its pore size distribution is shifted to larger pores sizes. In any case, its fouling with BSA (J_{p2}/J_0) is hardly different from the untreated membrane.

Because the concentration of NVP in the grafting solution affected the amount grafted onto the PES membrane surface (Fig. 4), and because all the filtration results reported in Table IV were for a 5 wt % NVP in solution, it is of interest to determine the effect of NVP concentration on NVP-grafted PES UF membrane filtration performance. The filtration results from 0.5 to 10 wt % NVP are summarized in Table VII. Even at low NVP concentrations of 0.5 wt %, the filtration performance was superior to that of the unmodi-

Table VII Results for the NVP Grafted 10 kDa PES Membranes as a Function of NVP Concentration in the Grafting Solution[a]

Experiment	J_0 (L/m^{2}h)	J_{p1}/J_0	J_{p2}/J_0	J_1/J_0	J_3/J_0	[BSA] (g/L)	R (%)	J_s (g/L)	Plasma Conditions
PES–NVP (0.5%)[b]	78.9	0.684	0.497	0.654	0.722	10.2	99.9	0.475	30 s, 0.2 Torr, 25 W
PES–NVP (2%)	82.4	0.757	0.519	0.626	0.811	11.2	99.9	0.588	30 s, 0.2 Torr, 25 W
PES–NVP (5%)[c]	67.5	0.624	0.560	0.708	0.674	11.4	99.9	0.655	30 s, 0.2 Torr, 25 W
PES–NVP (10%)	90.1	0.514	0.381	0.581	0.612	10.9	94.9	24.11	30 s, 0.2 Torr, 25 W

[a] See footnotes in Table IV.
[b] (wt) (%) NVP.
[c] Average of the two runs reported in Table IV.

fied (virgin) membranes listed in Table IV. At a concentration of NVP of 10 wt %, however, BSA retention was decreased and a concomitant large protein flux (J_s) was observed. The explanation for these observations is that NVP, very much like *N*-methyl-2-pyrrolidone, is a good solvent for aryl sulfones at these high concentrations.[28] Thus, the skin layer of the asymmetric PES membrane was probably damaged at the high NVP concentrations. Also, at these concentrations, the T_g of the skin region could have been reduced by the presence of NVP.

CONCLUSIONS

The goal of this work was to evaluate the efficacy of using a low-temperature helium plasma treatment followed by grafting of *N*-vinyl-2-pyrrolidone (NVP) to modify poly(ether sulfone) (PES) UF commercial membranes. This was motivated by the search for optimal conditions of plasma treatment time and NVP graft concentration so as to reduce membrane fouling during the filtration of solutions containing bovine serum albumin. This has been successfully accomplished using a procedure consisting of plasma excitation, brief oxidation in air, and grafting at 50°C in NVP solution. The main conclusions from this work are:

1. Treatment with He plasma alone drastically changed the surface properties of PES UF membranes. The exposed membrane surfaces were hydrophilized (as measured by captive bubble contact angles) and showed good stability for at least 3 weeks, especially when kept in water. However, plasma treatment is known to be unstable with time, especially if the modified surface is exposed to air or the hydrophobic core of a protein. Then, surface restructuring is expected for this type of modification.[13–17,27] Although pore etching due to plasma excitation was expected, this was not significant for the mild plasma conditions studied.
2. NVP was grafted onto PES membranes via formation of surface polymer peroxides by plasma excitation, as evidenced by FTIR/ATR spectroscopy. The degree of modification was adjusted during a thermally induced polymerization step. A relatively low degree of grafting (0.42–1.27 μmol/cm^2) of NVP yielded a significantly large surface hydrophilicity when compared with the parent PES membrane. With NVP concentrations of 0.5–5 wt % in the grafting solution, the filtration performance was superior to that of the unmodified membranes. Higher concentrations damaged the membrane probably due to dissolution by NVP. Plasma treatment times from 30–60 s were optimal and practical for large scale.
3. Both the plasma treatment alone and the plasma-induced grafted NVP modification exhibited strongly reduced protein adsorption, resulting in favorable filtration performance. While the modified membranes were easier to clean with pure water, they also showed lower irreversible fouling compared with the virgin membranes. This is of commercial interest because frequent cleaning with water rather than with caustic may be possible with these modified membranes, saving chemical and disposal costs.
4. The filtration results, together with contact angle measurements, confirm that plasma treatment and subsequent NVP grafting hydrophilized the membranes, resulting in

higher filtration performance (water and protein solution fluxes) with less total and irreversible fouling.

5. The permeation rate values, permeation rate ratios, and short-term contact angle measurements were quite similar for the plasma-treated (no grafting) and the plasma-grafted membranes. The main difference being the detection of NVP in the surface region by ESCA and ATR/IR. The expected long-term instability of the plasma-treated (no grafting) compared with the NVP-grafted membranes favors the latter modification.[13] Surface restructuring is not expected to be as significant for long periods for the NVP-grafted PES UF membranes (it is more difficult for large polymeric pendent groups compared with relatively small functional groups such as hydroxides, carboxylic acids, etc., to diffuse into the bulk PES polymer).[17] Although this was not confirmed here, extensive results in the literature suggest this to be the case.[12,29]

This work lays the foundation for extending the research using low-temperature plasma-induced grafting to a variety of other molecules, some hydrophilic monomers for comparison with NVP, and other charged or hydrophobic monomers. Biologically active surfaces through the binding of enzymes and ribozymes could also be pursued. The low-temperature plasma technique for inducing radicals and peroxides on the surface of PES needs to be compared with other approaches, such as ultraviolet radiation, currently being pursued in our laboratory.[30] These techniques could be used for preparing/modifying polymeric surfaces for applications other than membrane filtration.

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