

# Surface Modification of Polysulfone Membranes by Low-Temperature Plasma–Graft Poly(ethylene glycol) onto Polysulfone Membranes

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Received 23 July 1999; accepted 11 January 2000

**ABSTRACT:** A novel and general method of modifying hydrophobic polysulfone (PSF) to produce highly hydrophilic surfaces was developed. This method is the low-temperature plasma technique. Graft polymer-modified surfaces were characterized with the help of Fourier transform infrared attenuated total reflection (FTIR–ATR) and X-ray photoelectron spectroscopy (XPS). Study results demonstrated that poly(ethylene glycol) (PEG) could be grafted onto the PSF membrane surface by low-temperature plasma. The hydrophilic character of the modified surfaces was increased in comparison with that of the parent membrane. The contact angle for a modified PSF membrane was reduced apparently. We analyzed the effectiveness of this approach as a function of plasma operating variables including plasma treatment power and treatment time. Hence, plasma-induced graft polymer modification of membranes can be used to adjust membrane performance by simultaneously controlling the surface hydrophilicity and hemocompatibility. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 979–985, 2000

**Key words:** low-temperature plasma; polysulfone membrane surface modification; graft poly(ethylene glycol)

## INTRODUCTION

Thrombus formation is a serious problem in surgical therapy and clinical application of artificial organs. Therefore, the need for the creation of highly antithrombogenic biomaterials has been increasing. Although a substantial amount of work in the improvement of the blood compatibility of polymeric materials has been carried out, the results are still inconclusive. This is caused partly by the fact that the relationship between surface properties and surface-induced thrombosis has not been thoroughly evaluated.<sup>1</sup>

Many polymer membranes have been employed in the field of biomedicine. But, most poly-

mer membranes are relatively inert and hydrophobic and they have low surface energies, such as polypropylene ( $\gamma = 29.5$  mN/m), poly(vinylidene fluoride) ( $\gamma = 42$ – $47$  mN/m), poly(ethylene terephthalate) ( $\gamma = 24.2$  mN/m), and polyarylsulfone ( $\gamma = 49$  mN/m).<sup>2</sup> There is therefore much interest in the modification of the membranes to improve their hydrophilicity and hemocompatibility.

Several different surface-modification techniques have been pursued: One approach involved heterogeneous chemical modifications,<sup>3–5</sup> and another used irradiation methods such as with UV.<sup>3</sup> Low-temperature plasma techniques have been used to prepare highly selective composite membranes for reverse osmosis and gas separation.<sup>6</sup> A very thin modified selective layer (some nanometers) is obtained by this method. Simple treatment with inert gas, nitrogen, or ox-

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*Journal of Applied Polymer Science*, Vol. 78, 979–985 (2000)  
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xygen plasma enhanced the surface hydrophilicity of asymmetric ultrafiltration (UF) membranes made from poly(vinyl chloride), but the pores were also enlarged.<sup>7</sup>

The aim of this work was to optimize the plasma excitation condition to obtain a modified membrane with improved hydrophilicity and hemocompatibility compared to an unmodified membrane.<sup>8</sup> In this study, we chose polysulfone (PSF) because it is widely used as a material for UF membranes with its excellent film- and membrane-forming properties and its high mechanical and chemical stability. We use poly(ethylene glycol) (PEG) to graft onto the PSF membrane surface because PEG is hydrophilic, very compatible with peptides and proteins, and nontoxic in the body. Therefore, it is expected that PSF membrane surfaces grafted with PEG will curtail surface-induced thrombus formation.

## EXPERIMENTAL

### Materials

The PSF ( $\eta = 0.56\text{--}0.63$ ) polymer was supplied by DaLian No. 1 Plastics Factory (DaLian, China). Commercially available *N,N*-dimethylacetamide (DMAC) (TianJin No. 2 Reagent Factory, Tianjin, China, special grade) was used as a solvent. PEG (molecular weight 4000) was obtained from the Tiantai Chemical Co. (TianJin, China). The additive was PEG (molecular weight 400). Iospropyl alcohol (Ledai Chemical Co. Tianjin, China) and diiodomethane (Xingfu Chemical Research Institute, Beijing, China) were used. All these liquid chemicals were used without further purification.

### Membrane Preparation

The PSF membranes were prepared by a phase-inversion technique. The polymer was dried in an oven (over 100°C) for 6 h to remove absorbed water vapor before use. The casting solution was made of 12.5 wt % PSF, 62.5 wt % DMAC, and 25 wt % PEG. The dissolved and degassed solution was cast onto a glass plate to form a flat film. After partial evaporation of the solvent, the membrane was immersed into a coagulation media in which there was a nonsolvent of the polymer. In the coagulation bath, solvent exchange and phase inversion took place and solidification of the polymer film occurred.

### Modification of Membranes

PSF membranes were immersed in 0.5% PEG-4000 in a solution composed of 25 wt % isopropyl alcohol (IPA) and 75 wt % water for 24–36 h and air-dried. The PSF membranes were then treated with plasma using a glow-discharge reactor in nitrogen (99.99%). After the treatment, the PSF membranes were washed with water and removed the PEG which could not be grafted.

### Surface Analytical Methods

Attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectra of the unmodified PSF and the PEG-modified membranes were measured with a Bio-Rad Corp. FTS6000 FTIR spectrometer. An internal reflection element (ZnSe) was used in the ATR accessory at an incident angle of 45°, giving an IR penetration depth of 0.42–4.2  $\mu\text{m}$ .

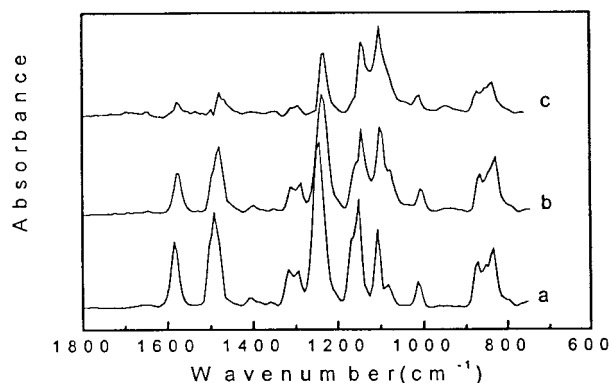
For XPS measurements, a Perkin–Elmer Corp. PHI-1600 spectrometer with a  $\text{MgK}\alpha_{1,2}$  ( $h\nu = 1253.6$  eV) radiation source was used to record the spectra for the membrane sample. The power of the source was 150 W at 25 mA. During the measurements, the spectrometer worked with a constant pass energy of 23 eV. Data accumulation and analysis were performed on an IBM PC using the Matlab software routine. The backgrounds of the peaks were subtracted according to the Shirley method. Fitted parameters of the component peaks were the peak maximum position, the full-width half-maximum (fwhm), the peak area, and the Gaussian–Lorentzian ratio.

### Contact Angle Test

The measurement of the contact angle between water and a membrane surface is one of the easiest ways to characterize the hydrophilicity of a membrane. When water is applied to the surface, the outmost surface layers interact with the water. A hydrophobic surface with low free energy gives a high contact angle with water, whereas a wet high-energy surface allows the drop to spread, that is, gives a low contact angle. The measurement of the contact angle of water or diiodomethane was carried out with a JY-82 contact angle instrument at 25°C. The values for the contact angles were averaged over 10 different water drops.

### Determination of the Grafting Degree

The grafting degree ( $g_w$ ), defined as the mass ratio of the main chain, was determined by the



**Figure 1** FTIR/ATR spectra of the surface of polysulfone membranes: (a) unmodified PSF; (b) PSF-g-PEG; (c) subtracting.

difference of the membrane mass before ( $W_0$ ) and after ( $W$ ) grafting according to the following equation:

$$g_w = \frac{w - w_0}{w_0} \times 100\% \quad (1)$$

## RESULTS AND DISCUSSION

### FTIR-ATR Analysis

Figure 1 shows the ATR spectra PSF and PSF-g-PEG. The strongest band of PSF is at  $1250 \text{ cm}^{-1}$  [ $\nu(\phi\text{-o-}\phi)$ ] and around  $1300\text{--}1335 \text{ cm}^{-1}$  [ $\nu(\text{S}=\text{O})$ ] and  $830 \text{ cm}^{-1}$  [ $\delta(\text{CH})$ ] are characteristic for the original PSF [Fig. 1(a)]. Similar spectra were obtained for the PSF membranes grafted with PEG [ $\nu(\text{S}=\text{O}) = 1295, 1333 \text{ cm}^{-1}$   $\delta(\text{CH}) = 835 \text{ cm}^{-1}$ ]. Figure 2 shows a schematic diagram of the grafting.

The graft polymer on PSF is easily identified using FTIR/ATR spectra of the modified membrane [Fig. 1(b)] compared with the parent PSF membrane surface [Fig. 1(a)]. The characteristic bands of the graft polymer (PSF-g-PEG) originates from ether structures [ $\nu(\text{C}-\text{O}-\text{C}) = 1110\text{--}$

$1150 \text{ cm}^{-1}$ ]. The intensity of the ether bands strongly increased and the specific absorption bands of PSF are simultaneously reduced. The changes are very apparent and can be observed from the subtracting spectrum [Fig. 1(c)].

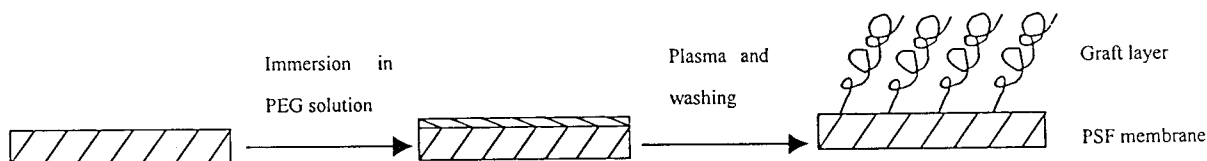
Figure 3 shows the FTIR spectrum of PEG-4000.  $\nu(\text{C}-\text{O}-\text{C}) = 1125\text{--}1148 \text{ cm}^{-1}$  is clearly obtained. So, it proves that PEG can be grafted onto PSF membrane surfaces by low-temperature plasma.

### XPS Analysis

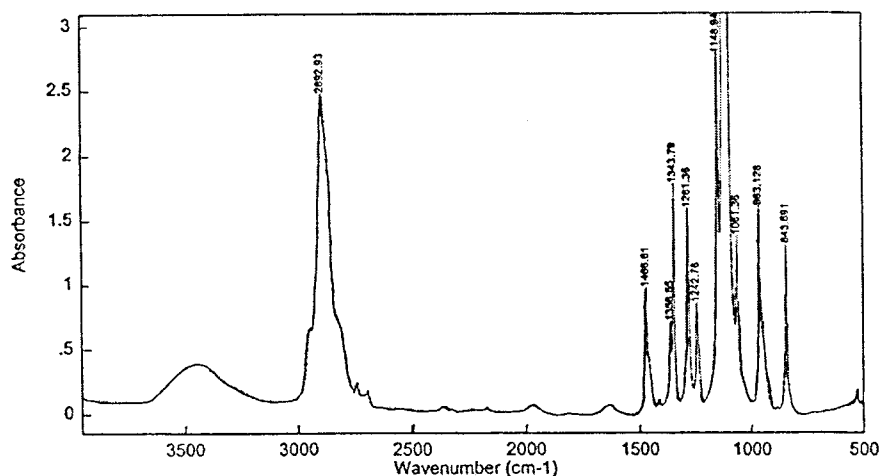
In an attempt to gain further information about the composition of the surface of the PSF membranes, membranes were subjected to XPS. Surface compositions by X-ray photoelectron spectroscopy (XPS) of the PSF membranes before and after plasma treatment are summarized in Table I and are shown in Figure 4.

The stoichiometrical atomic ratio of carbon : oxygen : sulfur (C : O : S) of the unmodified PSF membrane was 1.0 : 0.2076 : 0.0309. After PEG-4000 grafting, the atomic ratio of C : O : S became 1.0 : 0.3006 : 0.0260. The atomic O : C ratio increased and the atomic S : C ratio decreased. Sulfur was still observed in the spectrum after grafting PEG onto the PSF membrane surface. So, this analysis indicates that the membrane surface was not thoroughly covered by the thick layer of the grafted PEG chains, but PEG grafting clearly occurred. Note that the same conclusions were drawn from FTIR-ATR.

The C signal in the high-resolution spectra of the unmodified samples could be deconvoluted into three peaks [Fig. 4(a,d)]. Carbon atoms attached to hydrogen/carbon, sulfone, and ether groups exhibit C(1s) core-level binding energies of 284.71, 285.31, and 286.34 eV, respectively [Fig. 4(a)].<sup>8</sup> Low-energy  $\pi\text{-}\pi^*$  shake-up transitions accompanying core-level ionization at around 291.80 eV were fitted with a Gaussian peak of different fwhm to assess the level of aromaticity present before and after plasma treatment. The O(1s) peak is a doublet with the peaks



**Figure 2** Schematic description of graft PEG onto PSF membrane by low-temperature plasma.



**Figure 3** FTIR spectrum of PEG-4000.

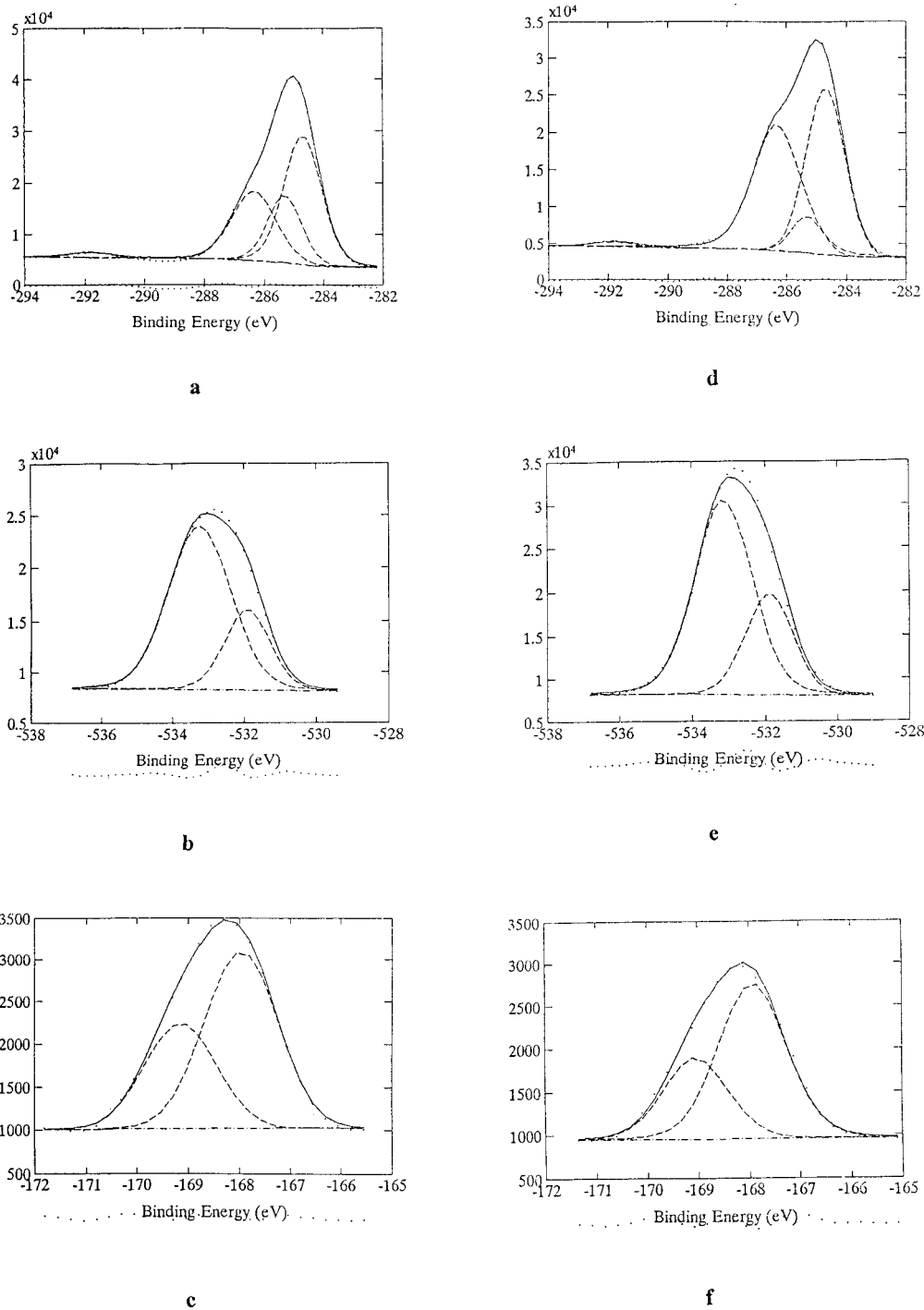
centered at 531.91 and 533.24 eV [Fig. 4(b)], corresponding to oxygen-bonded to sulfur (sulfone groups) and oxygen-bonded to carbon in the backbone (ether linkages), respectively. The S(2*p*) peak was found to be a doublet with the peaks centered at 167.92 eV [S(2*p*<sub>3/2</sub>)] and 169.06 eV [S(2*p*<sub>1/2</sub>)], this can be taken as being characteristic of the sulfone group [Fig. 4(c)]. Compared with Figure 4(a), after PEG grafting, the intensity of the —C—O—C component in Figure 4(d) increased. Table I shows that the —C—O—C component increased from 28.99 to 46.44%. Therefore, the peak (286.34 eV) [Fig. 4(d)] can be considered for the —C—O—C of the PSF membrane

and the —C—O—C of the PEG grafted onto the PSF membrane surface. It also supports the grafting of PEG.

To demonstrate a gradient composition of the grafting membrane surface, angular-dependent XPS was used to quality the surface composition. The take-off angle (TOA) is defined as the angle between the horizontal axis of the surface and the axis of the analyzer lens system. The TOA of 30°, 60°, and 90° employed led approximately to sampling depths of 2, 5, and 10 nm, respectively. Table II shows the elemental composition for the PSF membrane treated under 30 W power for 60-s conditions. As shown in Table II, the outmost

**Table I** XPS Data of Unmodified and Modified PSF Membranes

Sample	Peak	Position	2σ = fwhm	Assignment	Intensity %
Unmodified PSF	C(1s)	284.70	1.52	—C—H—	47.12
		285.31	1.34	—C—S—	21.82
		286.34	1.74	—C—O—	28.99
		291.80	1.74	—π—π*—	2.07
	O(1s)	531.91	1.49	O=S=O	26.65
		533.24	2.06	—C—O—	73.35
	S(2p)	167.92	1.64	2 <i>p</i> <sub>3/2</sub>	57.09
169.06		1.71	2 <i>p</i> <sub>1/2</sub>	42.92	
Modified PSF	C(1s)	284.70	1.53	—C—H—	44.58
		285.31	1.20	—C—S—	7.71
		286.34	1.91	—C—O—	46.44
		291.83	1.49	—π—π*—	1.28
	O(1s)	531.90	1.55	O=S=O	29.53
		533.14	1.85	—C—O—	70.47
	S(2p)	167.95	1.64	2 <i>p</i> <sub>3/2</sub>	71.21
		169.11	1.45	2 <i>p</i> <sub>1/2</sub>	28.79



**Figure 4** High-resolution XPS spectra of unmodified and modified PSF membrane surfaces. Unmodified PSF: (a) C(1s); (b) O(1s); (c) S(2p). Modified PSF: (d) C(1s); (e) O(1s); (f) S(2p).

surface at 30° TOA consists of 80.36% C, 17.25% O, and 1.7% S, while the C, O, and S values are 80.03, 16.56, and 2.44% at 90° TOA, respectively. The O/C atomic ratios decrease, whereas the S/C

atomic ratios increase from 30° TOA to 90° TOA, indicating that PEG was grafted onto the PSF membrane surface. But the changes of the O/C and S/C atomic ratios are not clear from 30° TOA

**Table II Results of Modified PSF Membrane XPS at Different Take-off Angles**

Sample	Take-off Angle Degree	Atomic %		
		Carbon	Oxygen	Sulfur
PSF	30	80.36	17.25	1.70
	60	80.23	17.22	2.08
	90	80.03	16.56	2.44

to 60° TOA. Thus, it is substantiated that the PEG chain grafted onto the PSF membrane surface is about 5 nm. All the XPS data obtained here confirmed the occurrence of the surface grafting of PEG onto the PSF membrane.

### Surface Hydrophilicity Measured with Contact Angle

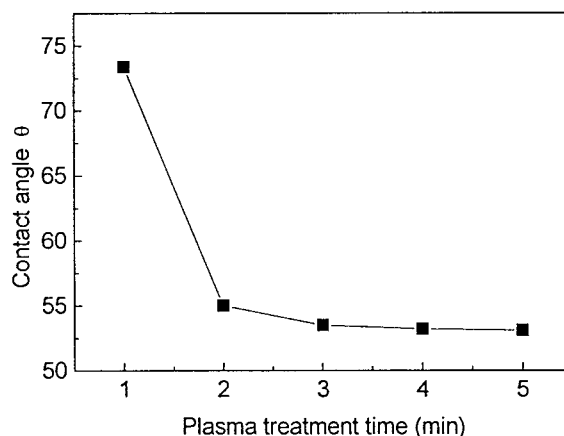
The PEG-grafted membranes were analyzed for their hydrophilic properties by carrying out water and diiodomethane contact angle measurements. Wu<sup>9</sup> thought that the surface free energy ( $\gamma$ ) could be separated into a dispersing parameter ( $\gamma^d$ ) and a polar parameter ( $\gamma^p$ ). This procedure leads a harmonic mean equation to the Young equation.  $\gamma$ ,  $\gamma^d$ , and  $\gamma^p$  can be calculated by solving the system of equations as follows:

$$\gamma_1(1 + \cos\theta_1) = \frac{4\gamma_1^p\gamma_s^p}{\gamma_1^p + \gamma_s^p} + \frac{4\gamma_1^d\gamma_s^d}{\gamma_1^d + \gamma_s^d} \quad (2)$$

$$\gamma_2(1 + \cos\theta_2) = \frac{4\gamma_2^p\gamma_s^p}{\gamma_2^p + \gamma_s^p} + \frac{4\gamma_2^d\gamma_s^d}{\gamma_2^d + \gamma_s^d} \quad (3)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (4)$$

To investigate the effectiveness of various plasma operating conditions, the contact angle is evaluated as a function of different factors. Although the grafting degree was not high, the sur-

**Figure 5** Contact angle as a function of plasma-treatment time.

face properties of the membranes changed drastically (see Table III). The PEG-grafted membranes showed a considerable decrease in the water contact angle from 74.0° to 37.2° for unmodified membranes and modified membranes, respectively, as shown graphically in Table III, which indicates an increase in hydrophilicity after the grafting of PEG. So, the blood compatibility of the polymer was improved. This is due to the hydrophilic environment of the blood-material interface, which appears to reduce protein and platelet adhesion. The advantages of using PEG include a high water contact of the surface, high dynamic motion, and extended chain conformation at the blood-material interface.

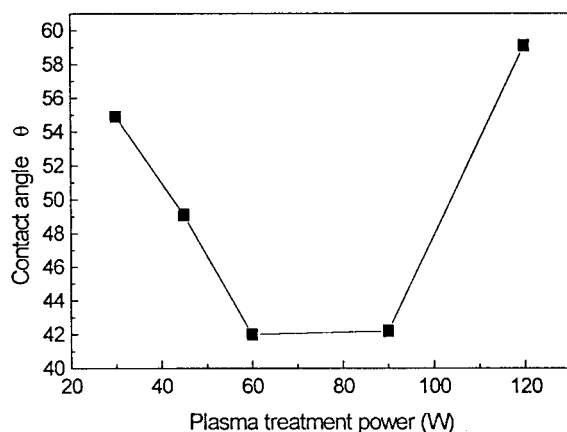
### Plasma Treatment Time

The values obtained for the modified membranes at different plasma treatment times are represented in Figure 5. A tendency to decrease the contact angle with increasing treatment time was observed. This is due to the hydrophilic groups generated at the PSF membrane surface. However, the increasing contact angle decreased

**Table III Contact Angle, Surface Energy, and Grafting Degree Results of Unmodified and Modified PSF Membranes**

	Contact Angle		$r^d$	$r^p$	$r$	$g_w$
	H <sub>2</sub> O	CH <sub>2</sub> I <sub>2</sub>				
Unmodified	74.0	43.2	28.92	13.64	42.56	0
Modified	37.2	28.1	31.43	32.37	63.80	2.7





**Figure 6** Contact angle as a function of plasma-treatment power.

sharply at the beginning of the treatment time and became stable at the later stage of the treatment time. This is because the hydrophobic groups by the introduction of PEG reached equilibrium on the PSF membrane surface and gradually developed to the inferior surface of membrane.

#### Plasma Treatment Power

The effect of the plasma treatment power, presented in Figure 6, showed a maximum contact angle at a special power. It can be explained that the energies of all kinds of particles were decided by the plasma-treatment power. When the plasma-treatment power is low, the concentration of high-energy particles increases with the growth of the treatment power. So, it is beneficial to the grafting. But, if the plasma-treatment power is over some limit, the properties of the polymer can be changed. Perhaps some small molecules can be produced. It is not beneficial to the grafting and so the contact angle was increased at high power.

## CONCLUSIONS

The goal of our work was to develop and understand the effects of a surface-modification method such as low-temperature plasma treatment and subsequent grafting for improving membrane hydrophilicity. This has been successfully accomplished using a procedure consisting of long-time immersion in PEG solutions, plasma excitation, and grafting.

The results from FTIR-ATR and XPS measurements consistently indicate that PEG can be grafted onto the surface of the PSF membrane by low-temperature plasma. The results of the contact angle and surface energy show that the surface properties of the PSF membrane changed drastically. The membranes become hydrophilic after treatment. With suitable plasma treatment, the optimal performance of the PSF membrane surface can be achieved.

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