

# Improvement of the Water Selectivity of ULTEM Poly(ether imide) Pervaporation Films by an Allylamine-Plasma-Polymerized Layer

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**ABSTRACT:** The wettability and surface energy of extruded ULTEM poly(ether imide) films strongly increased (the water contact angle varied from 75 to 38° and the surface energy varied from 45.3 to 59.5 mJ m<sup>-2</sup>, respectively) with the deposition of an allylamine-plasma-polymerized layer and were characterized with X-ray photoelectron spectroscopy, scanning electron microscopy, and atomic force microscopy according to the experimental parameters. Pervaporation tests for dehydrating the water/ethanol azeotropic mixture were performed at 40°C with nontreated and

plasma-treated ULTEM films for 15, 30, 60, and 120 min. No significant difference was noticed in the total flow (ca. 2.5 g/m<sup>2</sup> h) among the various films. However, for the 30-min duration, a great increase in the water selectivity from 850 to 10,850 was measured, and it was related to the higher N/C ratio and the presence of amide groups on the surface. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2088–2096, 2005

**Key words:** membranes; plasma polymerization; polyimides; surfaces

## INTRODUCTION

The development of dense membranes, especially for pervaporation and vapor permeation, is an area of much research. These techniques are key technologies for azeotropic separation and for the recovery of volatile organic compounds at low concentrations from water (H<sub>2</sub>O) in the strict frame of pollution prevention. There has been increased interest in these applied developments at the industrial level for the last several years.<sup>1</sup> This has been caused by the profitable energetic outcome, separation effectiveness, and clear aspects of these technologies. Polyimides, particularly polyimides based on aromatic structures, have been widely investigated in this field because these thermoplastic-glassy polymers have good chemical and thermal stability and mechanical properties.

For evaluating the behavior of pervaporation membranes, the dehydration of ethanol (EtOH) is in common use. Among the first polyimides tested for the separation of aqueous EtOH solutions, we can point out polyimides prepared by the step reaction of 3,3',4,4'-biphenyltetracarboxylic anhydride or

3,3',4,4'-benzophenontetracarboxylic anhydride with 4,4'-diaminodiphenyl ether, which brought flexibility to the macromolecular chain because of the ether linkage. Another preparation involved simultaneous deposition by vapor deposition and polymerization of the two monomers on a porous substrate.<sup>2–4</sup> A composite membrane with a deposition layer thicker than 0.2 μm exhibited an optimal separation factor or water selectivity ( $\alpha_{\text{H}_2\text{O}}$ ) of 1300 and a flow in the range of 10–40 g/m<sup>2</sup> h at 25°C.<sup>4</sup> The combination of interfacial polymerization and thermal imidization, starting from toluene-soluble 2,5-bis(methoxycarbonyl)terephthaloyl chloride and H<sub>2</sub>O-soluble diamines, was also investigated to create a composite membrane with a dense skin layer of about 1–10 μm, an  $\alpha_{\text{H}_2\text{O}}$  value of 240, and a flow of approximately 70 g/m<sup>2</sup> h at 40°C for a 10/90 (w/w) H<sub>2</sub>O/EtOH mixture.<sup>5</sup>

Briefly, the separation and transfer mechanism through the membrane can be divided into three stages: the sorption on the top face, the diffusion inside the material, and the desorption from the opposite face. The sorption is often the preferential stage that determines  $\alpha_{\text{H}_2\text{O}}$ ; indeed,  $\alpha_{\text{H}_2\text{O}}$  is well connected to the H<sub>2</sub>O swelling degree of the polymer. However, the diffusion step plays a strong role by facilitating the transfer of the small H<sub>2</sub>O molecules and should also be considered. Overall, the separation performance is depen-

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dent on the hydrophilic–hydrophobic balance of the membrane, and numerous experiments for modifying the bulk or surface of membranes have been carried out to improve their hydrophilic or hydrophobic nature.<sup>6</sup>

Poly(ether imide) (PEI; ULTEM 1000, General Electric and Plastics), prepared from bisphenol A diphthalic anhydride and *m*-phenylene diamine, has an aromatic structure and an ether linkage, which provide good processability. Its great properties make possible its use in the semiconductor and electronic-packaging industries; in membrane separation domains, it is widely studied for gas separation. For such a pervaporation membrane used to dehydrate a 10/90 (w/w) H<sub>2</sub>O/EtOH mixture,  $\alpha_{\text{H}_2\text{O}}$  of PEI can reach 350.<sup>7</sup> Various methods have been employed to improve the hydrophilicity of PEI for various applied domains. The main methods are as follows, and generally they come from the same teams. Because polyvinylpyrrolidone (PVP) is hydrophilic, it may increase the sorption coefficient of H<sub>2</sub>O when membranes are prepared with various amounts of PVP in the initial casting solution of PEI in *N*-methylpyrrolidone.<sup>8,9</sup> Moreover, blend membranes prepared from PEI and sulfonated PEI<sup>10,11</sup> with polybenzimidazole<sup>12</sup> or poly(ethylene glycol)<sup>13</sup> as a polymer additive can have improved hydrophilicity.

A recent technique involves the surface modification of a PEI membrane, with the active-layer side against a diethylene triamine solution (used as a modifier) for 120 min.<sup>14</sup> As a result of the functionalization, the wettability of the membrane was considerably pronounced after the treatment; this was shown by a strong reduction in the contact angle with long treatment times, from 75 to 20°. The hydrophilic imide group of PEI is reactive toward nucleophilic substitution at the active carbonyl group. Thus, the functionalization occurs via the nucleophilic attack of the appropriate amine on the carbonyl function in the imide moiety of the polymer chain. According to the mechanism proposed by the authors, the modification generates covalently bonded amine groups, and the hydrophobic imide group is transformed into the more hydrophilic amide group.<sup>15</sup>

During the past 2 decades, the plasma grafting and polymerization technique has been widely used to prepare permselective membranes, including reverse-osmosis, ultrafiltration, and pervaporation membranes. The plasma, obtained by the ionization of a gas or monomer vapor by means of electrical discharge at a radio frequency of 13.56 MHz, leads to a thin dense layer on a porous or dense substrate.<sup>16</sup> Surprisingly, the plasma technique has not been used to modify PEI membranes. Only a few articles cite experimental results about the plasma treatment of PEI in the field of adhesion.<sup>17,18</sup>

The aim of our work was to demonstrate that surface modification by plasma treatment is a high-performance method for increasing the hydrophilicity of PEI films and, consequently, their  $\alpha_{\text{H}_2\text{O}}$  values. For this purpose, among the hydrophilic monomers described in the scientific literature, we selected allylamine as the plasma-polymerized monomer and a PEI film 75  $\mu\text{m}$  thick. A reference PEI film with a high  $\alpha_{\text{H}_2\text{O}}$  value (850) was treated to determine more completely the ability of the allylamine-plasma layer to increase this property. The other gases and monomers that we tested (particularly argon, oxygen, H<sub>2</sub>O, and acrylic acid) were not as efficient as the allylamine-plasma treatment in improving hydrophilicity, and they had absolutely no effect on  $\alpha_{\text{H}_2\text{O}}$ . Therefore, we report only the results concerning the allylamine plasma. The H<sub>2</sub>O/EtOH azeotropic mixture was in fact used to evaluate the ability of the plasma layer of the PEI composite membrane to transfer H<sub>2</sub>O selectively. These performances, obtained under drastic experimental conditions (a thick membrane with a very high  $\alpha_{\text{H}_2\text{O}}$  value even before the plasma modification and a separation mixture containing only 4.4 wt % H<sub>2</sub>O), could be beneficial for enhancing the hydrophilicity of porous PEI membranes or in other applied domains.

## EXPERIMENTAL

PEI ULTEM 1000 films and granules and bisphenol A diphthalic anhydride were kindly supplied by General Electric and Plastics; *m*-phenylene diamine, allylamine, and *N*-methylpyrrolidinone (Aldrich Chemical Co.) were used as received.

Static contact angles with H<sub>2</sub>O and diiodomethane (Merck) were measured with a Kruss G device immediately after the drop was deposited to avoid evaporation or adsorption by the substrate. Ten measurements on different surface locations were averaged for each sample. The error of measurement was  $\pm 1^\circ$ . The surface energy ( $\gamma_s$ ) and its polar ( $\gamma_s^d$ ) and dispersive ( $\gamma_s^d$ ) components were calculated with the Owens method.<sup>19</sup> The accuracy was about  $\pm 1 \text{ mJ m}^{-2}$ .

The Fourier transform infrared (FTIR) spectra were recorded with a Bruker YEWS 48 device with an attenuated total reflectance (ATR) attachment with a KRS 5 crystal.

The X-ray photoelectron spectroscopy (XPS) surface analyses were carried out with a Surface Science Instruments M Probe spectrometer with an Al K $\alpha$  monochromatic and focalized source (10 kV, 12 mA, 600- $\mu\text{m}$  spotlight diameter, and 35° takeoff angle). The pressure was approximately  $10^{-8}$  Pa. The binding energies (BEs) were measured with reference to the aliphatic, aromatic, and contamination carbon C1s peak situated at 284.6 eV. The spectra were recorded at a constant pass energy (50 eV). A

TABLE I  
Contact Angles ( $\theta_{\text{H}_2\text{O}}$  and  $\theta_{12\text{CH}_2}$ ;  $\pm 1^\circ$ ),  $\gamma_s$  ( $\pm 1 \text{ mJ/m}^2$ ),  $\alpha_{\text{H}_2\text{O}}$ , Total Flow (at  $40^\circ\text{C}$  for a  $\text{H}_2\text{O}/\text{EtOH}$  Azeotropic Mixture), and Thickness of Dense Membranes Made by the cast-Evaporation Method from ULTEM Granules, synthesized UPEI, and Extruded PEI Film

Starting material	$\theta_{\text{H}_2\text{O}}$ ( $^\circ$ )	$\theta_{12\text{CH}_2}$ ( $^\circ$ )	$\gamma_s$ ( $\text{mJ m}^{-2}$ )	$\alpha_{\text{H}_2\text{O}}$	Total flow ( $\text{g/m}^2 \text{ h}$ )	Thickness ( $\mu\text{m}$ )
ULTEM granules	93	27	46.8	114	2–5	60–80
Synthesized UPEI	88	32	42.6	290	2–5	60–80
ULTEM film	75	32	45.3	850	2–5	75

5-eV flood gun was used to compensate for the charge effects. Experimental and theoretical (80% Gaussian and 20% Lorentzian) bands were fitted with a nonlinear baseline (Shirley type<sup>20</sup>) with a least-square algorithm. The proportions of the elements were determined on the basis of the intensity factors calculated by Scofield.<sup>21</sup> The assignment of BEs was based on the literature data.<sup>22,23</sup>

The reactor contained a pair of parallel aluminum electrodes (12 cm in diameter and 3 cm apart) coupled with an rf generator (13.56 MHz). The round samples, cut to the same size as the pervaporation cell (19.6-cm<sup>2</sup> surface), were placed on the bottom electrode. A vacuum was established at 3 Pa, and an argon-plasma pretreatment (10 W, 40 Pa, and 5 min) was performed. Allylamine vapor flow was monitored with a Pirani gauge and was regulated to obtain the desired pressure of 40 Pa. The rf power was turned on, and the plasma treatment was performed at 75 W for 15, 30, 60, and 120 min. For the completion of the treatment, the rf power was turned off, and the allylamine vapor flow was continued for 10 min more. Then, the system was pumped down to 3 Pa for about 2 h before the reactor was opened.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed at the Laboratoire de Microscopie of Montpellier II University.

Pervaporation experiments were performed with a cell of steel with two removable parts. The top part had a volume of 100 mL and contained a  $\text{H}_2\text{O}/\text{EtOH}$  (4.4 wt %/95.6 wt %) azeotropic mixture. It was connected to a 2-L flask, which provided a continuous supply of liquid. Beforehand, the ULTEM films were placed for 1 night in the azeotropic mixture for swelling, and then they were placed on the porous support of the bottom part. Repetitive gravimetric analysis did not enable us to correctly measure the swelling of the samples before and after the treatment. In any case, it was very low. The pressure downstream from the film was 2–4 mmHg. The experiment was carried out at  $40^\circ\text{C}$ , and the pervaporate was condensed with liquid air traps. The mass of the liquid condensed during given times up to 70 h continuously allowed us to calculate the total flow ( $\text{g/m}^2 \text{ h}$ ). The pervaporate was analyzed by the Karl Fisher technique (Kf 684, Metrohm) to determine the weight percentage of  $\text{H}_2\text{O}$ .

The results are expressed by  $\alpha_{\text{H}_2\text{O}} = (C'_{\text{H}_2\text{O}}/C'_{\text{EtOH}})/(C_{\text{H}_2\text{O}}/C_{\text{EtOH}})$ , where  $C'$  and  $C$  are the weight percentages of  $\text{H}_2\text{O}$  and alcohol, respectively, in the pervaporate and in the azeotropic mixture that dehydrate. The values were calculated when the system was stabilized.

Pervaporation tests were carried out with nontreated, argon-pretreated, and allylamine-treated samples. We verified that the nontreated and argon-pretreated films had the same performances; that is, the argon plasma could not change  $\alpha_{\text{H}_2\text{O}}$ .

## RESULTS AND DISCUSSION

### Preparation and plasma modification of the PEI films

To select the process leading to the reference membrane that showed the best  $\alpha_{\text{H}_2\text{O}}$  value before the plasma treatment, we compared membranes that we made ourselves, with supplied extruded PEI films kept at ambient atmospheric conditions.  $\alpha_{\text{H}_2\text{O}}$  was evaluated for the  $\text{H}_2\text{O}/\text{EtOH}$  azeotropic mixture (Table I).

Dense membranes were prepared from supplied PEI granules and also from PEI obtained in our laboratory with a similar structure (UPEI) by a two-step polymerization of bisphenol A diphthalic anhydride and *m*-phenylene diamine according to the well-known synthesis. The cast-evaporation technique was carried out with a 25 wt % polymer solution in *N*-methylpyrrolidone. The solution, slowly stirred at  $80^\circ\text{C}$  for 4 h, was cast onto a glass plate and dried at  $120^\circ\text{C}$  *in vacuo* for 24 h.

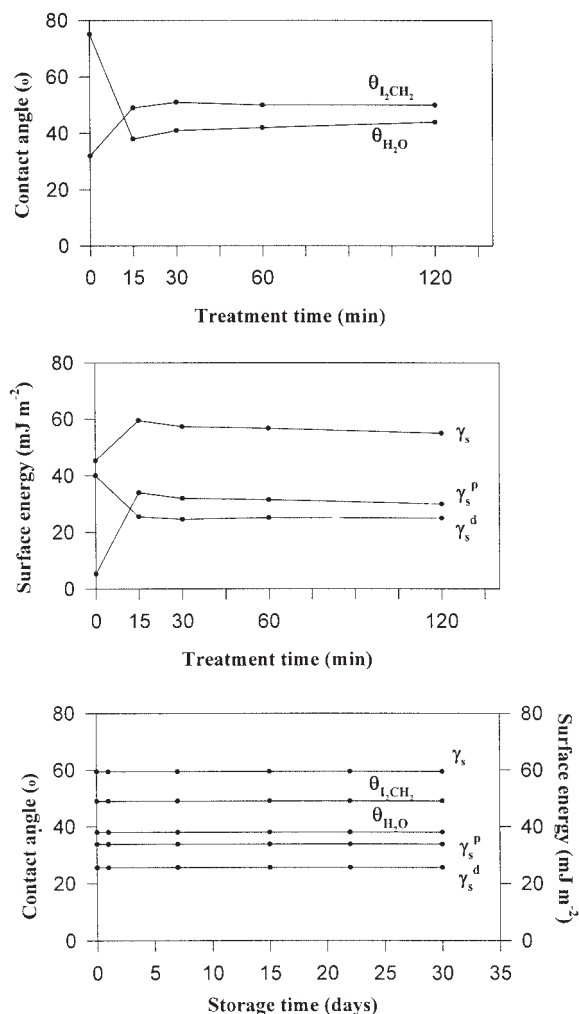
The  $\gamma_s$  values and the thicknesses were close for the three samples, but the marketed PEI film yielded the greatest value  $\alpha_{\text{H}_2\text{O}}$ , about 850. This high value could be explained by the very consistent structure of the bulk and the constant thickness of the film due to the homogeneous temperature and composition of the matter during the extrusion, which led to a good-quality film. No samples among the membranes that we made by varying the cast-evaporation parameters (essentially the time and the temperature of drying) showed an  $\alpha_{\text{H}_2\text{O}}$  value greater than 290. This method led to the formation of structural flaws notably related

to the difficult control of the experimental conditions (the evaporation rate of the solvent and the ambient moisture).

The wettability [water contact angle ( $\theta_{\text{H}_2\text{O}}$ ) = 75°], the density, and the suitable interchain accessible volume for the  $\text{H}_2\text{O}$ -molecule transfer could properly account for the best  $\alpha_{\text{H}_2\text{O}}$  value of the homogeneous film. As a result, the film tended to have a low flow, as discussed later. These preliminary results confirmed for us that the allylamine-plasma polymerization could improve  $\alpha_{\text{H}_2\text{O}}$  by combining the expected good hydrophilicity of the deposited superficial layer with the optimized density of the polymer support. Therefore, the surface modification of the marketed PEI film was studied. We performed long-duration treatments to obtain a layer thick enough to affect the pervaporative transfer at the risk of preparing a fragile layer because of a lack of cohesion. The power and the monomer vapor pressure were tested in the range of 20–100 W and in the range of 20–50 Pa, respectively, to find the most homogeneous and easily reproducible glow discharge in the 3-L reactor. The minimum  $\theta_{\text{H}_2\text{O}}$  value and the maximum  $\gamma_s$  and  $\gamma_s^p$  values were obtained at 75 W and 40 Pa, and they demonstrated the optimized hydrophilicity of the plasma-treated film. The thickness and its regularity and the homogeneous texture of the plasma layer increased with the treatment duration, which was at least 15 min. As shown in Figure 1(a,b),  $\theta_{\text{H}_2\text{O}}$  decreased from 75 to 38° and  $\gamma_s$  increased (because of an increase in  $\gamma_s^p$ ) from 45.3 to 59.5  $\text{mJ m}^{-2}$  for the nontreated and treated films, respectively. Beyond 15 min,  $\theta_{\text{H}_2\text{O}}$  and  $\gamma_s$  roughly stabilized. Generally, one of the main criticisms against plasma modification is the partial loss of hydrophilicity due to macromolecular chain movement and functional group reorientation onto the surface. For the allylamine-plasma polymerization developed in our study, the properties of the coating were permanent, and this means that the crosslinked structure of the coating was not affected by the storage time under ambient conditions [Fig. 1(c)].

### XPS analysis

The XPS analysis of the reference sample (nontreated PEI film) was in good agreement with the expected values for BE and the atomic percentages of the elements (Table II). The high-resolution C1s spectrum could be resolved into three peaks, with a relative surface area that seemed suitable in light of the likely contamination. The first at 284.6 eV corresponded to aromatic and aliphatic carbons 1, 2, and 3 and contamination carbon; the second at 286.2 eV corresponded to carbons 4 and 5 bonded to nitrogen and to oxygen 2. The peak at 288.3 eV was assigned to the  $\text{O}=\text{C}-\text{N}$  imide groups. The wide and asymmetrical O1s spectrum could be curve-fitted in two peaks at-



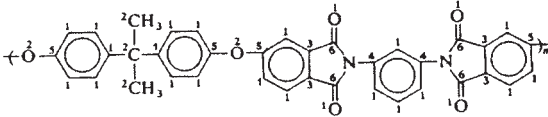
**Figure 1** Contact angles and  $\gamma_s$ ,  $\gamma_s^d$ , and  $\gamma_s^p$  values ( $\pm 1 \text{ mJ m}^{-2}$ ) for allylamine-plasma-treated PEI films versus (a,b) the treatment time and (c) the storage time under ambient conditions for a 30-min plasma treatment.

tributed to  $\text{O}=\text{C}-\text{N}$  at 531.7 eV and  $\text{O}-\text{C}$  at 533.2 eV. The surface area percentage should have been 66–33, whereas about 70–30 was obtained; this was a satisfactory proportion. The N1s peak at 400.3 eV was obviously attributable to  $\text{O}=\text{C}-\text{N}-\text{C}=\text{O}$ .

The surface concentration of nitrogen strongly increased after the allylamine-plasma treatment (Table III). On the C1s spectra (Fig. 2), the characteristic peak of the  $\text{N}-\text{C}=\text{O}$  imide group located at 288.3 eV disappeared. The peak in the range of 285.9–286.1 eV could be attributed to  $\text{C}-\text{N}$  and  $\text{C}-\text{O}$  groups but preferably to the  $\text{C}-\text{N}$  group in light of the highest N atom percentage for 15, 30, and 60 min and otherwise to  $\text{C}-\text{O}$  for 120 min. We noticed a new peak in the range of 287.0–287.3 for all durations, which was attributed to  $\text{O}-\text{C}-\text{O}$ ,  $\text{N}-\text{C}-\text{O}$ , or  $\text{C}=\text{O}$ . Another new peak appeared in the range of 288.1–288.6 eV, showing a shift to a higher BE for 30, 60, and 120 min. This new peak could be attrib-



TABLE II  
BEs and Atomic Percentages of Elements of the PEI Reference Film



Atomic element	1	2	3	4	5	6	1	2	N1s
BE (eV)	284.6			286.2		288.3	531.7	533.2	400.3
Experimental atom %	72			7		4	9.5	4	3.5
Theoretical atom %	60.0			13.3		8.9	8.9	4.4	4.4

uted to the N—C=O amide group and/or the O—C=O ester group, which bore out the oxidation of the layer. According to the increase in the corresponding energy (from 288.1 to 288.6 eV), the population of ester groups increased with the treatment time, in agreement with the increase in the oxygen concentration. The origin of the incorporated oxygen was widely solved by the combination of residual oxygen inside the reactor with allylamine species during the plasma treatment and by, more than anything, the reaction of atmospheric oxygen with the still active plasma layer even pumping down the system before the reactor was opened.

The O1s spectrum showed two resolved peaks, at 530.6–531.4 and 532.0–532.8 eV, lower than those of the PEI reference, and this confirmed the probable presence of N—C=O, O—C=O, and C—O groups different from the initial imide group.

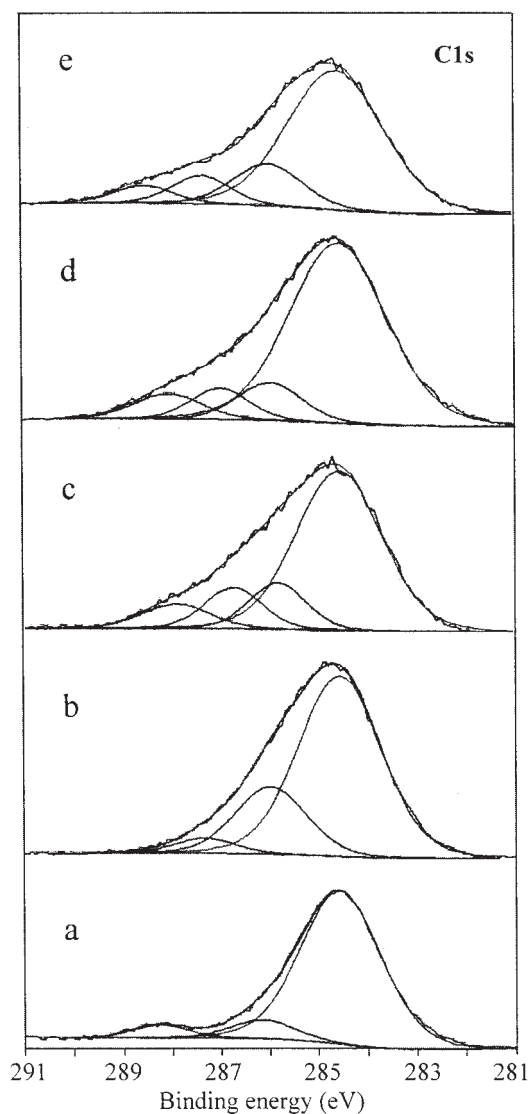
The most obvious modification concerned the N1s spectrum. The N1s peak of the nontreated sample

was sharp and symmetric, whereas it became broad and shifted toward lower BEs after treatment (Fig. 3). This broadening showed the presence of several types of nitrogen. The maximum of this band was shifted toward higher energies when the treatment time increased. This observation was in agreement with the increase in the oxygen concentration. Thus, the N1s band could be associated with C—N groups (BE ~ 399 eV) and N—C=O amide groups (BE ~ 400 eV), the latter increasing with the treatment time.

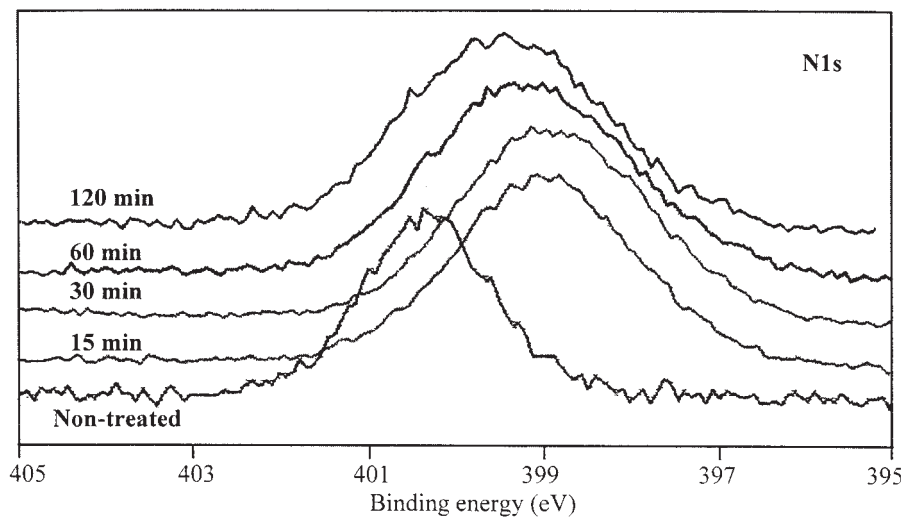
Unfortunately, no real evidence for amide and ester groups, no N—H clear-cut absorption band, could be detected in the FTIR-ATR spectra (not shown) because the nontreated and treated PEI spectra were similar. This difficulty could be related to the similarity of the functional groups in both samples and to the FTIR-ATR technique itself. Indeed, the IR beam often crossed the weak thickness layer and reached the support below it. Additional attempts to highlight and

TABLE III  
Functional Groups, Approximative BEs, and C1s, O1s, and N1s Atomic Percentages of the PEI Reference and Allylamine-Treated PEI Films (75 W, 40 Pa) for 15, 30, 60, and 120 min

Functional groups	Allylamine-plasma-treatment time									
	Reference		15 min		30 min		60 min		120 min	
	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %
C1s										
C=C, C—C	284.6	72	284.6	62	284.6	50	284.6	55	284.6	48
C—N, C—O	286.2	7	286.1	15	285.9	10	286.1	10	286.0	12
O(N)—C—O or C=O			287.3	4	287.0	8	287.3	6	287.3	6
O=C—N—C=O	288.3	4								
N—C=O, O—C=O					288.1	5	288.4	3	288.6	5
C atom %		83		81		73		74		71
O1s										
O=C	531.7	9.5	531.2	4	530.6	5	530.7	4	531.4	11
O—C	533.2	4	532.3	1.5	532.0	4	532.1	7	532.8	8
O atom %		13.5		5.5		9		11		19
N1s										
C—N, N—C=O			399.0		398.9		399.2		399.5	
O=C—N—C=O	400.3									
N atom %		3.5		13.5		18		15		10



**Figure 2** C1s XPS spectra of (a) the PEI reference film and (b–e) films treated with allylamine plasma for 15, 30, 60, and 120 min, respectively.



**Figure 3** N1s XPS spectra of the PEI reference film and films treated with allylamine plasma for 15, 30, 60, and 120 min.

determine the amine content by protonation<sup>14</sup> did not allow us to clearly confirm this.

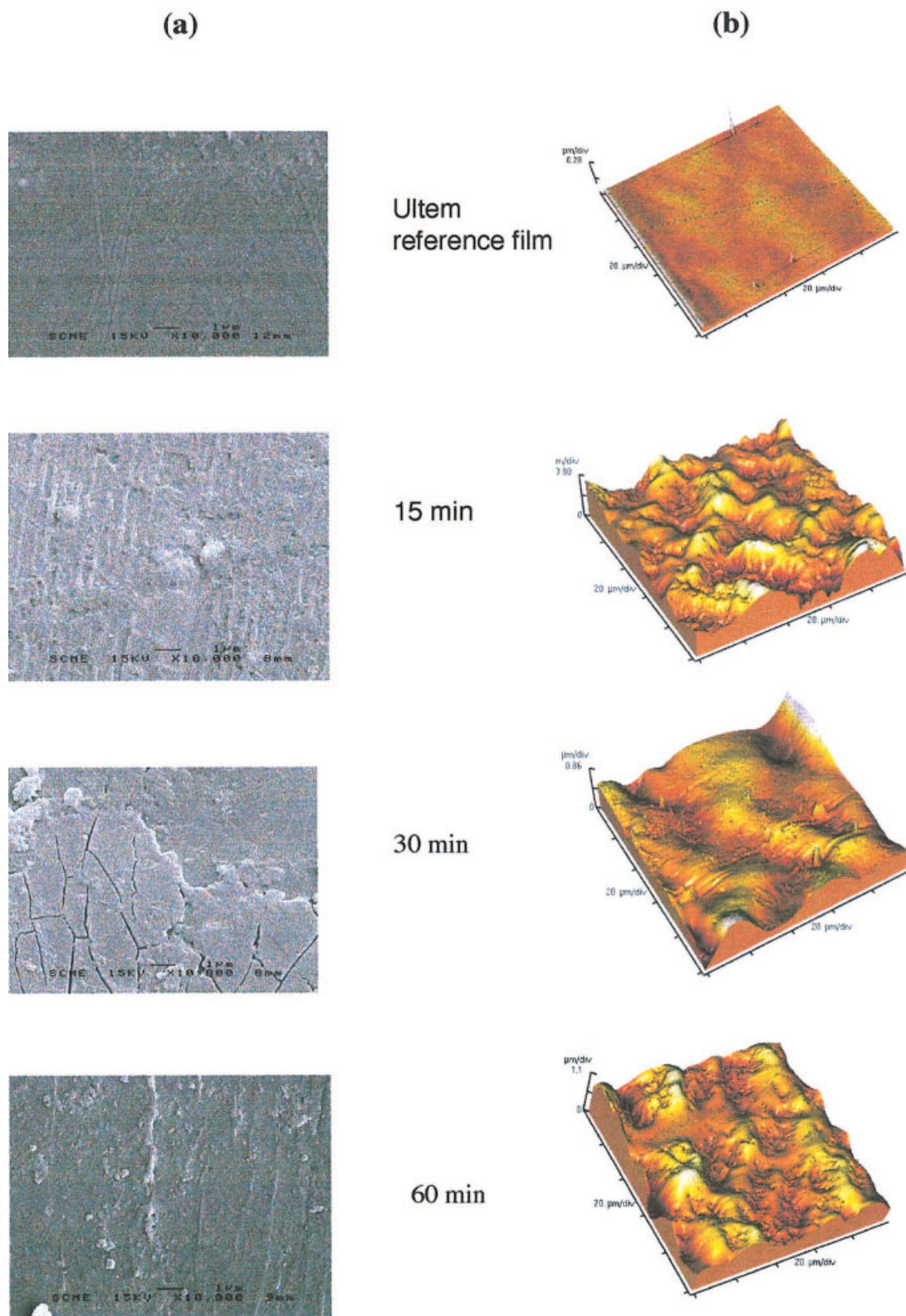
It is well known that the structure of a plasma deposited layer is strongly dependent on the processing parameters. Moreover, the XPS analysis has to be carefully manipulated. Nevertheless, we can suggest in a logical way that 75-W and 40-Pa allylamine plasma can form a layer containing an amide group, an ester group, or both.

#### SEM and AFM

SEM and AFM views showed a smooth and homogeneous surface that turned into a rough surface by plasma treatment (Fig. 4). In places, we found slightly cracked domains with limited surface area because of the relaxation of high tension in a too thick localized layer. The thickness range of 0.2–0.6  $\mu\text{m}$  usually increased with the treatment duration, and this led to thick plasma layers characterized by a poor mechanical strength and a weaker density than those at the beginning of the deposition.

#### Pervaporation tests at 40°C

Pervaporation tests for dehydrating the H<sub>2</sub>O/EtOH azeotropic mixture were carried out at 40°C to make possible a more rigorous temperature control than the ambient temperature. This selected temperature was lower than the boiling point of the azeotrope (78.2°C) and brought no negative implications to the mechanical behavior of the samples, given that PEI is an amorphous–vitreous solid (glass-transition temperature = 217°C) under such conditions. As expected from the density and the compaction of the film support, the total flow remained weak, and no significant difference was noticed between the non-

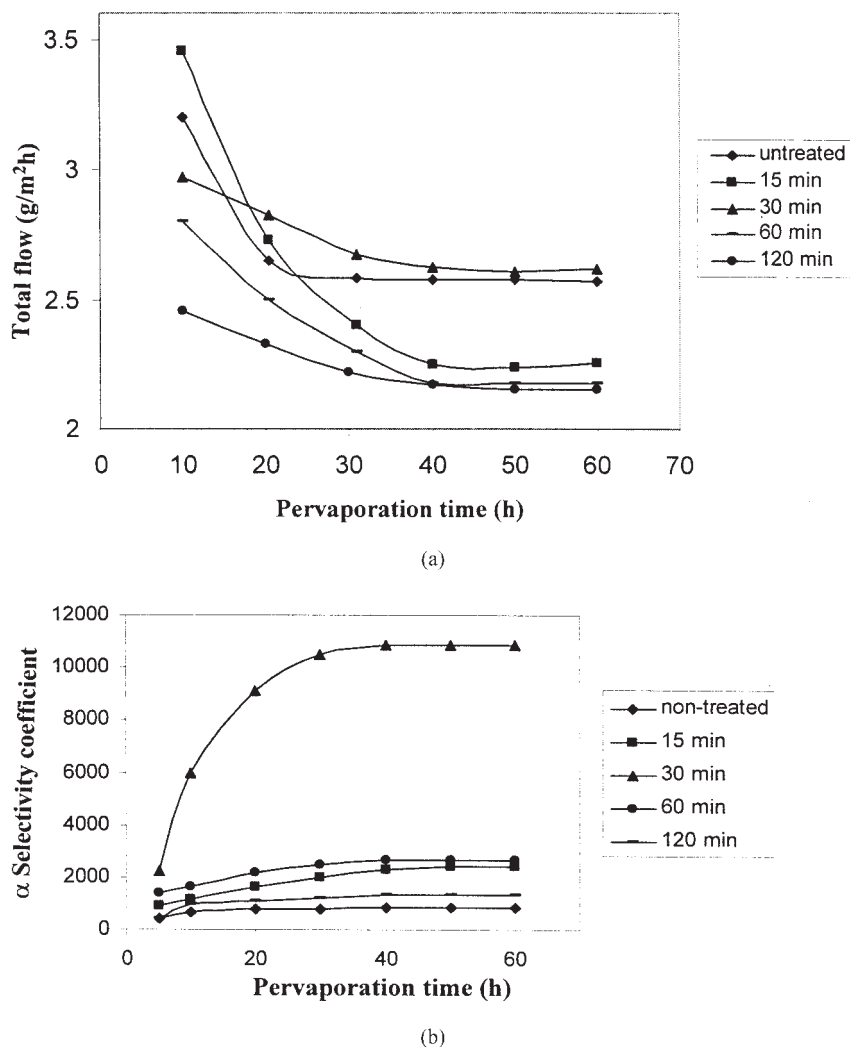


**Figure 4** (a) SEM and (b) AFM photographs of the PEI reference film and films treated with allylamine plasma for 15, 30, and 60 min.

treated and treated PEI films for various durations [Fig. 5(a)].

In all cases, the total flow regularly decreased for 20–30 h before being stabilized when the steady state of the trans-

fer was established. The structural characteristics of the film support seemed to limit the diffusion of molecules, particularly the almost complete lack of swelling even after a 12-h soaking of the film in the azeotropic mixture. The slight



**Figure 5** (a) Total flow and (b)  $\alpha_{\text{H}_2\text{O}}$  at 40°C versus the pervaporation time of a H<sub>2</sub>O/EtOH azeotropic mixture for the PEI reference film and films treated with allylamine plasma for 15, 30, 60, and 120 min.

reduction in flow of approximately 0.5 g/m<sup>2</sup> for the first pervaporation hours could be partially related to the draining of the sorbed liquid.

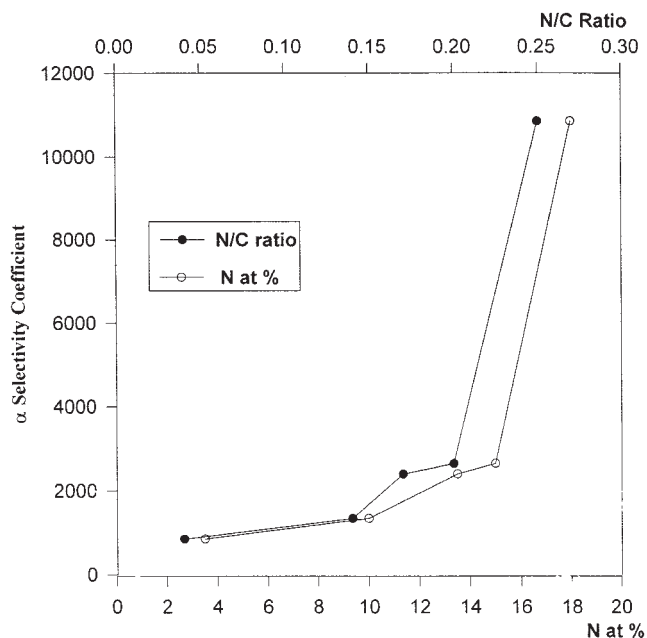
In contrast,  $\alpha_{\text{H}_2\text{O}}$  of the treated films was higher and had a stabilized optimal value for a 30-min plasma treatment [Fig. 5(b)]. There is no doubt about the role of the hydrophilic plasma layer in making the sorption of H<sub>2</sub>O molecules easier than the sorption of EtOH molecules. The H<sub>2</sub>O/EtOH liquid mixture should have been approximately 0.2/99.8 (i.e.,  $\alpha_{\text{H}_2\text{O}} = 10,850$ ) in the swollen allylamine-plasma layer. However, the diffusion through highly rigid PEI also contributed to the selective transfer of the H<sub>2</sub>O molecules because of the very different sizes of the H<sub>2</sub>O and EtOH molecules. A thorough analysis of the prevalence of the two elementary steps for the global mass transfer would require complementary sorption experiments.  $\alpha_{\text{H}_2\text{O}}$  increased from 850 to 10,850 according to the increases in the N atom percentage and N/C ratio and reached an optimal value at 18 atom % N and an N/C ratio of

0.25 for the 30-min duration (Fig. 6), which gave the best swollen layer. The other combinations that we tried [O atom percentage and O/C, (O + N)/C, and N/O ratios] did not lead to a such satisfactory correlation with  $\alpha_{\text{H}_2\text{O}}$ . The  $\alpha_{\text{H}_2\text{O}}$  increase and the swelling ability seemed to depend more on the presence of an amide group than on the presence of an ester group. Indeed, it seems that the amide group was present in a higher percentage than the ester group for 30 min if we consider the XPS results and the strong oxidation following the plasma treatment longer than 30 min. The  $\alpha_{\text{H}_2\text{O}}$  value can be probably related to the difference in the hydrophilicity between these groups and to the ability to create hydrogen bonding.

## CONCLUSIONS

We showed that the good  $\alpha_{\text{H}_2\text{O}}$  value of an extruded PEI film could be increased from 850 to 10,850; in other words, the H<sub>2</sub>O weight percentage in the pervaporate





**Figure 6**  $\alpha_{\text{H}_2\text{O}}$  for a  $\text{H}_2\text{O}/\text{EtOH}$  azeotropic mixture versus the atomic percentage of N and the N/C ratio of the reference and allylamine-plasma-treated PEI films.

increased from 97.5 to 99.8 without a significant change in the flow ( $2.5 \text{ g}/\text{m}^2 \text{ h}$  at  $40^\circ\text{C}$ ). This improvement at first sight seems to be modest; nevertheless, it is of great interest in a concentration range of the  $\text{H}_2\text{O}/\text{EtOH}$  mixture above the azeotropic concentration that is admitted as a test mixture. This result, better than the one cited in the reference, has its origins in the wettability and  $\gamma_s$  value of the allylamine-plasma-polymerized layer. The best deposition conditions were 75 W, 40 Pa, and 30 min, which led to the strongest N/C ratio that showed a large proportion of amide functional groups. During the glow discharge, the allylamine monomer ( $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{NH}_2$ ,  $\text{C}_3\text{H}_7\text{N}$ ) polymerized via a crosslinked structure with 73, 9, and 18 atom % C, O, and N, respectively, or just  $(\text{C}_7\text{ON}_2)_n$ .

The properties of this allylamine-polymerized layer can be worked for other separation techniques with PEI porous membranes (e.g., ultrafiltration and microfiltration) and in other industrial applications.

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