Improvement of the water selectivity of ULTEM poly(ether imide) pervaporation films by an allylamine-plasma-polymerized layer
Meriyam Kaba, Nabil Raklaoui, Marie Françoise Guimon, André Mas

To cite this version:
Meriyam Kaba, Nabil Raklaoui, Marie Françoise Guimon, André Mas. Improvement of the water selectivity of ULTEM poly(ether imide) pervaporation films by an allylamine-plasma-polymerized layer. Journal of Applied Polymer Science, Wiley, 2005, 97 (5), pp.2088-2096. 10.1002/app.21684. hal-00383332

HAL Id: hal-00383332
https://hal.archives-ouvertes.fr/hal-00383332
Submitted on 12 May 2009

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Improvement of water selectivity of ULTEM polyetherimide pervaporation film by an allylamine plasma-polymerized layer

M. Kaba 1, N. Raklaoui 1, M.-F. Guimon 2, A. Mas 1

1 Organisation Moléculaire, Evolution et Matériaux Fluorés UMR 5073 CNRS, USTL Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

2 Laboratoire de Physico-Chimie Moléculaire UMR 5624 CNRS, Hélioparc Pau-Pyrénées, Avenue du Président-Angot, 64053 Pau Cedex 9, France

Abstract

The wettability and surface energy of extruded ULTEM polyetherimide film were strongly increased (θH2O varies from 75° to 38° and γs varies from 45.3 to 59.5 mJ m⁻² ) by depositing an allylamine plasma-polymerized layer characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM) according to the experimental parameters. Pervaporation tests for dehydrating the H₂O/EtOH azeotropic mixture were performed at 40 °C using non-treated and ULTEM plasma-treated films for 15, 30, 60 and 120 min. No significant difference was noticed in total flow (about 2.5 g/m²h) between the various films. However for 30 min duration a great increase of the selectivity αH₂O from 850 to 10850 was measured and related to the higher N/C ratio and the presence of amide group onto the surface.

* Correspondence to: A. Mas (mas@univ-montp2.fr)

Key words: plasma polymerization, membranes, polyimides, surfaces.
1. Introduction

The development of dense membranes specially for pervaporation and vapour permeation is the subject of a large research. These techniques are key technologies for azeotropic separation and for the recovery of volatile organic compounds at low concentration from water in the strict frame of the pollution prevention. An increase in interest for these applied developments at industrial level was noticed for the last years.¹ This updating was caused by the profitable energetic outcome, separation effectiveness and clear aspect of these technologies. Polyimides, more particularly polyimides based on aromatic structure, are widely investigated in this field because these thermoplastic-glassy polymers own good chemical and thermal stability and mechanical properties.

To evaluate the behaviour of a pervaporation membrane, the dehydration of ethanol is in common use. Among the first polyimides tested for the separation of aqueous ethanol solutions, we can point out the polyimides prepared by step-reaction of 3,3’,4,4’-biphenyltetracarboxylic anhydride (BPDA) or 3,3’,4,4’-benzophenonetetracarboxylic anhydride (BTDA) with 4,4’-diaminodiphenyl ether (ODA) that brings flexibility to the macromolecular chain thanks to the ether linkage. Another preparation involved the simultaneous deposition by vapour deposition and polymerization (VDP) of the two monomers on a porous substrate.²-⁴ The 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/m²h at 25 °C.⁴ The combination of interfacial polymerization and thermal imidization starting from 2,5-bis(methoxycarbonyl)terephthaloylchloride (BMTC) soluble in toluene and water-soluble diamines was also investigated to elaborate a composite membrane with a dense skin layer of about 1-10 μm showing \( \alpha_{\text{H}_2\text{O}} = 240 \) and a flow about 70 g/m²h at 40 °C for the 10/90 w/w H₂O/EtOH mixture.⁵

Briefly, the separation and transfer mechanism through the membrane is divided in 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 which determines the selectivity, indeed the selectivity is well-connected to the water swelling degree of the polymer. However the diffusion step plays a strong role by facilitating the transfer of the small water molecules and should be also considered. Overall, the separation performances are dependent on the hydrophilic-hydrophobic balance of the membrane and numerous experimentations for modifying the bulk or the surface of membranes have been carried out to improve the hydrophilic or hydrophobic nature of them.⁶
The polyetherimide (PEI, ULTEM 1000) prepared from bisphenol-A diphthalic anhydride (BPDA) and m-phenylene diamine (m-PDA) has also an aromatic structure as well as an ether linkage that provide good processability. Its great properties made it possible to use it in semiconductor and electronic packaging industry; in membrane separation domains it is widely studied for gas separation. As such pervaporation membrane for dehydrating the 10/90 w/w H₂O/EtOH mixture, \( \alpha_{\text{H}_2\text{O}} \) of PEI reaches 350. Various methods have been employed to improve the hydrophilicity of PEI for various applied domains. The main methods are following, generally they come from the same teams. Since polyvinylpyrrolidone (PVP) is hydrophilic, it may increase the sorption coefficient of water when membranes are prepared with varying amounts of PVP in the initial casting solution of PEI in N-methylpyrrolidone (NMP). It was also found that blend membranes prepared from PEI and sulfonated polyetherimide as well as polybenzimidazole or poly(ethylene glycol) as polymer additives, led to the improvement of hydrophilicity.

A recent technique involves a surface modification of PEI membrane at the active-layer side being against a diethylene triamine (DETA) solution as modifier until 120 min. As a consequence of the functionalization, the wettability of membranes was considerably pronounced after treatment, which was shown by a strong reduction in contact angle with long treatment times from 75° to 20°. The hydrophilic imide group of PEI is reactive towards nucleophilic substitution at the activated carbonyl group. Thus the functionalization occurs via 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 bond amine groups and the hydrophobic imide group is transformed into the more hydrophilic amide group.

During the two past decades, the plasma grafting and polymerization technique was widely used to prepare permselective membranes including reverse osmosis, ultrafiltration and pervaporation membranes. The plasma being obtained by the ionisation of a gas or monomer vapour by means of electrical discharge at rf 13.56 MHz leads to a thin dense layer upon a porous or dense substrate. Surprisingly, the plasma technique was not used to modify the PEI membranes. Only a few articles cite experimental results about plasma treatment of PEI in adhesion field.

The aim of our work was to investigate and to show that the surface modification by plasma treatment is a high-performance method to increase the hydrophilicity of PEI film and, consequently, its water selectivity. For this purpose, among the hydrophilic monomers described in the scientific literature, we selected allylamine as plasma-polymerized monomer.
and PEI film 75 μm thick. Reference PEI film with high water selectivity \((\alpha_{H2O} = 850)\) was treated to point out more completely the ability of the allylamine plasma layer to increase this property. The other gas and monomers that we tested (particularly argon, oxygen, water, acrylic acid...) were not as efficient as allylamine plasma treatment in improving hydrophilicity and they yield absolutely no effect on selectivity. So we report only the results concerning the allylamine plasma. The H2O/EtOH azeotropic mixture is in fact used to evaluate the ability of the plasma layer of the PEI composite membrane to transfer water selectively. These performances obtained by working under drastic experimental conditions (a thick membrane with a very high selectivity even before the plasma modification and a mixture to separate containing only 4.4 %w water) could be of benefit to enhance the hydrophilicity of porous PEI membranes or in other kinds of applied domains.

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

Static contact angles with water 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 ±1°. Surface energy \((\gamma_s)\), polar \((\gamma_s^p)\) and dispersive \((\gamma_s^d)\) components were calculated with the Owens method.\(^{19}\) The accuracy was about ±1mJ m\(^{-2}\).

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

The X-ray photoelectron spectroscopy (XPS) surface analyses were carried out with a Surface Science Instruments spectrometer, M Probe model, using the AlKα monochromatic and focalized source (10 KV, 12 mA, 600 μm spotlight diameter, take-off angle 35°). The pressure used was about 10\(^{-8}\) Pa. Binding energies (BE) were measured with reference to the aliphatic, aromatic and contamination carbons C1s peak situated at 284.6 eV. The spectra were recorded at constant pass energy (50 eV). A 5 eV flood gun was used to compensate the charge effects. Experimental and theoretical (80% Gaussian, 20% Lorentzian) bands were fitted using non-linear baseline (Shirley type\(^{20}\)) with a least-square algorithm. The proportions of the elements were determined on the basis of the intensity factors calculated by Scofield\(^{21}\).

The assignment of binding energies was based on the literature data.\(^{22,23}\)
The reactor contains a pair of parallel aluminium electrodes (12 cm in diameter, 3 cm distance) coupled with a rf generator (13.56 MHz). The round samples cut at the same size as the pervaporation cell (19.6 cm² surface) are placed on the bottom electrode. Vacuum was established at 3 Pa and an argon plasma pre-treatment (10 W, 40 Pa, 5 min) was made. Allylamine vapour flow was monitored with a Pirani gauge and was regulated to obtain the desired pressure 40 Pa. The rf power was turned on and the plasma treatment was performed at 75 W for 15, 30, 60 and 120 min. To complete the treatment, the rf power was turned off and the allylamine vapour flow was pursued for 10 more min. Then the system was pumped down to 3 Pa for about 2 hours before the reactor was opened.

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were performed at the Laboratoire de Microscopie of the Montpellier II University.

Pervaporation experiments were achieved using a cell of steel with two removable parts. The top part had a volume of 100 ml and contained the H₂O/EtOH (4.4/95.6 weight %) azeotropic mixture. It was connected to a 2 l flask to provide a continuous supply of liquid. Beforehand the ULTEM films were put one night in the azeotropic mixture for swelling 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 treatment. In any case it is very low. The pressure downstream from the film was 2-4 mm Hg. The experiment was carried out at 40 °C and the pervaporate was condensed using liquid air traps. The mass of the liquid condensed during given times up to 70 h continuously allowed us to calculate the total flow (g/m²h). The pervaporate was analyzed by the Karl Fisher technique (Metrohm, Kf 684) in order to determine the weight percentage of water.

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

Pervaporation tests were carried out with non-treated, argon pretreated and allylamine treated samples. We verified that non-treated and argon pretreated films had the same performances, ie argon plasma can not change the water selectivity.

3. Results and discussion

Preparation and plasma modification of PEI film
In order to select the process leading to the reference membrane that showed the best selectivity before plasma treatment we compared membranes that we did ourselves, with supplied extruded-PEI films then kept at ambient atmospheric conditions. The selectivity of water ($\alpha_{\text{H}_2\text{O}}$) was evaluated in the case of H$_2$O/EtOH azeotropic mixture (Tab. 1).

Dense membranes were prepared from supplied PEI granules and also from polyetherimide obtained in our laboratory with a similar structure (called UPEI) by two-step polymerization of BAPA and m-PDA according to the well-know synthesis. The cast-evaporating technique was carried out using a 25 % weight polymer solution in NMP. The slow-stirred solution at 80 °C for 4 h was cast on a glass plate and dried at 120 °C under vacuum for 24 h.

The surface energy and the thickness are close for the three samples, however marketed PEI film yield the $\alpha_{\text{H}_2\text{O}}$ greatest value about 850. This high value can be explained by considering the very consistent structure of the bulk and the constant thickness of the film because of the homogeneous temperature and composition of the matter during the extrusion that lead to a good-quality film. No samples among the membranes that we did by varying the cast-evaporating parameters (essentially the time and the temperature of drying) showed a $\alpha_{\text{H}_2\text{O}}$ greater than 290. This method led to the formation of structural flaws notably related to a difficult control of the experimental conditions (evaporation rate of the solvent, ambient moisture).

The wettability ($\theta_{\text{H}_2\text{O}} = 75^\circ$), the density and the suitable interchain accessible volume for the H$_2$O molecules transfer can properly account for the best selectivity of the homogenous film. As a result, the film tends to have a low flow as mentioned below. These preliminary results confirmed us in such opinion as the allylamine plasma-polymerization could improve the selectivity by combining the expected good hydrophilicity of the deposited superficial layer with the optimized density of the polymer support. Therefore the surface modification of marketed PEI film was studied. We did long duration treatments in order to obtain layer thick enough to affect the pervaporative transfer at the risk of preparing a fragile layer possibly due to a lack of cohesion. The power and the monomer vapour pressure were experimented in the range of 20-100 W and 20-50 Pa respectively in order to find the most homogenous and easily reproducible glow discharge in the 3 l reactor. The $\theta_{\text{H}_2\text{O}}$ minimal value and the $\gamma_s, \gamma_s^p$ maximal values were obtained from 75 W, 40 Pa processing parameters and testify to the optimized hydrophilicity of the plasma treated film. The thickness and its regularity as well as the homogenous texture of the plasma layer increased with the treatment duration that should be at least 15 min. As shown in Fig. 1ab, $\theta_{\text{H}_2\text{O}}$ decreases from 75° to 38° and $\gamma_s$ increases (due to
γ_s increased from 45.3 to 59.5 mJ m⁻² for non-treated and treated film respectively. Above 15 min, θ_H₂O and γ_s are roughly stabilized. Generally one of main criticism against the plasma modification is the partial loss of hydrophilicity because of macromolecular chain movement and functional groups reorientation onto the surface. In the case of allylamine plasma polymerization developed in our study, the properties of the coating were permanent which means that the cross-linked structure of the coating is not affected by the storage time in ambient conditions (Fig. 1c).

**XPS analysis**

XPS analysis of reference sample (non-treated PEI film) is in good agreement with the expected values for the binding energies (BE) and the percentages (at %) of the elements (Tab. 2). The high resolution C1s spectrum can be resolved in three peaks with a relative surface area that seems suitable considering the likely contamination. The first at 284.6 eV corresponds to aromatic and aliphatic carbons 1, 2, 3 and contamination carbon; the second at 286.2 eV to carbons 4 and 5 bonded to nitrogen and to oxygen; the peak at 288.3 eV is assigned to the O=C-N imide groups. The wide and asymmetrical O1s spectrum can be curve-fitted in two peaks attributed to O=C-N at 531.7 eV and O-C at 533.2 eV. The surface area percentage should be 66-33 whereas about 70-30 was obtained, that is a satisfactory proportion. The N1s peak at 400.3 eV was obviously attributed to O=C-N-C=O.

Surface concentration of nitrogen strongly increases following the allylamine plasma treatment (Tab. 3). On the C1s spectra (Fig. 2) the characteristic peak of the N-C=O imide group located at 288.3 eV disappeared. The peak in the range 285.9-286.1 eV can be attributed to C-N and C-O groups but preferably to C-N group considering the highest N at % for 15, 30 and 60 min and otherwise to C-O for 120 min. We noticed a new peak in the range 287.0-287.3 for all duration, attributed to O-C-O, N-C-O or C=O. Another new peak appeared in the range 288.1-288.6 eV, showing a shift to higher BE for 30, 60 and 120 min. This new peak could be attributed to N-C=O amide group and/or O-C=O ester group that bore out the oxidation of the layer. According to the increase of corresponding energy (from 288.1 eV to 288.6 eV), it seems that the population of ester groups increases with the time of treatment, in agreement with the increase in 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 as well as, more than anything, by 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 eV and 532.0-532.8 eV lower than those of PEI reference, this confirms the probable presence of N-C=O, O-C=O, C-O groups different from the initial imide group.

The most obvious modification concerns the N1s spectrum. The N1s peak of non-treated sample is sharp and symmetric whereas it becomes broad and shifts toward lower binding energies after treatment (Fig. 3). This broadening shows the presence of several types of nitrogen. The maximum of this band is shifted toward higher energies when the treatment time increases. This observation is in agreement with the increase of the oxygen concentration. Thus, the N1s band could be associated with C-N groups (BE at about 399 eV) and N-C=O amide groups (BE at about 400 eV), this latter increasing with the treatment time.

Unfortunately no real evidence for amide and/or ester groups, no N-H clear-cut absorption band, could be detected on FTIR-ATR spectra (not shown) because the non-treated and treated PEI spectra appear similar. This difficulty can be related to the similarity of the functional groups in both samples as well as to the FTIR-ATR technique itself. Indeed the IR beam often crosses the weak-thickness layer and reaches the support below. Additional attempts to highlight and determine amine content by protonation did not allow us to clearly confirm.

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

**Scanning Electron and Atomic Force Microscopies**
SEM and AFM views showed a smooth and homogenous surface that turned into a rough surface by plasma treatment (Fig. 3). 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 0.2-0.6 μm usually increased with the treatment duration leading to thick plasma layers characterized by a poor mechanical strength and a weaker density than at the beginning of the deposition.

**Pervaporation tests at 40 °C**
Pervaporation tests for dehydrating H2O/EtOH azeotropic mixture were carried out at 40 °C to make it possible a more rigorous temperature control than at ambient temperature. This selected temperature was lower than the boiling point of the azeotrope (78.2 °C) and brought...
no negative implication on the mechanical behaviour of the samples given that PEI is an amorphous-vitrous solid (glass temperature Tg = 217 °C) in such conditions. As expected by considering the density and the compaction of the film support, the total flow remained weak and no significant difference was noticed between the non-treated and treated PEI films for various durations (Fig. 5a).

In all cases the total flow regularly decreased for 20-30 hours before being stabilized when the steady-state of the transfer was established. The structural characteristics of the film support seem to put up a limit for the diffusion of molecules, mainly the almost lack of swelling even after 12 hours soaking the film in the azeotropic mixture. The slight reduction in flow about 0.5 g/m²h for the first pervaporation hours could be partly related to the draining of the sorbed liquid.

In contrast the water selectivity of the treated films is higher and took a stabilized optimal value for a 30 min plasma treatment (Fig. 4b). There is no doubt about the role of the hydrophilic plasma layer in making easier the sorption of H₂O molecules than the EtOH molecules. The H₂O/EtOH liquid mixture should be about 0.2/99.8 (that is α_{H₂O} = 10850) in the swollen allylamine plasma layer. However, the diffusion through the highly rigid PEI also contribute to the selective transfer of the water molecules owing to the very different sizes of H₂O and EtOH molecules. A thorough analysis of the prevailing of either of both elementary steps on the global mass transfer would require complementary sorption experiments.

α_{H₂O} increases from 850 to 10850 according to the N at % and N/C ratio increases and reaches an optimal value for N at % = 18 and N/C = 0.25 in the case of 30 min duration (Fig. 5) that gave the best swollen layer. The other combinations that we tried (O at % and O/C, (O+N)/C, N/O ratio) did not lead to a such satisfactory correlation with α_{H₂O}. The α_{H₂O} increase and the swelling ability seem to be mainly dependent on the presence of amide group more than ester group. Indeed it seems that amide group is in higher percentage than ester group for 30 min if we consider the XPS results and the strong oxidation following the plasma treatment longer than 30 min. The α_{H₂O} value can be probably related to the difference of hydrophilicity between these groups as well as the ability to create hydrogen-bonding.

4. Conclusions
We showed that the strong selectivity of extruded PEI film could be increased from 850 to 10850 in other words the H₂O weight % in the pervaporate increased from 97.5 to 99.8 without significant change in the flow (2.5 g/m²h at 40 °C). This improvement at first sight
seems to be modest nevertheless it is of great interest in a concentration range of H$_2$O/EtOH mixture above the azeotropic concentration that is admitted as a test-mixture. This result, better than the one cited in reference, has its origins in the wettability and surface energy of the allylamine plasma-polymerized layer. The best deposit conditions were 75 W, 40 Pa, 30 min leading to the strongest N/C ratio that showed a large proportion of amide functional group. During the glow discharge, the allylamine monomer (H$_2$C=CH-CH$_2$-NH$_2$, C$_3$H$_7$N) polymerized via a cross-linked structure with 73, 9, 18 respectively C, O, N at % or just (C$_7$ON$_2$)$_n$.

The properties of this allylamine-polymerized layer can be worked for other separation techniques using PEI porous membranes (ultra- and microfiltration for example) as well as in other industrial applications.
List of tables and figures

Table 1: Contact angle ($\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{I}_2\text{CH}_2} \pm 1^\circ$), surface energy ($\gamma_s \pm 1 \text{ mJ m}^{-2}$), water selectivity and total flow (at 40 °C for H$_2$O/EtOH azeotropic mixture), thickness of dense membranes made by cast-evaporating method from ULTEM granules (a), synthesized polyetherimide (UPEI) (b) and of extruded PEI film (c).

Table 2: Binding energies (BE) and atomic percentages of elements (at %) of PEI reference film.

Table 3: Functional groups, approximative binding energies (BE), C1s, O1s and N1s atomic percentage of PEI reference and allylamine treated PEI film (75 W, 40 Pa) for 15, 30, 60 and 120 min.

Figure 1: Contact angle and surface energy ($\gamma_s$), dispersive ($\gamma_s^d$) and polar ($\gamma_s^p$) components ($\pm 1 \text{ mJ m}^{-2}$) of allylamine plasma treated PEI film versus treatment time (a) (b) and storage time under ambient conditions for 30 min plasma treatment.

Figure 2: C1s XPS spectra of PEI reference film (a) and allylamine plasma treated films for 15 min (b), 30 min (c), 60 min (d) and 120 min (e) treatment time.

Figure 3: N1s XPS spectra of PEI reference film and allylamine plasma treated film for 15, 30, 60 and 120 min treatment time.

Figure 4: Scanning Electron Microscopy (a) and Atomic Force Microscopy (b) photographs of PEI reference film and allylamine plasma treated film for 15, 30 and 60 min.

Figure 5: Total flow (a) and $\alpha_{\text{H}_2\text{O}}$ selectivity factor (b) at 40 °C versus pervaporation time of H$_2$O/EtOH azeotropic mixture for PEI reference film and allylamine plasma treated film for 15, 30, 60 and 120 min treatment time.

Figure 6: $\alpha_{\text{H}_2\text{O}}$ selectivity factor for H$_2$O/EtOH azeotropic mixture versus at % N and N/C ratio of reference and allylamine plasma treated PEI film.
References


<table>
<thead>
<tr>
<th>Starting material</th>
<th>( \theta_{\text{H}_2\text{O}} ) (°)</th>
<th>( \theta_{\text{I}_2\text{C}_2\text{H}_2} ) (°)</th>
<th>( \gamma_s ) (mJ.m(^{-2}))</th>
<th>( \alpha_{\text{H}_2\text{O}} )</th>
<th>Total flow (g/m(^2)h)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM granules (^{(a)})</td>
<td>93</td>
<td>27</td>
<td>46.8</td>
<td>114</td>
<td>2-5</td>
<td>60-80</td>
</tr>
<tr>
<td>UPEI synthesized (^{(b)})</td>
<td>88</td>
<td>32</td>
<td>42.6</td>
<td>290</td>
<td>2-5</td>
<td>60-80</td>
</tr>
<tr>
<td>ULTEM film (^{(c)})</td>
<td>75</td>
<td>32</td>
<td>45.3</td>
<td>850</td>
<td>2-5</td>
<td>75</td>
</tr>
<tr>
<td>Atomic element</td>
<td>C1s</td>
<td>O1s</td>
<td>N1s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE (eV)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>284.6</td>
<td>286.2</td>
<td>288.3</td>
<td>531.7</td>
<td>533.2</td>
<td>400.3</td>
</tr>
<tr>
<td>Experimental at %</td>
<td>72</td>
<td>7</td>
<td>4</td>
<td>9.5</td>
<td>4</td>
<td>3.5</td>
</tr>
<tr>
<td>Theoretical at %</td>
<td>60.0</td>
<td>13.3</td>
<td>8.9</td>
<td>8.9</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Functional groups</td>
<td>Reference</td>
<td>Allylamine plasma treatment time</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------</td>
<td>---------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BE (eV)</td>
<td>at %</td>
<td>15 min</td>
<td>BE (eV)</td>
<td>at %</td>
<td>30 min</td>
</tr>
<tr>
<td></td>
<td>BE (eV)</td>
<td>at %</td>
<td>15 min</td>
<td>BE (eV)</td>
<td>at %</td>
<td>30 min</td>
</tr>
<tr>
<td>C1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡C , C-C</td>
<td>284.6</td>
<td>72</td>
<td>284.6</td>
<td>62</td>
<td>284.6</td>
<td>50</td>
</tr>
<tr>
<td>C-N , C-O</td>
<td>286.2</td>
<td>7</td>
<td>286.1</td>
<td>15</td>
<td>285.9</td>
<td>10</td>
</tr>
<tr>
<td>O(N)-C-O or C=O</td>
<td>287.3</td>
<td>4</td>
<td>287.0</td>
<td>8</td>
<td>287.3</td>
<td>6</td>
</tr>
<tr>
<td>O=C-N-C=O</td>
<td>288.3</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N=C=O , O=C=O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C at %</td>
<td>83</td>
<td>81</td>
<td>73</td>
<td>74</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>O1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O=C</td>
<td>531.7</td>
<td>9.5</td>
<td>531.2</td>
<td>4</td>
<td>530.6</td>
<td>5</td>
</tr>
<tr>
<td>O-C</td>
<td>533.2</td>
<td>4</td>
<td>532.3</td>
<td>1.5</td>
<td>532.0</td>
<td>4</td>
</tr>
<tr>
<td>O at %</td>
<td>13.5</td>
<td>5.5</td>
<td>9</td>
<td>11</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>N1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-N , N-C=O</td>
<td>399.0</td>
<td></td>
<td>398.9</td>
<td>399.2</td>
<td>399.5</td>
<td></td>
</tr>
<tr>
<td>O=C-N-C=O</td>
<td>400.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N at %</td>
<td>3.5</td>
<td>13.5</td>
<td>18</td>
<td>15</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1

(a) Contact angle (°) vs. Treatment time (min)

(b) Surface energy (mJ.m⁻²) vs. Treatment time (min)

(c) Contact angle (°) vs. Storage time (days)
Figure 2

![Graph showing binding energy (eV) vs. C1s peaks for different samples labeled a to e.](image)
Figure 3

![Graph showing NIs binding energy over time](image)
Figure 4

(a) ULTEM reference film

(b)

15 min

30 min

60 min
Figure 5a

![Graph showing total flow vs. pervaporation time for untreated and treated samples.](image)

- Untreated
- 15 min
- 30 min
- 60 min
- 120 min

**Axes:**
- Y-Axis: Total flow (g/m²h)
- X-Axis: Pervaporation time (h)
Figure 5b
Figure 6

The figure shows a graph with the x-axis labeled as 'N at %' ranging from 0 to 20 and the y-axis labeled as 'Selectivity Coefficient' ranging from 0 to 12000. Two lines are plotted:
- The black line represents the 'N/C ratio'.
- The grey line represents 'N at %'.

The graph illustrates the relationship between the selectivity coefficient and the N/C ratio at various N at % values.