

Surface Modification of Polyamide and Poly(vinylidene fluoride) Membranes

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ABSTRACT: Experimental results from the gas-plasma treatment and electron-beam irradiation of polyamide (PA) and poly(vinylidene fluoride) (PVDF) membranes to improve their wettability and to evaluate protein adsorption at their surface are presented. The wettability of the membrane surface was determined by contact angle measurements; the analysis of the surface composition was performed by X-ray photoelectron spectroscopy (XPS). We observed that a reduction in the water contact angle was not always indicative of a reduction in the protein adsorption and, furthermore, that a charge at the surface of the modified membrane seemed to be a major factor in the protein adsorption process. Furthermore, the XPS results shed some light on the modification mechanism of PVDF and PA by electron-beam irradiation. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Protein adsorption and fouling is of great importance in many fields, from bioengineering to membrane filtration processes, as they affect the performances of the materials and, therefore, industrial processes.^{1,2} Among the relevant surfaces, many are polymeric materials, and it has been widely acknowledged that hydrophobic polymer surfaces present higher protein adsorption and fouling than their hydrophilic counterparts. As a result, many efforts have been focused on making these surfaces more hydrophilic.^{2–10} Various techniques can be used to this end, such as the introduction of surfactants, grafting of hydrophilic molecules to the polymer surface,^{6,8–10} gas-plasma treatments,^{5,11–15} and other techniques, such as electron-beam irradiation.^{16–18}

Protein adsorption appears to be a very complex phenomenon; first of all, as proteins differ in their structures, the nature and number of their hydrophilic or hydrophobic side chains, their sizes, and their overall resulting chemical and physical properties, it affects the way they interact with different surfaces, whose chemical nature and physical properties have a role to play in the protein adsorption.

Adesso and Lund¹⁹ observed that the Teflon surface, which has a lower critical surface tension than the metal surfaces used in their studies led to similar rates and levels of protein adsorption. Their study emphasized that when the surface energy of a solid surface influenced the rate and amount of adsorbed pro-

tein at a surface, the fouling of the milk whey protein used in their study on a given surface was not predictable from the measurements of surface tension determined by contact angle measurements. Davies et al.²⁰ observed that in polystyrene treated with argon plasma, bovine serum albumin (BSA) adsorption appeared to be more uniform across the treated surface, whereas on the untreated surface the adsorption was sporadic. Furthermore, they stressed that plasma treatment has been used to improve the binding characteristics of proteins to polymer surfaces; this was in contrast with the assumption that oxygen functionalities created by plasma exposure at the surface to increase its wettability should reduce the protein adsorption. As stated by Haynes and Norde,² no single experimental or theoretical approach can answer all of the questions concerning the protein adsorption at solid surfaces. However, further experimental works across different fields of science could help elucidate this protein adsorption process.

In this article, we present our experimental results on combined plasma and electron-beam-treated polymer membranes and the resulting adsorption of selected proteins. At our institute, Schulze et al.¹⁸ observed a decrease in the water contact angle and a systematic decrease in the protein adsorption with electron-beam irradiation under specific conditions. Also, we have used gas plasma for polymer surface modification.^{21,22} Both techniques are quite different; electron-beam irradiation leads to the degradation or crosslinking of polymer chains via radical mechanisms,¹⁶ whereas gas plasma is a mixture of ions,

electrons, radicals, and photons in short-wave UV, which have different actions on different types of surfaces. It is often assumed that gas-plasma surface treatment etches, functionalizes, and brings radicals to polymer surfaces. A small experiment already showed that when radicals are formed by plasma, they are short lived, but that ionic species do remain active at the surface long enough to react with molecules deposited at their surface.²¹ Thus, we explored and compared the two types of surface treatments and their combinations to study the influence of the surface treatment on the wetting properties of the membranes and the adsorption of some single proteins at their surfaces.

Aliphatic polyamide (PA) and poly(vinylidene fluoride) (PVDF) membranes were chosen for this study for their interesting properties: they are chemically resistant to alkaline solutions and organic solvents and are used for particle removal in filtration processes. However, despite the higher hydrophilic character of the PA membrane compared to that of PVDF, they both present high nonspecific adsorption, which limits their applications.

The modified membranes were characterized through measurements of contact angle and protein adsorption, and an investigation by X-ray photoelectron spectroscopy (XPS) into the surface composition after the surface treatments was also carried out.

EXPERIMENTAL

Materials and methods

Materials. PA and PVDF membranes (Roti-Nylon and Roti-PVDF) were obtained from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). The measured thicknesses of the membranes were 150 μm for Roti-Nylon and 130 μm for Roti-PVDF on average. The announced values for the porosities were 0.2 μm for the Roti-Nylon and 0.45 μm for the Roti-PVDF, but upon measurement on a PoreMaster-33 GT from Quantachrome GmbH & Co. KG (Odelzhausen, Germany) in high- and low-pressure modes, the membranes porosities were found to be 59% with an average pore size of 0.63 μm for the Roti-Nylon and 66% with an average pore size of 0.94 μm for the Roti-PVDF. BSA (fraction V, pH 5) [isoelectric point (iep) = 4.7, molecular mass (M_s) = 67,200 Da, acidic protein] was obtained from Acros Organics (Geel, Belgium). Myoglobin (Mb) from equine skeletal muscle (95–100%, essentially salt-free, lyophilized powder, iep = 7.0, M_s = 17,800 Da, neutral protein) and lysozyme (Lys) from chicken egg white (lyophilized powder, protein \geq 90%, \geq 40,000 units/mg of protein, iep = 11.1, M_s = 14,600 Da, basic protein) were obtained from Sigma-Aldrich (Hamburg, Germany). Phosphate-buffered saline (PBS; 50 mM) was used at pH 7. Millipore-grade distilled water was used in all of the surface modifications.

Surface modification

Plasma treatment. The membranes were exposed to gas plasma with an radio frequency (RF) plasma system (Junior Plasma System, Europlasma NV, Oudenaarde, Belgium) equipped with a 300-W kHz generator. During all surface treatments, the gas flow, or mixture of gases, was set at 20 sccm, the power was set at 100 W, and the base pressure was set at 120 mT. After the

base pressure was reached, the gas was let into the chamber during a stabilization phase of 3 min. Samples were exposed to plasma for 5 min at a working pressure of 180–195 mT with an RF of 6–7 W and the temperature inside the chamber varying between 25 and 29°C. These conditions were chosen on the basis of previous experience with plasma modification of other substrates with the same plasma system.^{21,22}

Electron-beam treatment. The PA and PVDF membranes were surface-modified in a one-step procedure: the membranes were immersed in Millipore-grade water for 0.5 h and subject to electron-beam treatment. The typical applied irradiation dose was 100 kGy. The irradiation was performed in a nitrogen atmosphere with oxygen quantities controlled to be less than 10 ppm with a homemade electron accelerator. The voltage and current were set to 160 kV and 10 mA, respectively. The absorbed dose was adjusted by the speed of the sample transporter.

Water flux and bubble-point measurements. Water flux and bubble point were measured with an in-house setup comprising a Sartorius Stedim Biotech GmbH (Goettingen, Germany) stainless steel holder with a 220-mL capacity connected directly to a pressure source. The area of the tested membrane was 17.35 cm². The membrane samples were first soaked in water for 1 min in the case of the PA membranes. For the PVDF membranes, a preliminary dip of a couple of seconds in ethanol was carried out before soaking in water to improve the membrane wettability. The water flux was determined by measurement of the time necessary for a given volume of water (100 mL for PA and 200 mL for PVDF) to go through the membrane samples under a pressure of 1 bar. All flux data reported in this study are relative fluxes:

$$J = J_m/J_o \quad (1)$$

where J_o and J_m , respectively the fluxes of the unmodified and modified membranes, were calculated according to the following formulas

$$J_o = V_o/(S \times t_o) \quad (2)$$

$$J_m = V_m/(S \times t_m) \quad (3)$$

where V_o is the volume of permeated water for the unmodified membrane, V_m is the volume of permeated water for the modified membrane, S is the virtual area of the tested samples, t_o is the record time for the original membrane, and t_m is the record time for the modified membrane.

We measured the bubble points with the same holder by dipping the lower end of the stainless steel holder into a volume of water, filling up the volume on the upper side of the membrane with water, and applying increasing pressure until the first bubble of air appeared, at which point the corresponding pressure was recorded.

Surface characterization. For static water contact angle measurements, two different liquids were used: ultrapure water (MilliQ, Millipore GmbH, Schwabach/Ts, Germany) and diiodomethane (DIM; Sigma-Aldrich, Hamburg, Germany). The measurements were carried out on a DSA II (Krüss GmbH, Hamburg, Germany) equipped with Drop Shape Analysis 2.1

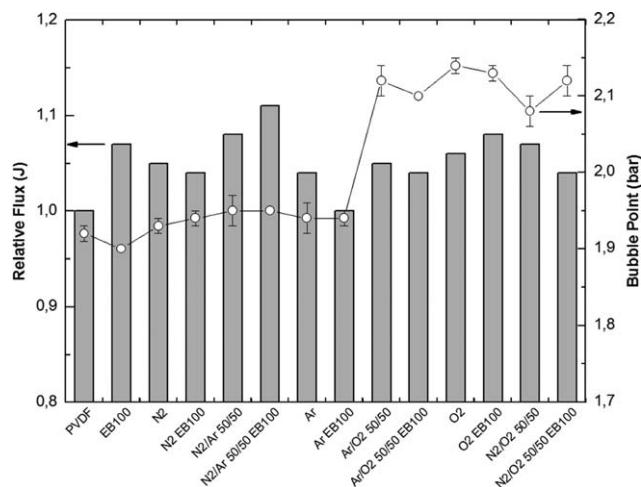


Figure 1. Relative water flux through the untreated and treated PVDF membranes and corresponding bubble-point values.

software. Before measurement, the PA membrane samples were pressed into dense films ($30 \times 9 \text{ mm}^2$) to eliminate the immediate absorption of the water droplet into the membrane pores. This was carried out with nonadherent paper to prevent some of the modified membrane from sticking to the metallic jaws of the press. All contact angles are the mean value of five measurements with each test liquid on different parts of the sample's surface.

XPS analyses were carried out on a Kratos Axis Ultra (Kratos Analytical, Ltd., Manchester, United Kingdom) with a monochromatized Al excitation source at 150 W (15 kV, 10 mA, with a pass energy of 40 eV). Surface spectra were collected over a range of 0–1200 eV. The nominal resolutions were 1.0 eV for the survey (pass energy = 160 eV) and 0.1 eV for the high-resolution scans (pass energy = 20/40 eV), respectively. The binding

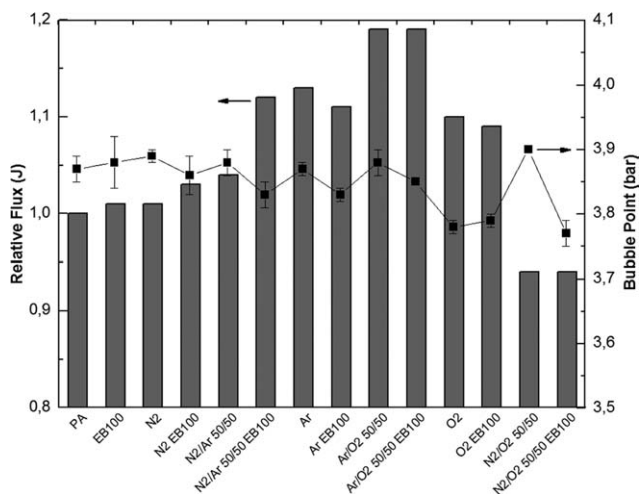


Figure 2. Relative water flux through the untreated and treated PA membranes and corresponding bubble-point values.

energies were corrected for the static charging of the samples by reference to the C1s peak set at a binding energy of 285.0 eV.

Scanning electron microscopy (SEM) was carried out on a Carl Zeiss SMT Ultra 55 (Oberkochen, Germany). The samples were preliminarily coated with a 50-nm layer of chrome to improve the conductivity.

Protein adsorption studies. Protein adsorption experiments on the polymer membrane surfaces were investigated with a bicinchoninic acid (BCA) based assay (Pierce)^{23,24} and the following proteins: BSA, Mb, and Lys. Membrane samples were cut to fit into the wells of a 48-well microtiter plate (diameter of the wells = 1 cm). In the case of the PVDF membrane, the samples were preliminarily conditioned by the addition of 250 μL of ethanol to the membrane pieces in the wells and were placed on a

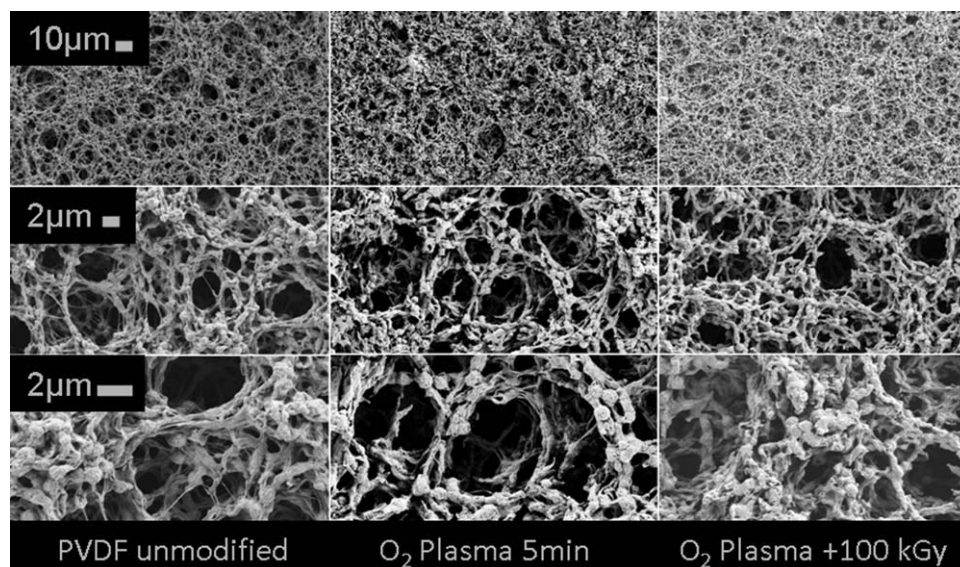


Figure 3. SEM images of the PVDF membrane samples: unmodified (left), treated with oxygen plasma (middle), and treated with oxygen plasma followed by electron-beam irradiation (right).

Table I. Water and DIM Contact Angles of the Unmodified and Modified PVDF Membranes

	Contact angle		Surface energy (mN/m ²)	Contribution	
	Water (°)	DIM (°)		Dispersive	Polar
PVDF	138.3 ± 0.4	77.8 ± 2.5	22.1	18.6	3.5
EB100	128.6 ± 1.9	67.8 ± 0.6	26.8	24.1	2.7
N ₂	137.5 ± 1.2	90.4 ± 1.8	14.0	12.5	1.5
N ₂ -EB100	110.8 ± 2.3	80.9 ± 1.0	17.2	17.0	0.1
N ₂ /Ar-50/50	137.3 ± 2.5	94.4 ± 2.3	11.9	10.8	1.1
N ₂ /Ar-50/50-EB100	126.5 ± 1.7	77.7 ± 1.2	19.8	18.7	1.1
Ar	132.9 ± 1.6	100.0 ± 0.3	8.9	8.7	0.2
Ar-EB100	129.6 ± 2.1	89.3 ± 1.5	13.6	13.0	0.6
O ₂ /Ar-50/50	126.0 ± 2.9	101.3 ± 2.0	8.2	8.2	0.6
O ₂ /Ar-50/50-EB100	102.2 ± 2.7	85.0 ± 2.5	16.7	15.0	1.7
O ₂	65.1 ± 2.6	82.8 ± 2.3	37.0	16.1	20.9
O ₂ -EB100	68.9 ± 2.7	71.0 ± 2.3	36.1	22.3	13.8
O ₂ /N ₂ -50/50	127.4 ± 0.8	72.6 ± 2.2	23.3	21.4	1.9
O ₂ /N ₂ -50/50-EB100	116.8 ± 3.3	77.4 ± 2.8	19.0	18.9	0.1

mechanical shaker for 10 min before they were rinsed three times with water. To each membrane sample, 200 mL of a protein solution (2.0 mg/mL) in 50 mM PBS (pH 7.0) was added, and the plates were shaken for 1 h at ambient temperature. The samples were washed three times with 1 mL of PBS, respectively. Then, the BCA reagent was added to the samples, and the plate was incubated for 25 min at 37°C. The plate was then shaken for 5 min at ambient temperature, the solution was transferred to a 96-well microtiter plate, and the light adsorption at 562 nm was measured with a microtiter plate reader (Infinite M200, Tecan, Männedorf, Switzerland). For calibration, several protein concentrations, ranging between 0 and 30 mg/mL, were used per the BCA test instructions.

RESULTS AND DISCUSSION

Surface modification by plasma and electron-beam treatments

PA and PVDF flat-sheet membranes were treated by either gas-plasma treatment, electron-beam treatment, or both treatments successively, that is, gas plasma followed by electron-beam irradiation. The idea to combine both surface treatments came from the observation that gas plasma is generally quite efficient in increasing the hydrophilicity of a polymer surface. However, with this type of treatment, the polymer surfaces may undergo hydrophobicity recovery.^{25–28} In parallel, surface treatment with electron-beam irradiation in the conditions developed by Schulze et al.¹⁸ provides a significant decrease in the water

Table II. Atomic Composition and C1s Deconvolution at the Surface of the Treated and Untreated PVDF Membrane Samples as Determined by XPS

	Elemental ratio (relative atom %)				C1s deconvolution (eV; relative %)					
	F	O	N	C	284.9 —C—C—	286.4 —CH ₂ —	287.5 C—O	288.5 C—O _x	290.9 —CF ₂ —	292.1 —CF _x —
PVDF	51.8	—	—	48.2	—	51.0	—	—	49.0	—
EB100	44.6	3.2	0.3	51.9	7.0	53.0	—	—	40.0	—
N ₂	46.4	3.7	0.6	49.3	—	47.0	—	12.8	40.2	—
N ₂ -EB100	39.8	6.4	1.2	52.7	7.5	44.2	—	15.1	33.2	—
Ar	44.3	4.6	—	51.1	—	49.4	—	13.0	37.7	—
Ar-EB100	37.3	8.0	0.9	53.9	—	59.6	—	6.7	33.7	—
O ₂	48.5	4.2	—	47.3	—	41.7	10.7	—	47.6	—
O ₂ -EB100	44.3	5.6	—	49.5	4.9	45.1	—	5.6	44.4	—
N ₂ /Ar-50/50	47.1	4.2	0.3	48.3	—	47.7	—	12.5	37.3	2.5
N ₂ /Ar-50/50-EB100	39.0	6.8	0.7	53.5	4.4	49.0	—	7.6	39.0	—
Ar/O ₂ -50/50	48.6	4.0	—	47.5	—	37.2	9.0	—	53.8	—
Ar/O ₂ -50/50 EB100	42.7	6.2	0.3	50.8	1.6	51.6	—	4.0	42.8	—
N ₂ /O ₂ -50/50	48.5	4.1	0.1	47.3	—	44.1	—	8.5	47.3	—
N ₂ /O ₂ -50/50-EB100	40.4	8.2	0.8	50.7	6.3	44.8	—	13.1	35.8	—

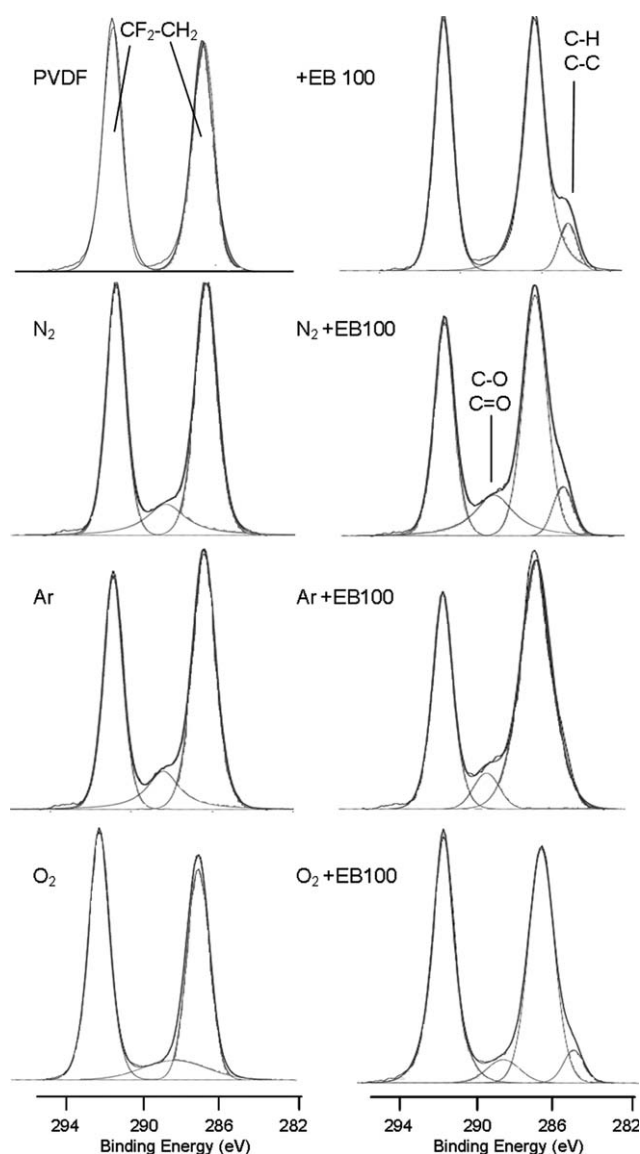


Figure 4. High-resolution C1s photoelectron spectra of pristine PVDF, PVDF membrane sample treated only with plasma (left: N₂, Ar, and O₂), and PVDF membrane sample treated with plasma plus electron-beam irradiation (+EB100) PVDF membrane samples.

contact angle and a systematic reduction in the protein adsorption. Thus, it could be possible to improve the surface modification through a combination of the treatments. By comparing both techniques and combining them, we aimed to determine what the resulting contact angles were and to evaluate the protein adsorption behavior on the modified membranes.

The techniques used in this study had the following effects on the filtration properties of the membranes: we observed an increase up to 15–20% in the water flux according to the surface treatment and the nature of the polymer membrane (Figures 1 and 2). For bubble-points values, there were no drastic changes observed, except in the PVDF membranes treated with oxygen-containing plasma, where an increase in the bubble point was observed (Figure 1). For these samples, the changes in the

bubble-point values could have been symptomatic of a modification of the pore size. However, the SEM images did not reveal a difference in the pore size, as shown in the selected images presented in Figure 3.

PVDF modification and surface characterization

Polymers such as PVDF present a challenge in terms of surface modification because of their high hydrophobicity induced by the CF₂ group. Any technique used would have to severely attack the polymer unit to break the C–F bond or remove CF₂ groups of the surface to achieve a significant change in the surface properties.

Table I presents the contact angles with water and DIM and the mean values of the total surface free energy as a function of the PVDF membrane surface treatments. We noted that although the electron-beam irradiation treatment alone was able to somewhat reduce the water contact angle, its effect was more compelling when the irradiation was carried out after plasma treatment. However, it did not induce a meaningful change in the surface polarity. This would be in agreement with a crosslinking of the PVDF chains upon exposure to electron-beam irradiation and the fact that the process produces a chain rearrangement rather than a chemical surface modification.

A more significant reduction in the contact angle was observed after the treatment with oxygen plasma or with a combination of nitrogen and oxygen gas plasma. With oxygen plasma alone, the polar contribution to the surface energy was greatly increased; this is generally attributed to the presence of polar functions at the surface upon plasma treatment,^{20,29–33} but it also showed that only the oxygen-containing-plasma treatments were efficient enough to produce chemical changes at the surface of the PVDF membrane. Because other treatments did not significantly raise the polar contribution to the surface energy, this indicated that the modification was more structural (etching) than chemical. Furthermore, the additional electron-beam treatment always tended to lower the water contact angle and, in some cases, the polar contribution of the surface energy. This could be explained by the formation of CH₂–CH₂ bonds via a radical mechanism, which was still of hydrophobic nature. Thus, the modified surface tended to have similar properties to that of a polyolefin.

Additionally, after several weeks, we measured the water contact angle values of samples taken from the same modified membranes and observed no significant change in the measured values; this indicated a stable modification over time.

XPS was used in this work to investigate the changes occurring at the surface of the membranes upon gas-plasma and electron-beam treatments. The data presented in Table II show an increase in the oxygen content after all surface treatments, and we also observed an increase with the additional electron-beam irradiation after the plasma treatment compared to plasma treatment alone. The C1s deconvolution results (Table II and Figure 4) show that the electron-beam irradiation alone, although it increased the oxygen content to 3 atom %, did not produce obvious oxidation species, such as hydroxyl or acid functions, at the surface as the plasma surface treatment

Table III. Water and DIM Contact Angles of the Unmodified and Modified PA Membranes

	Contact angle		Surface energy (mN/m)	Contribution	
	Water (°)	DIM (°)		Dispersive	Polar
PA	55.5 ± 2.4	23.1 ± 1.7	57.2	46.8	10.5
EB100	50.0 ± 1.2	35.2 ± 0.5	57.3	41.9	15.3
N ₂	34.3 ± 4.9	31.3 ± 2.8	66.6	43.7	22.9
N ₂ -EB100	38.6 ± 2.5	28.1 ± 1.9	65.0	45.0	20.0
N ₂ /Ar-50/50	33.5 ± 4.6	28.4 ± 0.7	67.5	44.9	22.7
N ₂ /Ar-50/50-EB100	43.0 ± 0.7	33.7 ± 2.6	61.5	42.6	18.9
Ar	26.8 ± 3.3	32.0 ± 1.6	70.0	43.4	26.6
Ar-EB100	35.0 ± 2.1	24.3 ± 2.0	67.6	46.4	21.2
O ₂ /Ar-50/50	38.3 ± 2.4	27.1 ± 2.2	65.4	45.4	20.0
O ₂ /Ar-50/50-EB100	37.7 ± 0.8	34.8 ± 2.9	64.1	42.1	22.0
O ₂	35.0 ± 3.2	25.7 ± 3.3	67.3	45.9	21.5
O ₂ -EB100	36.8 ± 1.5	37.7 ± 3.1	64.0	40.8	23.3
O ₂ /N ₂ -50/50	39.0 ± 1.8	30.0 ± 2.1	64.4	44.2	20.2
O ₂ /N ₂ -50/50-EB100	18.1 ± 0.6	26.5 ± 2.4	74.2	45.6	28.6

did.^{20,29,30,32} Thus, the 3 atom % oxygen was attributed to oxygen intake from air upon treatment. On the C1s deconvolution level, the increase in the oxygen content after the plasma treatment and combined plasma and electron-beam treatments, was underlined by the relative increases of 287.5 and 288.5 eV assigned to the C—O and C—O_x peaks, respectively (C—O_x = R—C—O, R—C=O, with R=C, O, etc.); this was definitely because of the action of the gas plasma but seemed to also be enhanced by electron-beam irradiation after plasma treatment, as if the prevalent mechanism in the electron-beam irradiation

of the plasma-treated PVDF was done through the recombination of these plasma-enhanced segments.

More interestingly, a peak at 284.9 eV always appeared after electron-beam irradiation and was assigned to the C—C/H bond of the CH₂—CH₂ chain segment. Figure 4 presents the C1s deconvolutions. We observed this 284.9-eV peak on most electron-beam-irradiated samples, located on the right side of Figure 4, but it was not obvious at first glance in the case of the PVDF sample treated by both Ar plasma and electron-beam irradiation. Therefore, we had to consider the full width at half-

Table IV. Atomic Composition at the Surface of the Treated and Untreated PA Membrane Samples as Determined by XPS

	Elemental ratio (relative atom %)				C1s deconvolution (relative %)				Atomic ratio		
	O	N	C	*	284.9 eV	285.5 eV	286.1 eV	288.1 eV	O/C	N/C	O/N
					C—C	C—N	C—O	C—O _x			
PA	12.1	11.5	76.4		46.4	19.2	17.2	17.1	0.16	0.15	1.05
EB100	13.7	11.2	75.1		29.1	40.0	13.6	17.3	0.18	0.15	1.22
N ₂	17.4	12.8	67.5	2.3	41.2	21.7	11.7	26.1	0.26	0.19	1.36
N ₂ -EB100	18.6	11.0	69.4	0.9	34.0	29.7	13.8	22.5	0.27	0.16	1.69
Ar	18.6	11.0	67.7	2.7	32.1	30.5	13.6	23.9	0.27	0.16	1.69
Ar-EB100	19.7	10.4	69.4	0.5	35.6	29.2	11.3	24.0	0.28	0.15	1.89
O ₂	18.7	12.5	68.8		38.7	24.4	11.0	25.9	0.27	0.18	1.50
O ₂ -EB100	17.2	11.5	71.3		36.2	25.3	15.2	23.3	0.24	0.16	1.50
N ₂ /Ar-50/50	17.8	11.7	68.6	2.0	36.0	29.2	10.6	24.2	0.26	0.17	1.52
N ₂ /Ar-50/50-EB100	18.3	10.6	70.4	0.7	33.5	27.1	17.3	22.1	0.26	0.15	1.73
Ar/O ₂ -50/50	18.7	12.0	69.3		35.6	28.8	9.9	25.7	0.27	0.17	1.56
Ar/O ₂ -50/50-EB100	18.6	10.8	70.6		28.3	20.2	14.9	36.6	0.26	0.15	1.72
N ₂ /O ₂ -50/50	18.5	11.7	69.8		35.0	30.0	9.7	25.0	0.27	0.17	1.58
N ₂ /O ₂ -50/50-EB100	18.5	11.4	70.1		34.6	26.0	15.2	24.3	0.26	0.16	1.62

An asterisk corresponds to impurities measured at the surface.

maximum (FWHM) of the peak centered at 286.4 eV, which was larger in the case of treatment with Ar plasma followed by electron-beam irradiation (FWHM = 2 eV) than on the other spectra (FWHM \approx 1.5 eV), to confirm the possible presence of this peak. During the C1s deconvolution step, the software could not fit a small shoulder peak at 284.9 eV, although the spectral curve did present a slight inflection at this binding energy position. This peak at 284.9 eV confirmed the crosslinking of PVDF through the formation of a CH₂—CH₂ bond during electron-beam irradiation.

PA modification and surface characterization

By nature, PA is a more hydrophilic type of membrane than PVDF, presenting a backbone and functionality, that is, the (CH₂)_n chain and amide function, which is more easily oxidized than the CF₂ groups of PVDF. Upon electron-beam and gas-plasma treatments, the water contact angle at the membrane surface decreased significantly (Table III), whereas the surface energy and its polar contribution increased. This indicated an increase in hydrophilic functionalities at the modified polymer surface. In contrast to what we observed with PVDF, the water contact angle increased slightly after the combined treatments of plasma and electron-beam irradiation compared to the corresponding plasma treatment alone. Once again, this was attributed to a crosslinking process generated by electron-beam irradiation, which led to an increase in CH₂—CH₂ bonds and slightly changed the overall hydrophilic character of the membrane surface.

As with the PVDF membranes, we measured the contact angles on samples taken from the same modified PA membranes after several weeks and noted that the values were again similar; this indicated the stability of our modifications.

The surface compositions determined by XPS and C1s deconvolutions (Table IV and Figure 5) showed an increase in the oxygen content after all of the surface treatments. Furthermore, we observed an additional increase with the electron-beam irradiation after plasma treatment compared to the plasma treatment alone. On the C1s deconvolution level, this was underlined by the relative increase of the —C=O peak at about 288 eV. The nitrogen content stayed about the same throughout the various surface treatments, even though we noted a regular increase upon treatment in the C1s peak located at 285.5 eV, which was associated with C—N bonds. From these observations, we developed the hypothesis that the generation of additional C—N bonds was the most plausible mechanism during the PA irradiation process and that the crosslinking of the PA was done through a C—N—C bridge formation.

Protein adsorption at the surface of the modified membranes

The membrane samples were tested for protein adsorption with the standard protocol of the BCA test described in the Experimental part and three proteins: BSA, Mb, and Lys. The variations in the adsorptions of the different proteins were calculated relative to the untreated membrane samples and are presented in Figure 6. At first glance, a reduction in the protein adsorption was observed in the case of BSA on the PA membrane, and this was observed only in certain conditions but also with PVDF after electron-beam irradiation as the sole treatment,

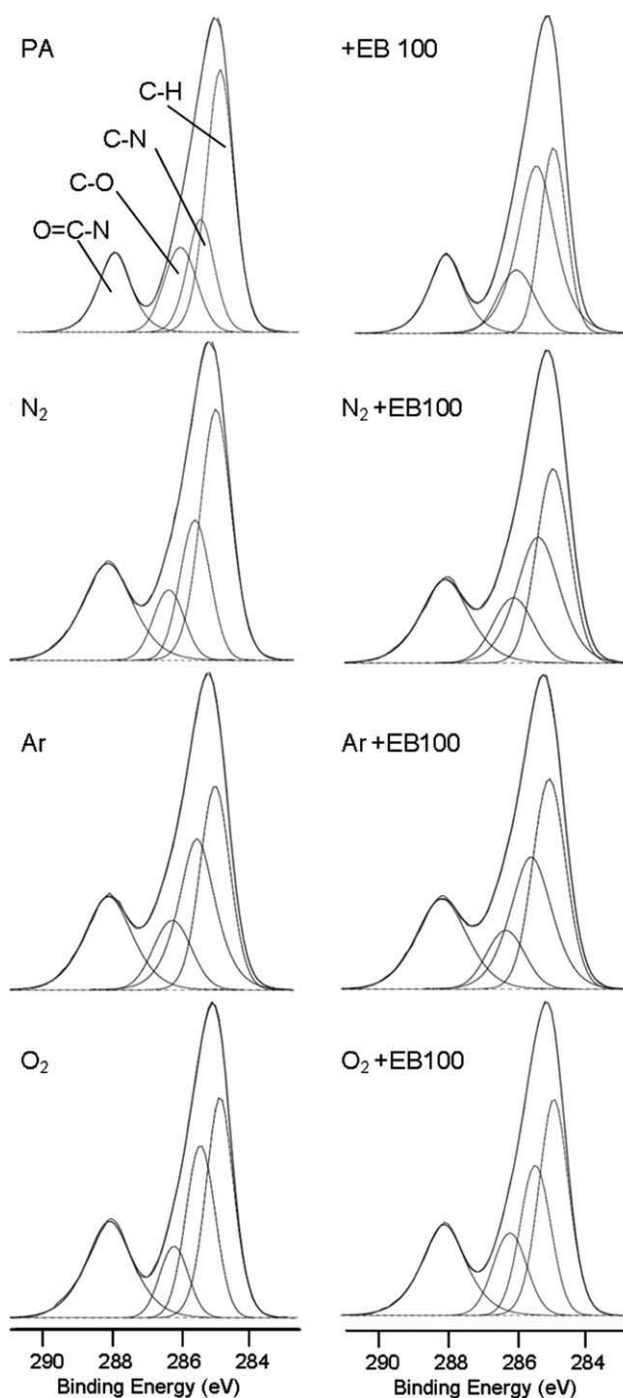


Figure 5. High-resolution C1s photoelectron spectra of pristine PA, PA membrane sample treated with plasma only (left: N₂, Ar, and O₂), and PA membrane sample treated with plasma plus electron-beam irradiation (+EB100).

where a small reduction of almost 3% was observed. In all other cases, whether with PA or PVDF membranes, the protein adsorption increased.

The adsorption of the various proteins differed significantly between PVDF and PA; this was expected due to the nature of the polymers themselves. However, the effect of oxygen plasma

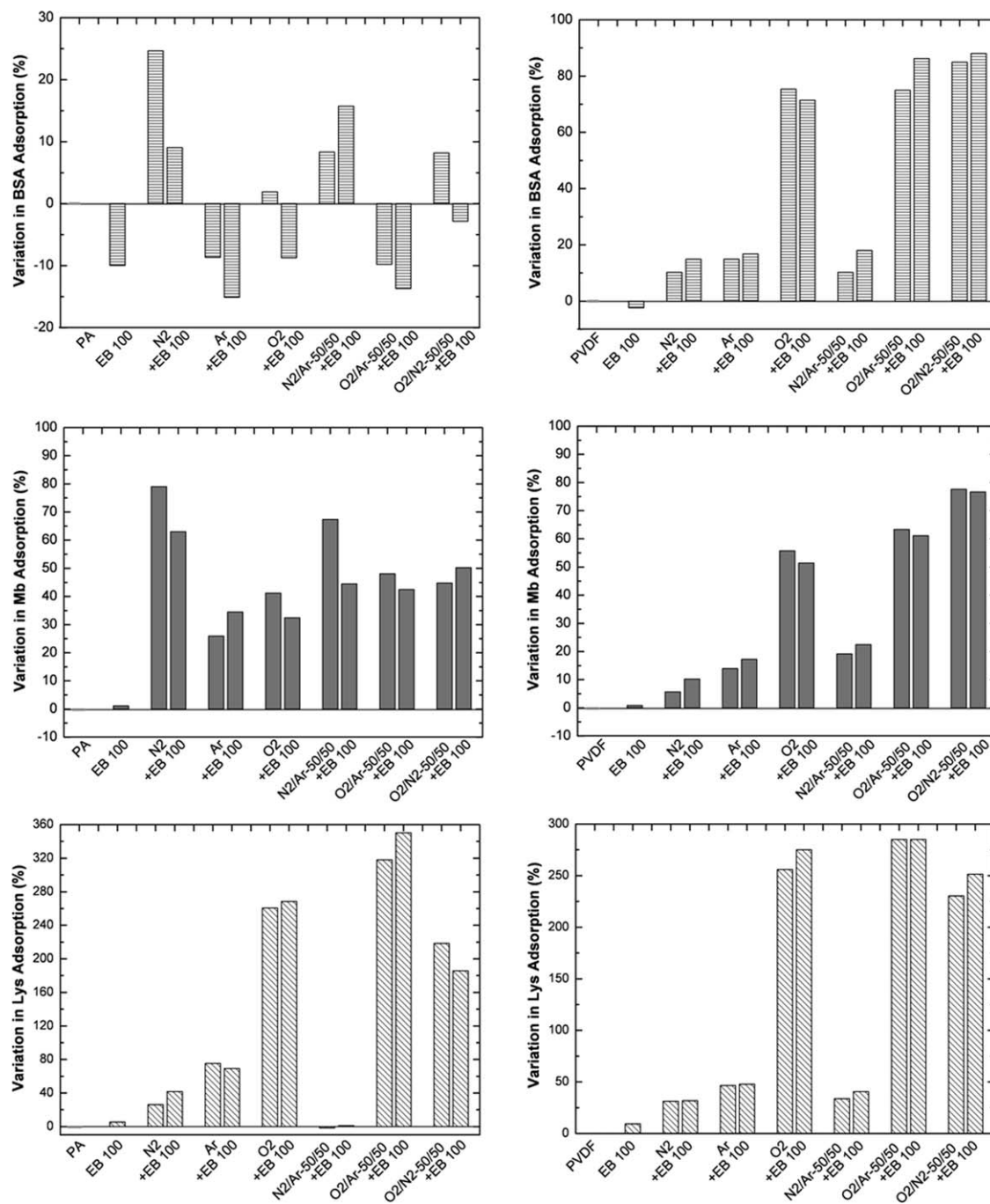


Figure 6. Variations in protein adsorption at the surface of the unmodified and modified PA (left) and PVDF (right) membranes. The proteins used in the BCA test were BSA (top), Mb (middle), and Lys (bottom).

exposure was quite different from one membrane to another. With the PVDF membranes, we observed the same pattern of adsorption with all three proteins, with the highest adsorption increase obtained after the treatments with oxygen-containing plasma. Treatments with nitrogen- and argon-containing plasma alone or followed by electron-beam irradiation seemed to provide an intermediate adsorption between that observed with the electron beam alone and oxygen-containing-plasma treatments. Because of the general assumption that argon plasma has a

milder effect than nitrogen or oxygen plasma on polymer surfaces²⁰ and because the argon atoms apparently do not react with the polymer as nitrogen and oxygen do but leave a high amount of unsaturated bonds for oxidation in ambient air, we might consider the argon plasma treatment as having a somewhat more neutral effect than the two others. Because of the high polarity created at the surface of the PVDF membranes by the oxygen-containing-plasma treatments, the charge at the surface was increased with the apparition of anionic species, contrary

to the treatment with nitrogen plasma, which tends to produce cationic species.³¹ However, with the contact angle values we obtained, we believed that nitrogen plasma only had an etching effect on the PVDF membrane surface with a small or negligible functionalization.

With regard to the effect of electron-beam irradiation after gas-plasma exposure, the treatment did not appear to have any additional influence on the protein adsorption, contrary to what was observed with the PA membrane surfaces. Indeed, with the PA membrane samples, we noted that the lowest BSA adsorption was reached after the electron-beam irradiation of the surface, alone or after plasma treatment, except with the nitrogen-containing-plasma treatments. In most cases, when the samples were irradiated after gas-plasma treatment, the BSA adsorption was significantly lower compared to that with plasma treatment alone. This indicated a further modification of the membrane by electron-beam irradiation. However, this trend did not correlate with the values of the water contact angles and, thus, did not appear to be dependent on the hydrophilicity of the surface.

The reason for an increase in the BSA adsorption on PA treated with nitrogen-based plasma was unclear, but it may have been related to the charges carried by the protein on one side and the charges at the adsorbent surface on the other side. BSA and Mb are both soft proteins³⁴ and can undergo conformational changes at the polymer surfaces, whereas Lys is considered to be a hard protein and would be less likely to undergo conformational changes at the hydrophilic PA surface. However, both Mb and Lys had their adsorption increased at the surface of the plasma-treated PA, whereas the adsorption of BSA differed. In addition to their sizes, BSA and Lys also differed by their iep's. On the nitrogen-plasma-treated surface, the charge at the surface might have reached a level inducing adsorption of BSA or enhancing its binding to the surface, whereas other treatments led to a reduction in adsorption. These observations tended to support the assumption that protein adsorption was controlled by the surface charge, the charges carried on the protein itself, and the nature of the interface rather than by the surface hydrophilicity.

CONCLUSIONS

The study of the effects of electron-beam and plasma surface treatments on PA and PVDF membranes and on the behavior of protein adsorption at their surface showed that only oxygen-based plasma treatments were efficient enough to increase the wettability and polarity of the PVDF membrane surface. The adsorption of several proteins on the PVDF surface increased with each plasma treatment, despite some reduction in the water contact angle. At the surface of PA, regardless of the hydrophilic character of the pristine and modified surface, the protein adsorption increased, except for BSA, whose adsorption increased after argon- or oxygen-based plasma treatment or electron-beam irradiation alone. The reasons for the selectivity in the BSA adsorption toward the different plasma-treated surfaces was unclear, but as for the other proteins, their behavior and ability to adsorb at the material's surface could be

linked to a difference in charges carried by the proteins and those present at the adsorbent surface, that is, to the protein and material surfaces and the interface conditions.

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