

Treatment of PET Nonwoven with a Water Vapor or Carbon Dioxide Plasma

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Received 13 January 1999; accepted 7 March 1999

ABSTRACT: Gas plasma treatment of poly(ethylene terephthalate) nonwoven (NW-PET) was used to increase the hydrophilicity of single- and multilayer NW-PET. NW-PET was treated with a pulsatile CO₂ or with a pulsatile H₂O glow discharge. X-ray photoelectron spectroscopy (XPS) showed significantly more oxygen with CO₂ glow-discharge-treated NW-PET than with H₂O glow-discharge-treated-NW-PET surfaces. Moreover, the introduction rate of oxygen at a single layer of NW-PET was higher for a CO₂ than for a H₂O glow-discharge treatment. Titration data revealed significantly higher surface concentrations of carboxylic groups for CO₂ glow-discharge NW-PET than for H₂O glow-discharge-treated NW-PET. Mass spectrometry analysis revealed that the entire internal surface of a single layer of NW-PET was modified. XPS and contact measurements confirmed the modification of the internal surface of multilayers of NW-PET. H₂O and CO₂ glow-discharge-treated substrates consisting of six layers of NW-PET had a nonuniform surface concentration of carboxylic acid groups as determined with titration experiments. The outside layers of the substrate contained a higher surface concentration of carboxylic acid groups than did the inside layers. XPS analysis and titration data showed that the rinsing of H₂O and CO₂ glow-discharge-treated NW-PET with water changed the surface composition considerably. Part of the carboxylic acid group-containing species were washed off. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 480–494, 2000

Key words: PET nonwoven; leukocyte filters; surface modification; gas plasma treatment; X-ray photoelectron spectroscopy; chemical composition; treatment stability

INTRODUCTION

Radio-frequency glow-discharge (RFGD) treatment is a frequently used method for altering the surface properties of a polymer while maintaining the beneficial physical characteristics of the bulk. Generally, RFGD treatment can change the chemical composition, the molecular weight of the polymer in the surface layer, and the topography

of the surface. For instance, when RFGD treatment with oxidative gases is used, a spectrum of oxygen-containing functional groups (hydroxyl, epoxide, ketone/aldehyde, carboxylic acid, and ester groups) can be introduced onto a polymer surface.^{1–3}

In this study, RFGD treatment of nonwoven poly(ethylene terephthalate) (NW-PET) was applied to increase the surface hydrophilicity, with the ultimate goal being to prepare a modified NW-PET surface with a high platelet compatibility. NW-PET can be used as a filter material for the removal of leukocytes from various blood products. However, when applying NW-PET in a filter for the removal of leukocytes from platelet

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Journal of Applied Polymer Science, Vol. 75, 480–494 (2000)

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CCC 0021-8995/00/040480-15

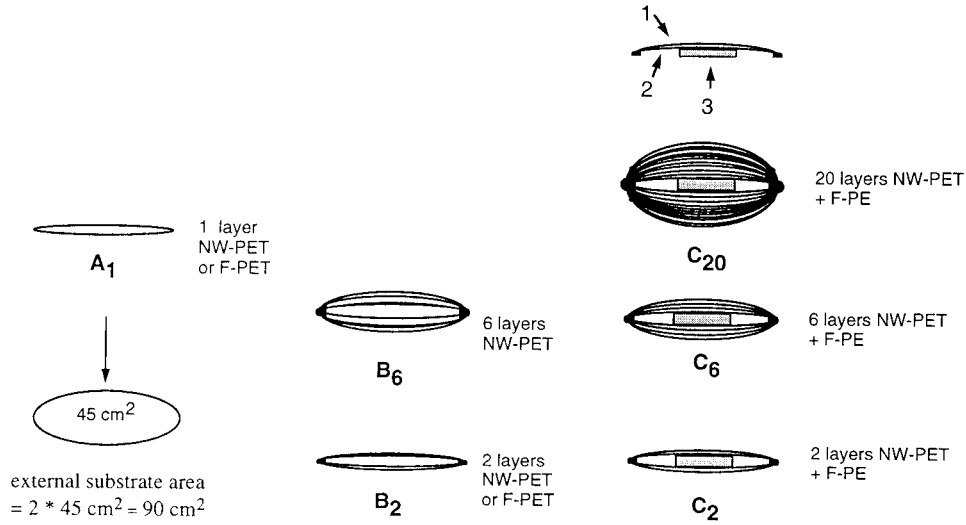


Figure 1 A schematic drawing of the various systems used for RFGD modification. System A₁: single-layer of NW-PET or PET film (F-PET); systems B₂ and B₆: multi-layer of NW-PET (two or six layers, respectively) or F-PET (two layers); and systems C₂, C₆, and C₂₀: multilayer of NW-PET (two, six, or 20 layers, respectively, which enclose a strip of four F-PEs. Arrows 1–3 point to (1): the (facial) external NW-PET surface, (2) the internal NW-PET surface, and (3) the F-PE surface.

concentrates (PCs), poor platelet recovery is obtained.⁴ In a previous study, NW-PET was treated with RFGD using different gases to study the effect of the discharged gas on the resulting surface modification. It was found that RFGD treatment of NW-PET using H₂O or CO₂ as a discharge gas improved the hydrophilicity of the nonwoven and reduced the adhesion of platelets onto the nonwoven surface.⁵

Glow discharges are produced by free electrons which are energized by an imposed direct current or radio frequency (rf) electric field and can only be maintained as long as the external source exists. Moreover, to generate and maintain a gas plasma, the dimensions of the volume in which the glow discharges are created must be much larger than is the distance over which a charge imbalance (Debye length) can exist.⁶ The Debye length (λ_D) can be calculated using eq. (1)⁷:

$$\lambda_D = \left(\frac{kT_e \epsilon_0}{n_e e^2} \right)^{1/2} \quad (1)$$

in which e (charge of proton) = 1.6022×10^{-19} C, k (Boltzmann constant) = 1.3807×10^{-23} J K⁻¹, ϵ_0 (vacuum permittivity) = 8.8542×10^{12} F m⁻¹, T (electron temperature) = 3.5×10 K, and n (electron density) = 0.5×10 per m

Recently, Takens determined the T_e and n_e of a CO₂ gas plasma (50 W, 10 cm³/min, and 0.05 mbar) established in the same reactor as used in this study.⁸ The discharge conditions were also similar. Using the results of Takens, λ_D can be calculated as 576 μ m, which is much larger than the average pore diameter of NW-PET (4–26 μ m). Therefore, it can be assumed that during RFGD treatment no plasma will be formed in the pores of NW-PET under the given conditions. Modification of the internal nonwoven surface will thus proceed differently as compared to modification of the external (facial) nonwoven surface. The modifications of the internal nonwoven surface will be more in the way of an afterglow-discharge treatment. During an afterglow-discharge treatment, energetic ions are absent and the concentrations of electrons or radiation-emitting species are strongly reduced. In this case, the surface modification is induced by (oxygen) radicals from the plasma phase.³ The reactive species need to diffuse into the pores of the nonwoven substrate. Therefore, a gradient in surface modification deeper into the nonwoven is to be expected.

In this study, various nonwoven configurations were used as indicated in Figure 1. To prevent reorientation of the macrostructure of the non-

woven, NW-PET was modified using a pulsatile RFGD treatment.⁵ This technique has been used by other researchers to treat polymers with "delicate" structures.¹ Previous work on RFGD treatment of NW-PET showed that no morphological changes took place when a pulsatile plasma treatment was used.⁵

The aim of this study was to investigate the surface modification of NW-PET using a H₂O or CO₂ glow discharge. Moreover, the chemical surface characteristics of the internal H₂O and CO₂ RFGD-treated nonwoven surface were compared with the chemical surface characteristics of the facial (external) RFGD-treated nonwoven surface.

Various techniques were used to investigate whether H₂O and CO₂ RFGD treatment modifies the internal NW-PET surface of multilayer systems (two, six, and 20 layers NW-PET). The internal modification of NW-PET was studied using mass spectrometry. The modification process of NW-PET was monitored on-line with a mass spectrometer to measure the concentrations of various gases. The results of treatments with single- and multilayer systems were compared. Furthermore, the results of the mass spectrometric analysis were used to calculate the mean etching rate of NW-PET during H₂O and CO₂ RFGD treatment. X-ray photoelectron spectroscopy (XPS) was used to measure the surface composition of the RFGD-treated nonwovens. The surface concentration of carboxylic acid groups of H₂O and CO₂ RFGD-treated NW-PET was determined by titration using aqueous sodium hydroxide (NaOH). The stability of the H₂O and CO₂ RFGD-treated NW-PET facial surfaces to rinsing with water was investigated by XPS analysis and titration. LDPE films were positioned in the multilayer systems to obtain additional chemical information of the processes inside the package of nonwoven. Consequently, Wilhelmy plate contact angle (CA) measurements and XPS analysis on enclosed polyethylene films (F-PEs) were performed. Finally, the uniformity of the surface modification of a multilayer system was studied by titration of carboxylic acid groups present at the surface of the separated NW-PET layers.

EXPERIMENTAL

Filter Material

NW-PET was obtained from NPBI International BV (Emmer-Compascuum, The Netherlands).

NW-PET had a porosity of $84 \pm 1.2\%$, a BET surface area of $0.74 \pm 0.19 \text{ m}^2/\text{g}$, an average fiber diameter of $2.6 \pm 0.2 \mu\text{m}$, and a mean-flow pore-size diameter of $8 \pm 1.1 \mu\text{m}$. The methods were given elsewhere.⁴ One layer of NW-PET has a thickness of approximately 0.35 mm. The NW-PET was used as received.

Chemicals

Porofil was purchased from Coulter Electronics. Low-density polyethylene film (abbreviated F-PE, thickness 0.2 mm, type 2300) was obtained from DSM (Geleen, The Netherlands). PET film was obtained from ICI (Rotterdam, The Netherlands) (hereafter abbreviated F-PET). CO₂ (purity $\geq 99.995\%$) and air were purchased from Hoekloos (Schiedam, The Netherlands). Water was purified using a Milli-Q-plus system (Millipore, Molsheim, France). CO₂-free water was double-deionized. Subsequently, the CO₂-free water was stored under a N₂ purge. All other chemicals were supplied by Merck (Darmstadt, Germany).

Cleaning of the Films

F-PE and F-PET were ultrasonically cleaned in toluene, acetone, H₂O, and acetone (10 m, three times in each liquid) and dried overnight at room temperature (RT, $20 \pm 3^\circ\text{C}$) *in vacuo*.

Test System Used

Figure 1 shows the various systems: System A₁ represents a single layer of F-PET or NW-PET. Systems B₂ and B₆ represent a multilayer substrate consisting of two or six layers, respectively, of F-PET or NW-PET. Systems C₂, C₆, and C₂₀ represent a multilayer substrate consisting of two, six, or 20 layers, respectively, of NW-PET, which enclose a strip of four F-PEs ($4 \times 13 \times 25 \text{ mm}$). The edges (2 mm) of systems B₂, B₆, C₂, C₆, and C₂₀ were sealed by heat treatment using a sealing apparatus (Sealbox, Andion Electro). The dimensions of the substrates are given when appropriate.

RFGD Treatment of Nonwoven

The RFGD treatment of systems A–C were performed in a tubular reactor with a length of 80 cm and an internal diameter of 6.5 cm equipped with three externally placed, capacitively coupled electrodes. The powered (hot) electrode was placed at the center of the tubular reactor. On both sides of

the powered electrode, a grounded (cold) electrode was placed at a distance of 13 cm from the powered electrode. The electrodes were connected to a 13.56 MHz rf generator (ENI Power Systems, Rochester, NY) through a matching network (ENI Power Systems).²

The substrate was mounted in a glass frame. Two glass frames were loaded in the reactor, each placed in the middle between a grounded electrode and the powered electrode. After evacuating the reactor to a pressure below 0.01 mbar, a gas flow of 25 cm³/min for CO₂ and a gas flow of approximately 2.5 ± 0.5 cm³/min for H₂O was established. The pressure was raised to 0.32 mbar. The RFGD treatment was computer-controlled: After 5 min, a pulsatile glow discharge (3–10,000 pulses, 1 s on, 1 s off) was applied with an input power of 50 W. After the pulsatile glow-discharge treatment, the gas flow was maintained for 2 min and the reactor was brought to atmospheric pressure with air. The H₂O or CO₂ RFGD-treated NW-PET (abbreviated NW-PET-H₂O and NW-PET-CO₂, respectively) were removed from the reactor and stored in a storage container at 4°C to prevent surface rearrangements until further use.^{9,10}

Mass Spectrometric Analysis of the Gas Composition

The gas composition in the reactor was analyzed using a thermostated quadrupole mass spectrometer at 100°C (type QMC 421, Balzers, Lichtenstein). The gas was sampled from the reactor (pressure 0.32 mbar) through a small sampling tube with a controllable leak valve at the pumping side of the reactor. The pressure in the mass spectrometer was typically 2 × 10⁻⁵ mbar. This setup enabled an on-line process control. The composition of the gas flow was calculated from empirically derived calibration data.

Determination of the Gas Composition as a Function of the Reactor Load

The concentration of the gases H₂, H₂O, CO, O₂, and CO₂ were measured on-line, before, during, and after a pulse plasma RFGD treatment as a function of the reactor load (e.g., NW-PET and F-PET, type A or type B). The concentration of other gases (e.g., He, Ar) were so small that they were neglected.

Rinsing of NW-PET

The NW-PET, NW-PET-H₂O, and NW-PET-CO₂ (system A) were cut into discs with a diam-

eter of 26 mm. The discs were subsequently rinsed with CO₂-free H₂O (50 mL) under a nitrogen atmosphere on a Vibrax VXR flat bed shaker (1 cycle/s, Labortechnik, Staufen, Germany) at RT. After 1 h, the nonwoven discs were rinsed once with fresh CO₂-free H₂O (25 mL, for 30 s). Subsequently, the samples were dried overnight *in vacuo* at RT. The water rinsed samples are marked with the superscript *w*.

X-ray Photoelectron Spectroscopy (XPS)

The surface composition of NW-PET and F-PE film was analyzed by XPS using a Kratos XSAM-800 apparatus (Kratos Analytical, Manchester, UK).⁴ Deconvolution of the XPS C1s spectra in various subpeaks was performed using the computer program Micro Origin 4.10. The C1s peak for aliphatic carbon was fixed at 284.6 eV.¹¹ The C1s peak of nonwovens was deconvoluted into the (a) —C—C— (284.6 eV), (b) —C—O— (286.3), (c) —C=O (287.5 eV), (d) O=C—OR (288.6 eV), and (e) π→π* shake-up satellite (290.7 eV). The peak width at half-maximum (1.4 eV) and the binding energy of the peaks were fixed during deconvolution of the C1s spectrum.

Titration of Carboxylic Acid Groups

Approximately 0.5 g nonwoven was cut into small pieces and added to 40 mL CO₂-free H₂O. The sample was kept under a nitrogen atmosphere throughout the analysis at RT. The pH of the sample was measured using an Orion pH electrode (Orion Research Inc., Boston, MA). The titration of carboxylic acid groups was performed by adding aliquots of 0.005 mL of a 2 mM NaOH solution to the sample. The addition of the 2 mM NaOH solution was computer-controlled (636 Titroprocessor, Methrom, Herisau, Switzerland). An aliquot of 0.005 mL of the 2 mM NaOH solution was added to the sample if the pH of the solution did not change with more than ±0.033 for a period of 3.2 s or after a total period of 100 s. The addition of the 2 mM NaOH solution was stopped after the pH value of the solution had reached a value of 9. The titer of the 2 mM NaOH solution was determined by titration with a 10.0 mM HCl solution.

Wilhelmy Plate CA Measurements of F-PE

The advancing and receding CAs of F-PE (13 × 25 mm) in H₂O were determined using the Wilhelmy plate method. F-PE was moved through the air-

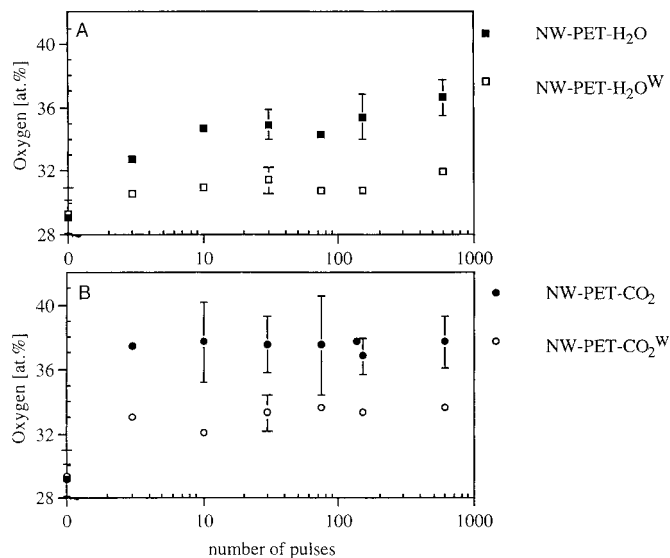


Figure 2 XPS measurements on RFGD-treated NW-PET. The atomic percentage of oxygen for (A) NW-PET-H₂O and (B) NW-PET-CO₂ as a function of the number of pulses (1 s off, 1 s on), (closed symbols) before and (open symbols) after water rinsing. For this experiment, system C₂ (total external NW-PET surface area of 180 cm²) was used and the facial surface was analyzed.

water interface with a controlled speed of 0.18 mm/s using an electrobalance (Model RM-2, Cahn/Ventron, Paramount, CA). After measuring the CA of a film, the water was refreshed.

Statistical Evaluation

Unless indicated otherwise, all values are expressed as the mean \pm standard deviation (sd). Statistical analyses were performed using the unpaired two-tailed Student *t*-test. Differences were considered significant if $p < 0.05$.

RESULTS

Oxidation of the External NW-PET Surface

RFGD treatment of NW-PET was performed to oxidize the NW-PET surface. Figure 2 shows the atomic percentage of oxygen of NW-PET as a function of the number of pulses of H₂O or CO₂ RFGD treatment. The surface concentration of oxygen of NW-PET increases with increasing number of pulses for the H₂O RFGD treatment, but levels off after 10 pulses. CO₂ RFGD treatment of NW-PET introduced more oxygen onto the external NW-PET surface than did H₂O RFGD treatment and the plateau value for the oxygen concentration was reached earlier. After

two pulses of the CO₂ RFGD treatment, the percentage of oxygen of NW-PET reached a plateau level of about 37.4%, compared to 36.6% oxygen after the 600-pulse H₂O RFGD treatment. Occasionally, the H₂O and CO₂ RFGD-treated nonwoven surfaces contained a small percentage of nitrogen (<0.5%, data not shown).

The C1s spectra were deconvoluted into five subpeaks to obtain qualitative information on the chemical composition of NW-PET-H₂O and NW-PET-CO₂ as a function of the number of pulses. The results in Table I confirmed that oxidation by the CO₂ RFGD treatment is faster than is oxidation by the H₂O RFGD treatment. With an increasing number of pulses, the concentration of —C—C— bonds decreases faster for the CO₂ RFGD treatment than for the H₂O RFGD treatment. Within three pulses of the RFGD treatment, —C=O bonds were formed for both treatments, which stayed more or less constant throughout the remainder of the treatment. For the CO₂ RFGD treatment, a plateau amount of —C—O— bonds was reached within three pulses. After prolonged RFGD treatment, the percentages of carbon in the various peaks of the C1s spectra of NW-PET-CO₂ were comparable to the percentages of carbon in the various peaks of the C1s spectra of NW-PET-H₂O. During both treat-

Table I Deconvolution of the C1s Spectra Obtained from XPS Measurements on NW-PET

	—C—C—	—C—O—	—C=O	O=C—OR	$\pi \rightarrow \pi^*$
	(%)	(%)	(%)	(%)	(%)
	(284.6 eV)	(286.3 eV)	(287.5 eV)	(288.6 eV)	(290.7 eV)
Nonwoven					
NW-PET	59	21	0	18	2
NW-PET-H ₂ O					
Pulses					
3	57	19	4	18	2
10	49	22	5	22	2
30	49	25	4	20	2
75	48	24	4	22	2
150	45	25	9	19	2
600	50	23	4	21	2
NW-PET-CO ₂					
Pulses					
3	50	25	5	18	2
10	48	25	5	20	2
30	47	26	4	21	2
75	48	25	5	21	2
150	48	25	5	21	2
600	45	25	6	22	2

The type of carbon bond, the binding energy (BE) of the fitted peak, and the percentage of surface area are given for NW-PET-H₂O and NW-PET-CO₂ treated for different times.

ments, the percentage of the surface area of the $\pi \rightarrow \pi^*$ shake-up peak stayed the same.

Titration experiments were performed to measure the concentration of carboxylic acid groups of NW-PET-H₂O and NW-PET-CO₂ as a function of the number of pulses. Figure 3 shows that the surface concentration of carboxylic acid groups of the RFGD-treated NW-PET increases with an increasing number of pulses. The concentration of

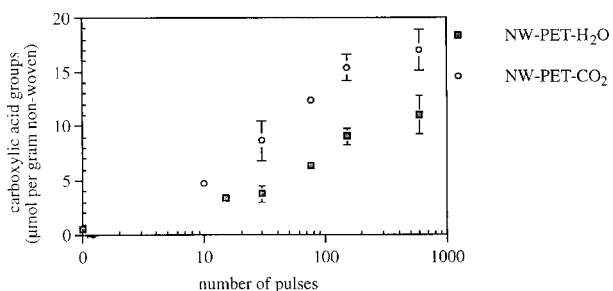


Figure 3 Titration of RFGD-treated NW-PET. The concentration of carboxylic acid groups of (■) NW-PET-H₂O and (○) NW-PET-CO₂ as a function of the number of pulses. The experiments were performed with system A₁ (facial surface area: 180 cm²).

carboxylic acid groups of NW-PET-H₂O was significantly lower than was the concentration of carboxylic acid groups of NW-PET-CO₂. For both cases, the concentration of carboxylic acid groups did not reach a plateau value.

Stability of NW-PET-H₂O and NW-PET-CO₂

The stability of the modified NW-PET surfaces toward rinsing with water was tested using XPS and titration. Figure 2 shows the percentages of oxygen on the surface of water-rinsed modified NW-PET as a function of the number of pulses of H₂O or CO₂ RFGD treatment. Water rinsing of the RFGD-treated NW-PET significantly reduced the surface concentration of oxygen. NW-PET-H₂O^w contained less oxygen than did NW-PET-CO₂^w. The percentage of oxygen of NW-PET-H₂O^w increased slightly from 29.3% oxygen for zero pulses to about 32% oxygen for 600 pulses, while NW-PET-CO₂^w contained about 33% oxygen, regardless of the number of pulses (3–600).

Titration of NW-PET-H₂O^w and NW-PET-CO₂^w with 2 mM NaOH revealed a significant decrease of the concentration of carboxylic acid groups as a result of the water-rinsing procedure

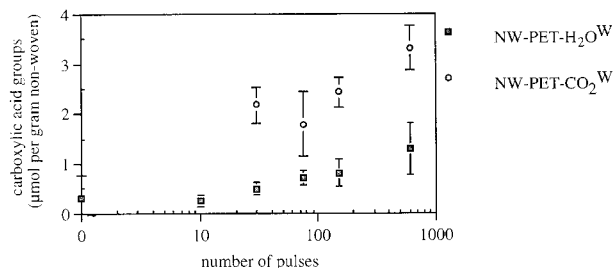


Figure 4 Titration of water-rinsed RFGD-treated NW-PET. The concentration of carboxylic acid groups of (■) NW-PET-H₂O^w and (○) NW-PET-CO₂^w as a function of the number of pulses. The experiments were performed with system A₁ (facial surface area: 180 cm²).

(Fig. 4). The concentration of carboxylic acid groups of NW-PET-H₂O^w was significantly lower than for NW-PET-CO₂^w.

The results in Table II show that the —C=O bonds introduced by the RFGD treatment were still present after rinsing with water. Moreover, the percentages of carbon in the —C—O— and

O=C—OR bonds of the C1s spectra of NW-PET-CO₂^w were higher than were the percentages of carbon in the —C—O— and O=C—OR bonds of the C1s spectra of NW-PET-H₂O^w.

Comparing the results of Tables I and II, it can be seen that rinsing with water causes the removal of highly oxidized material for both treatments: The concentration of O=C—OR bonds decreased, whereas the concentration of —C—C— bonds increased. This effect is illustrated for the 30-pulse H₂O and CO₂ RFGD-treated nonwovens in Figure 5.

Analysis of the Gas Composition by Mass Spectrometry

On-line-mass spectrometry was used to measure the gas concentrations (H₂, H₂O, CO, O₂, and CO₂) in the plasma reactor before and during RFGD treatment. Figure 6 shows the on-line measurements for H₂O RFGD treatment of an empty reactor and a reactor loaded with NW-PET (system A₁; 159 cm²). After 120 s, the RFGD treatment was started for 150 pulses (1 s on, 1 s off).

Table II Deconvolution of the C1s Spectra Obtained from XPS Analysis of Water-Rinsed NW-PET

Nonwoven	—C—C—	—C—O—	—C=O	O=C—OR	π → π*
	(%)	(%)	(%)	(%)	(%)
	(284.6 eV)	(286.3 eV)	BE (eV)	(288.6 eV)	(290.7 eV)
NW-PET ^w	60	21	0	17	2
NW-PET-H ₂ O ^w					
Pulses					
3	60	18	4	17	2
10	57	20	4	17	2
30	56	21	4	18	1
75	55	21	4	18	2
150	55	23	2	18	2
600	55	23	3	18	1
NW-PET-CO ₂ ^w					
Pulses					
3	52	23	4	19	2
10	51	24	4	19	2
30	50	24	4	20	2
75	49	26	4	19	2
150	51	25	3	19	2
600	50	25	4	19	2

The type of carbon bond, the binding energy (BE) of the fitted peak, and the percentage of surface area are given for NW-PET-H₂O and NW-PET-CO₂ treated for different times.

Subscript *w*: Prior to XPS analysis, the nonwovens were rinsed with water for 60 min at RT; thereafter, the nonwovens were dried overnight *in vacuo*.

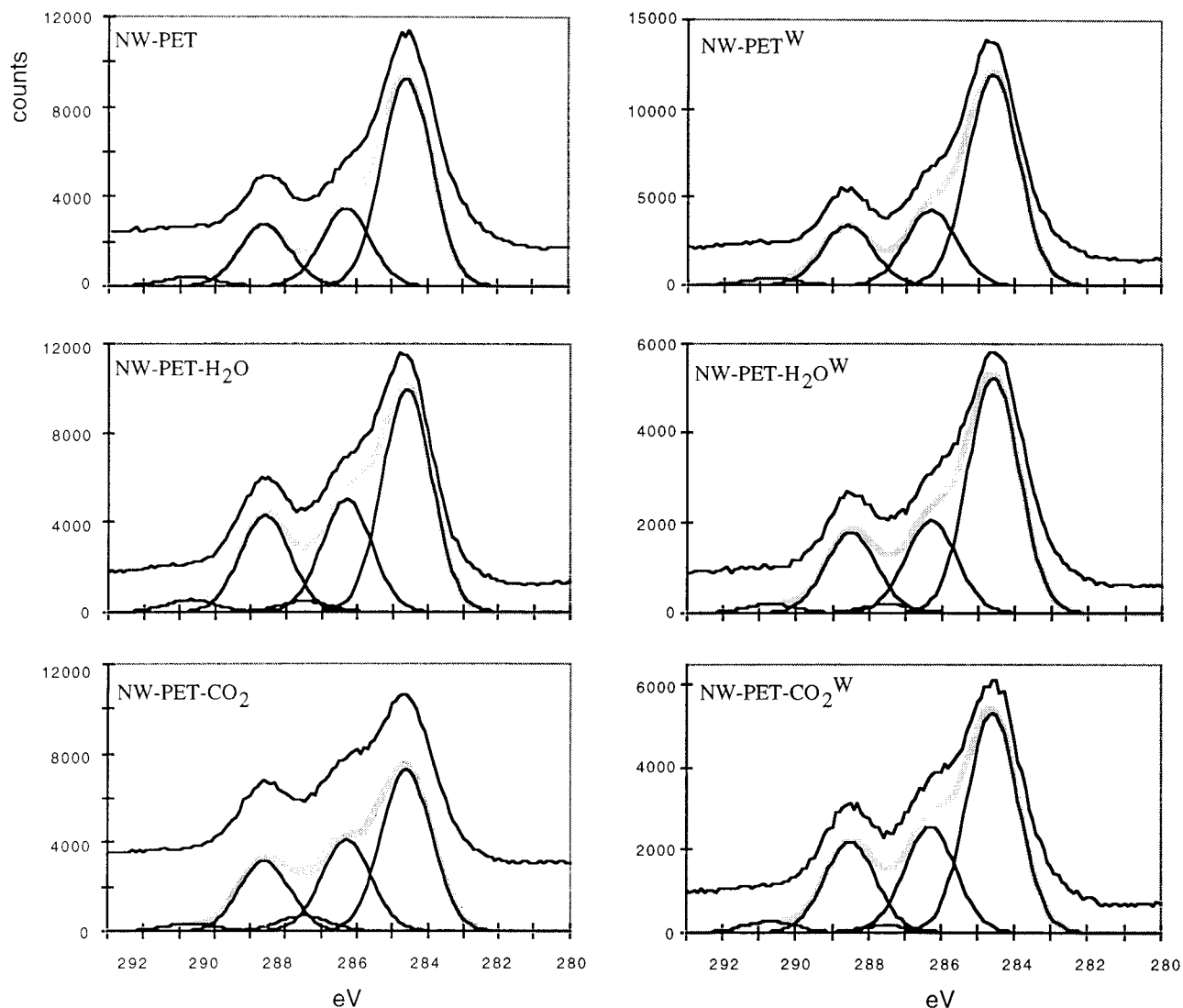


Figure 5 C1s spectra and C1s envelope of (A) NW-PET, (B) NW-PET^w, (C) NW-PET-H₂O, (D) NW-PET-H₂O^w, (E) NW-PET-CO₂, and (F) NW-PET-CO₂^w. The C1s envelope of the spectra were fitted according to Gaussian peaks for the —C—O— (286.3 eV), the —C=O (287.5 eV), and the O=C—OR (288.6 eV) groups and the $\pi \rightarrow \pi^*$ shake-up peak (290.7 eV). The binding energy of the —C—C— group was set at 284.6 eV. An offset was used for the C1s spectra.

During H₂O RFGD treatment of the empty reactor, the H₂ and the O₂ concentrations increased from 0.0 and 0.2% to about 30.1 and 15.4%, respectively. The CO₂ concentration slightly increased from 0.1% to about 0.8% and the H₂O concentration decreased from 99.4% to about 53.4%. The concentration of H₂, H₂O, CO, and CO₂ changed even more when NW-PET was present during the H₂O RFGD treatment. In a typical experiment, the concentrations of H₂, CO, and CO₂ increased further to about 37.6, 5.7, and 14.2%, respectively, and the H₂O concentration

decreased to 37.9%. The increase of the O₂ concentration was reduced to 4.6%.

The mean etching rate of NW-PET during H₂O RFGD treatment was determined from the measured gas composition.¹² The overall etching rate for H₂O RFGD treatment of NW-PET (system A₁) under the given conditions (0.32 mbar, 2.5 mL/min, 50 W, and a NW-PET surface area of 159 cm²) was about 245 Å/min.

Figure 7 shows the results of the on-line mass spectrometric analysis during the CO₂ RFGD treatment of the empty reactor and the reactor

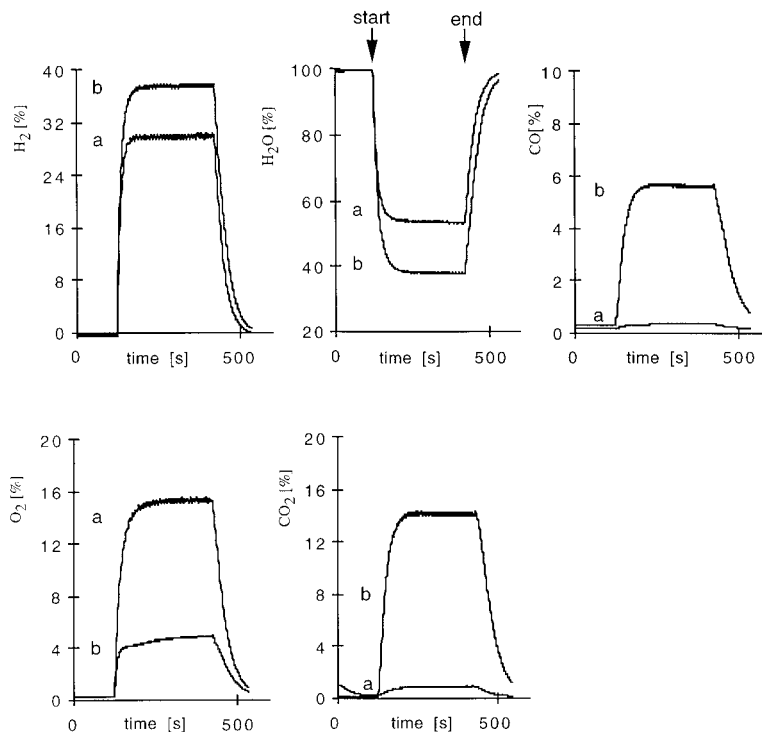


Figure 6 On-line mass spectrometric analysis of the concentration of H_2 , H_2O , CO , O_2 , and CO_2 before, during, and after H_2O RFGD treatment. During the entire process, the reactor was either (a) empty or (b) loaded with NW-PET (system A_1 ; facial surface area of 159 cm^2). The start and end of the RFGD treatment are indicated with arrows.

loaded with NW-PET. During CO_2 RFGD treatment of the empty reactor, the concentrations of CO and O_2 increased from 0 and 0.2% to about 10.9 and 5.1%, respectively, and the concentrations of H_2 and H_2O remained practically constant. Considerable changes in the various gas concentrations were observed during CO_2 RFGD treatment of NW-PET compared to CO_2 RFGD treatment without NW-PET (empty reactor).

In a typical experiment, the concentrations of H_2 and the H_2O increased from 0 and 0.3% to approximately 0.9 and 1.9%, respectively. The concentration of CO increased to about 17.3% and the concentration of CO_2 decreased to 76.8%. Moreover, the concentration of O_2 decreased to 3.2%.

The mean etching rate of NW-PET during CO_2 RFGD treatment was determined from the measured gas composition.^{8,12} The etching rate for CO_2 RFGD treatment of NW-PET (system A_1) under the given conditions (0.32 mbar, 25 mL/min, 50 W, and a NW-PET surface area of 159 cm^2) was about $629 \text{ \AA}/\text{min}$.

Modification of the Surface Within a Single Layer of NW-PET

To determine whether the surface within a single layer of NW-PET was modified, the changes in the gas composition into the reactor were measured as a function of the facial surface area of NW-PET loaded into the reactor. F-PET was used as a control. Figure 8 reveals that during H_2O RFGD treatment of NW-PET and F-PET H_2O was dissociated to a larger extent than without the presence of NW-PET and F-PET. The concentration of H_2 , CO , and CO_2 increased with increasing total facial NW-PET or F-PET surface area. A substantial increase of the concentration of H_2 , CO , and CO_2 was also observed after increasing the internal NW-PET surface area. The increase of the O_2 concentration during H_2O RFGD treatment of NW-PET and F-PET was less compared to RFGD treatment of the empty reactor. The increase of the O_2 concentration was further reduced with increasing total facial NW-PET or F-PET surface area. Furthermore, the O_2

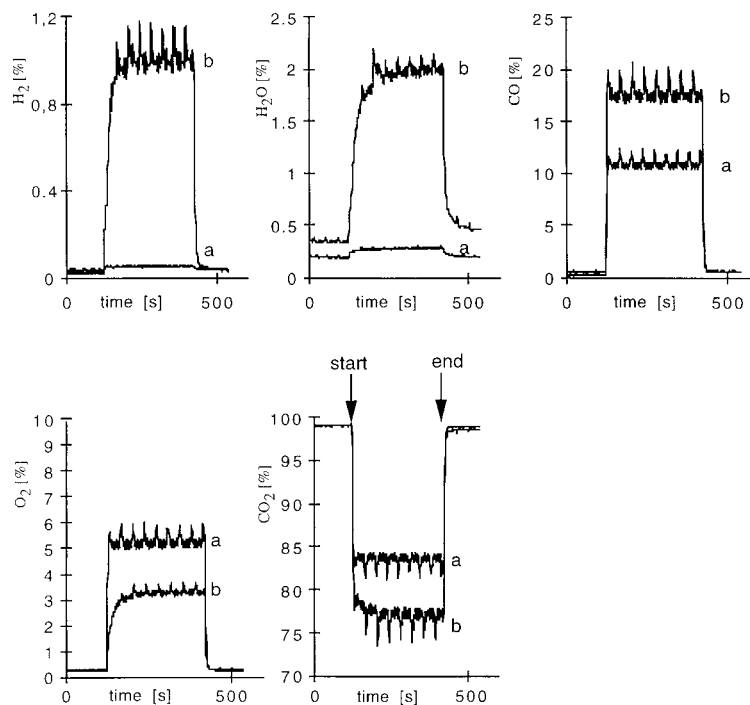


Figure 7 On-line mass spectrometric analysis of the concentration of H_2 , H_2O , CO , O_2 , and CO_2 before, during, and after CO_2 RFGD treatment. During the entire process, the reactor was either (a) empty or (b) loaded with NW-PET (system A₁; facial surface area of 159 cm^2). The start and end of the RFGD treatment are indicated with arrows. The saw-tooth pattern is caused by instability in the gas pressure.

concentration decreases with increasing internal NW-PET surface area.

Modification of the Surface Within Multilayers of NW-PET

Various systems C (Fig. 1) were used to determine whether the internal NW-PET surface area was modified. This was measured by XPS analysis of the internal and external nonwoven surface.

The introduction of oxygen onto the internal nonwoven surface of system C₂ by H_2O or CO_2 RFGD treatment was slower than for the facial nonwoven surface (Fig. 9). Only for the facial surface, a plateau value for the oxygen concentration was reached after about 10 pulses. After 100–150-pulse H_2O and CO_2 RFGD treatments, the differences in the atomic percentages of oxygen between the facial and the internal nonwoven surface disappeared.

A different and indirect way to determine whether the internal NW-PET surface area is modified is by determining the surface modification of F-PEs, which are present between two

layers of NW-PET (system C₂) during RFGD treatment. This was carried out by Wilhelmy plate CA measurements and XPS analysis. By using this system, it was also possible to determine the maximum amount of layers which can be modified at once.

Figure 10 shows the advancing and the receding CAs of RFGD-treated F-PEs enclosed between two layers of NW-PET as a function of the number of pulses. The advancing CA of F-PE decreases with an increasing number of pulses of H_2O and CO_2 RFGD treatment. After about 60 pulses of H_2O RFGD treatment and about 30 pulses of CO_2 RFGD treatment, the receding CA of F-PE was 0° , while the advancing CA of F-PE had reached a plateau level of about 55° .

Figure 11 shows the results of XPS measurements of F-PEs, which were present in between two layers of NW-PET during RFGD treatment. The atomic percentages of oxygen of F-PE increased with increasing number of pulses. No plateau value was reached. The atomic percentages of oxygen for 600-pulse H_2O and CO_2 RFGD-treated F-PE were about 21 and 25%, respec-

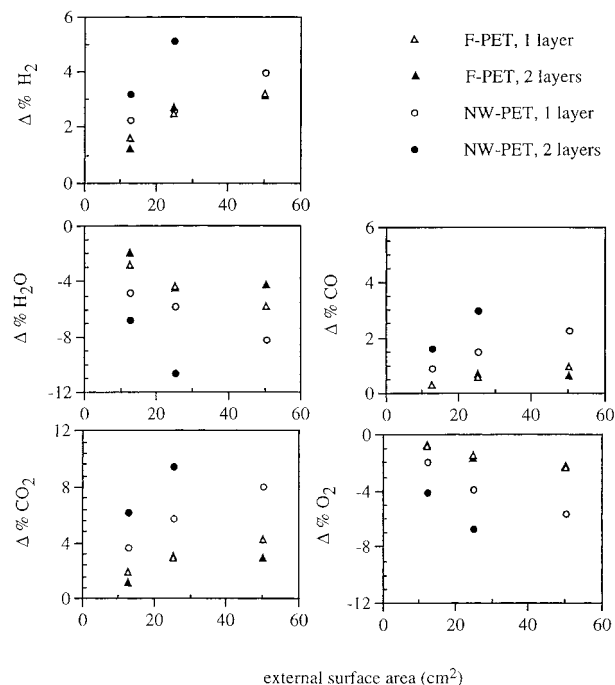


Figure 8 Mass spectrometric analysis of the gas composition during RFGD treatment of NW-PET and F-PET. Changes in the H_2 , H_2O , CO , O_2 , and CO_2 concentrations during H_2O RFGD treatment of system A_1 or B_2 as a function of the facial surface area of the substrate compared to RFGD treatment of the empty reactor. Either NW-PET or F-PET were used as the substrate.

tively, which is rather high compared to results reported by others.^{2,3}

To investigate whether more than two stacked layers could be modified, tests were performed with substrates consisting of six and 20 layers NW-PET. Figure 12 shows the advancing and receding CA of F-PEs, which were obtained from system C_6 , as a function of the number of pulses. For system C_6 , about 300 pulses were needed to achieve a receding CA of 0° . After 600 pulses, the advancing CA of F-PE had decreased to values of 20° and 45° for CO_2 and H_2O RFGD treatment, respectively.

CA measurements of H_2O RFGD-treated F-PEs which were present in between a substrate consisting of 20 layers NW-PET (system C_{20}) revealed that even after 6000 pulses the internal nonwoven surface was not completely modified (Fig. 13). To evaluate the homogeneity of the surface modification as a function of the depth in the nonwoven, the surface composition and surface concentration of carboxylic acid groups of RFGD-

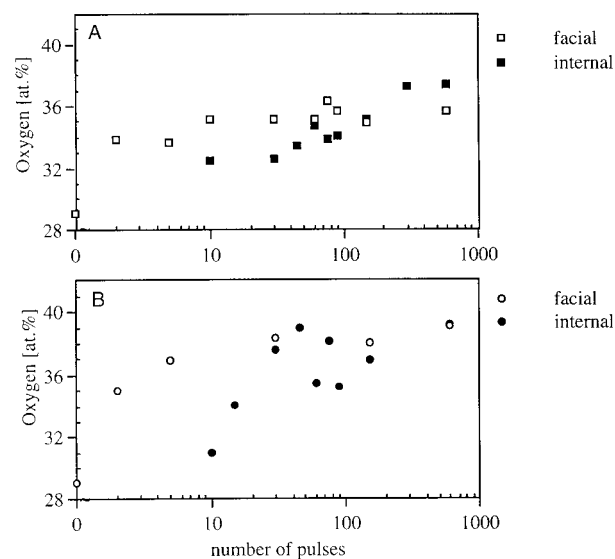


Figure 9 XPS analysis of (closed symbols) the internal side of the nonwoven and (open symbols) the external (facial) side of the nonwoven surfaces as a function of the number of pulses of (A) H_2O and (B) CO_2 RFGD treatment. System C_2 was used with a NW-PET facial surface area of 180 cm^2 .

treated nonwoven in the B_6 configuration were studied. This substrate consisted of six layers of NW-PET and was treated with either 600-pulse H_2O or 600-pulse CO_2 RFGD.

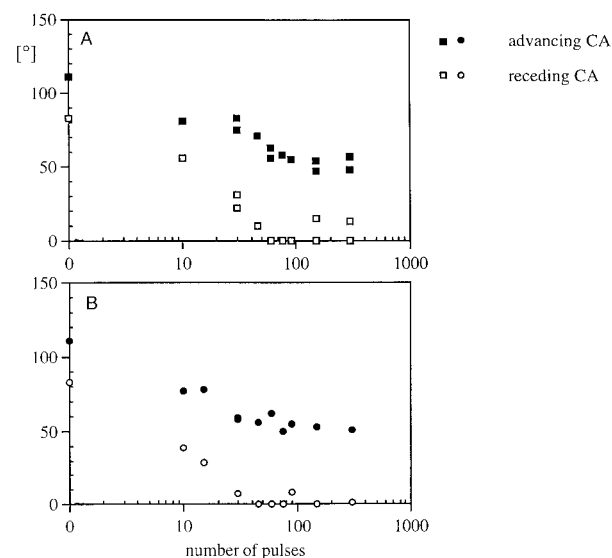


Figure 10 Advancing (closed symbols) and receding (open symbols) CAs of F-PE as a function of the number of pulses of (A) H_2O and (B) CO_2 RFGD treatment. The experiment was performed using system C_2 , with a facial surface area of 180 cm^2 .

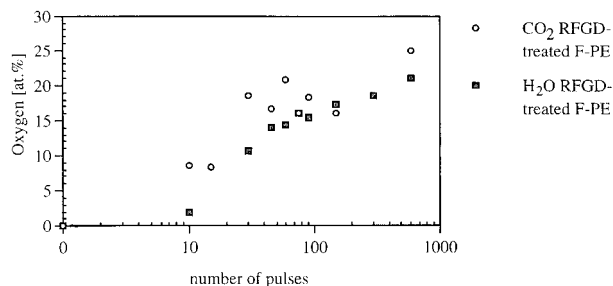


Figure 11 XPS analysis of F-PEs which were enclosed between NW-PET during RFGD treatment. The percentage of oxygen of F-PE as a function of the number of pulses of (■)H₂O and (○)CO₂ RFGD treatment. The experiment was performed using system C₂, of which the total external surface area was 180 cm².

The surface concentration of oxygen on the layers 1 and 6, 2 and 5, and 3 and 4 of NW-PET-H₂O and NW-PET-CO₂ did not significantly differ from each other [Fig. 14(A)]. In spite of this, the surface concentration of carboxylic acid groups decreases going from the outside layers (1 and 6) to the inside layers (2 and 5 and 3 and 4) for both the H₂O and CO₂ RFGD-treated systems [Fig. 14(B)].

The atomic percentage of oxygen of the 600-pulse H₂O RFGD-treated layers of NW-PET (≈34 at %) was lower than for the 600-pulse CO₂ RFGD-treated layers of NW-PET (≈38 at %). Moreover, the surface concentration of carboxylic acid groups of the 600-pulse H₂O RFGD-treated

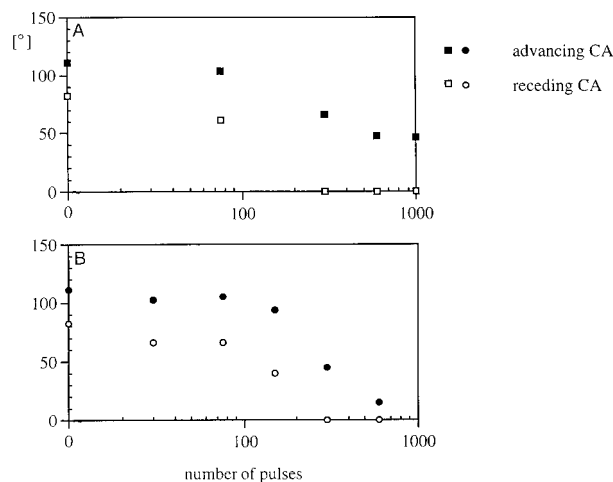


Figure 12 Wilhelmy plate advancing (closed symbols) and receding (open symbols) water CAs of (A) F-PE-H₂O and (B) F-PE-CO₂ as a function of the number of pulses of RFGD treatment. The F-PEs were obtained from system C₆, of which the total external NW-PET surface area was 180 cm².

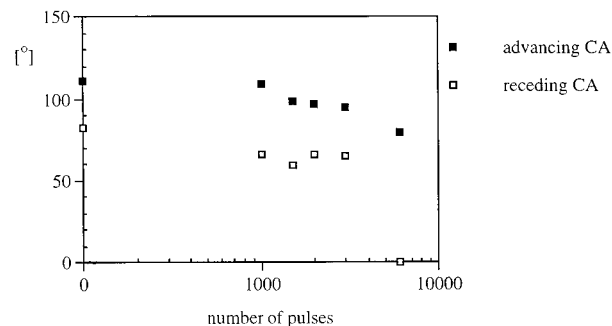


Figure 13 Advancing (closed symbols) and receding (open symbols) CA of F-PE as a function of the number of pulses of H₂O RFGD treatment. System C₂₀ was used with a facial surface area of 180 cm².

layers of NW-PET was significantly lower than that of the 600-pulse CO₂ RFGD-treated layers of NW-PET.

DISCUSSION

This study described the modification of NW-PET either using a pulsed H₂O or a CO₂ RFGD treatment. Of primary importance is the optimal number of pulses to treat NW-PET to ensure that the nonwoven surface is completely modified both internally and externally. A short treatment time can give an insufficient modification, resulting in a nonwoven of which the internal surface is not completely modified, whereas the use of too long treatment times will lead to highly oxidized sur-

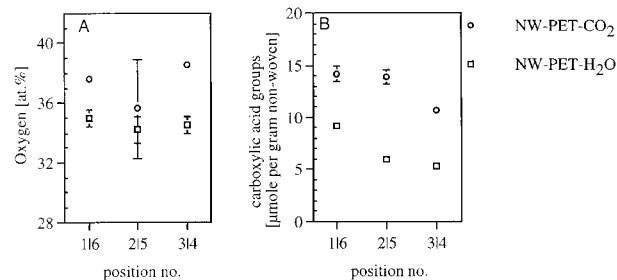


Figure 14 XPS analysis and titration of NW-PET layers treated as a package of six layers. (A) The atomic percentage of oxygen and (B) the surface concentration of carboxylic acid groups of the 600-pulse H₂O or CO₂ RFGD-treated system B₆ is given as a function of the nonwoven layer position in the system. The facial surface area of system was 180 cm². The layers 1|6 and the layers 3|4 represent the outside and inside layers, respectively.

faces which may be highly unstable in aqueous environments. This is important because our intention was to apply modified NW-PET in a filter for the removal of leukocytes from platelet concentrates. Therefore, the total NW-PET surface preferably has to be homogeneously modified.

When applying a H₂O plasma to treat NW-PET, it was observed that the introduction rate of oxygen onto the facial nonwoven surface was about two to three times lower in comparison to a CO₂ plasma. This correlates quite well with the difference in etching rates between H₂O RFGD treatment of NW-PET (245 Å/min) and CO₂ RFGD treatment of NW-PET (645 Å/min). In addition, H₂O RFGD treatment of NW-PET (system A₁, Fig. 2) introduced a lower amount of oxygen onto the facial nonwoven surface than did a CO₂ RFGD treatment.

The difference in oxygen levels between NW-PET-H₂O and NW-PET-CO₂ is probably caused by differences in oxidation reactions during H₂O and CO₂ RFGD treatment of NW-PET. Probably, various progressive oxidation reactions occur more extensively during CO₂ RFGD treatment than during H₂O RFGD treatment. This also explains the large difference in surface concentration of carboxylic acid groups between NW-PET-H₂O and NW-PET-CO₂ (Fig. 3).

Deconvolution of the C1s spectra of NW-PET-H₂O and NW-PET-CO₂ revealed only some small differences with respect to individual chemical moieties on the facial nonwoven surface. In unmodified NW-PET, 40% of the carbon atoms are present in oxygen-containing functional groups (e.g., —C—O— and O=C—OR) (Table I).

The percentage of carbon atoms in oxygen-containing groups was slightly increased to about 43% during the first three pulses of H₂O RFGD treatment of NW-PET. This was caused mainly by the introduction of —C=O groups.

Both the percentage of carbon atoms in the —C—O— and —C=O functional groups increases during the first three pulses of CO₂ RFGD treatment of NW-PET. After three pulses of CO₂ plasma, the percentage of carbon atoms in oxygen-containing groups remains constant.

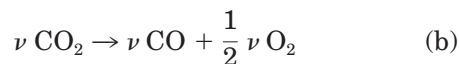
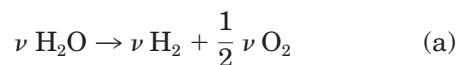
During exposure to plasma, the oxidative etching process of the nonwoven surface is believed to start by abstraction of the hydrogen atoms from the polymer backbone. Hydrogen atom abstraction can proceed via two routes: by bombardment of oxygen radicals and oxygen atoms and by UV radiation. The active sites on the polymer backbone can react with one another, resulting in the

formation of crosslinks, or they can react with species from the gas phase to form oxygen-containing groups on the polymer surface. With increasing treatment time, the surface-bound oxygen-containing groups can be oxidized to more highly oxidized groups.³

Based on the data in Table I, the following sequence of events may be deduced: At short exposure times to the plasma, carbonyl groups are mainly formed. In the case of CO₂ plasma, —C—O— (e.g., hydroxyl, ether) groups are also formed. Prolonged treatment with the H₂O and CO₂ plasmas leads to a higher concentration of O=C—OR (carboxylic acid and ester) groups, but in case of H₂O plasma, this also leads to a higher concentration of —C—O— groups.

After rinsing with water, the amount of oxygen on H₂O and CO₂ RFGD-treated surfaces is substantially reduced. Probably, a considerable number of the oxygen-containing groups was incorporated into the water-soluble material. This was supported by the finding that about 70–85% of the incorporated carboxylic acid groups were removed from the nonwoven surface by washing (Fig. 4). The surface density of carboxylic acid groups for the 600-pulse H₂O RFGD-treated NW-PET was about one group per 35 Å², and for the 600-pulse CO₂ RFGD-treated NW-PET, about one group per 12 Å². After rinsing with water, the surface density of carboxylic acid groups decreased considerably to a surface density of carboxylic acid groups of one group per 95 Å² and one group per 37 Å², for the 600-pulse H₂O and CO₂ RFGD-treated NW-PET, respectively. The removal of carboxylic acid groups due to rinsing with water is less clear if one considers the decrease in the concentration of oxygen in carboxylic acid bonds. This is possibly due to the shift in character of the oxygen atoms at the nonwoven surface, indicating an increase in ester groups at the cost of the carboxylic acid groups.

Mass spectrometry was used to characterize the H₂O and CO₂ RFGD treatment of NW-PET and to determine the etching rate of NW-PET (see Figs. 6 and 7). The dissociation of H₂O in H₂ and O₂ and the dissociation of CO₂ in CO and O₂ during RFGD in an empty reactor can be described with eqs. (a) and (b):



For both H₂O and CO₂ plasma treatments, high concentrations of oxygen in the gas-phase were measured. Mass spectrometrical measurements revealed a higher dissociation constant ν for H₂O (0.36) than for CO₂ (0.11). The differences in ν between H₂O and CO₂ plasma treatments can be explained by differences in the residence time of the gas in the reactor. This is longer for water vapor (about 2.5 mL/min, 0.32 mbar) than for carbon dioxide (25 mL/min, 0.32 mbar). It has been reported that the dissociation of the CO₂ molecules will be initiated by the excitation of the CO₂ molecules (e.g., by electron impact, by UV radiation, or by dissociative ionization). No reports of the dissociation mechanisms of H₂O molecules in a H₂O plasma are available.

During CO₂ RFGD treatment of NW-PET, only H₂, H₂O, CO, O₂, and CO₂ were detected and no other species (hydrocarbons) were present. Takens showed that hydrocarbons are probably immediately oxidized in the plasma phase.³ This was illustrated by the failure to detect toluene by mass spectrometry during CO₂ RFGD treatment of F-PE which was swollen with toluene.

Which oxidation products are preferentially formed during RFGD treatment of NW-PET depends on the amount of oxygen available for the oxidation.¹² By analyzing the gas flow leaving the reactor with a mass spectrometer (MS) during RFGD treatment of NW-PET, it was possible to make a mass balance. The mass spectrometrical data showed that carbon, oxygen, and hydrogen atoms present in the polymeric chain of NW-PET were converted to H₂, H₂O, CO, O₂, and/or CO₂. However, different oxidation regimes were found. During H₂O RFGD treatment, the main fraction of oxygen was used for complete oxidation of NW-PET into CO₂ and H₂O, whereas a small fraction was used for incomplete oxidation of NW-PET. During CO₂ RFGD treatment of NW-PET, equal fractions of oxygen were used for complete and incomplete oxidation of NW-PET and a small fraction of oxygen was used for "oxygen-deficient" oxidation (formation of H₂ and CO). From the mass balance determined by Takens,⁸ it can be calculated that the etching rate is about 245 and 645 Å/min, when applying a H₂O or CO₂ plasma to treat NW-PET, respectively.

MS analysis of the gas composition during H₂O RFGD treatment of NW-PET revealed that the internal surface of NW-PET layer is also modified. During H₂O RFGD treatment, the gas composition changes when the internal nonwoven

surface increases without increasing the external nonwoven surface (Fig. 8).

XPS measurements on multilayer NW-PET systems and CA measurements of F-PE, which were enclosed in the nonwoven packages, supported the occurrence of internal modification of NW-PET (Figs. 9–13). XPS analysis revealed that for a substrate consisting of two layers of NW-PET about 100–150 pulses were needed to modify the internal NW-PET surface compared to three to 10 pulses for the external nonwoven surface. CA measurements of RFGD-treated F-PEs, which were in between two layers of NW-PET, revealed that about 30–45 pulses were needed to obtain a plateau level of 55° for the advancing CA. The difference in the oxidation rate in the glow (facial surface) and afterglow (internal surface) is more generally observed.³ However, in this specific situation, the reactive species released by the PET nonwoven surface can participate in the modification of the most internal nonwoven surface. This is supported by the fact that a rather high surface concentration of oxygen at F-PE after H₂O and CO₂ RFGD treatment was found. For instance, F-PE, which was in between two layers of NW-PET, contained about 21 and 25% oxygen after 600-pulse H₂O or CO₂ RFGD treatment. Extensive studies of Terlingen et al. and Takens showed an introduction of 13–15% oxygen after prolonged CO₂ RFGD treatment of F-PE.^{2,3} These treatments were performed in the same reactor as for NW-PET. It is concluded that reactive species diffuse into the nonwoven pores and react with or deposit onto the F-PE surface, yielding a higher oxidation level. Consequently, the surface chemistry will be different from that observed for films treated directly in the plasma (Figs. 10 and 12).

From the results in this study, it can be concluded that when the number of layers of NW-PET was increased from two to six, 10–20 times more pulses were necessary to modify the external and internal nonwoven surface. Even more, at least 200 times more pulses were needed, after increasing the number of layers of NW-PET from two to 20 (Figs. 10, 12, and 13).

The facial surface of a package of nonwoven layers was treated more intensively than was the internal nonwoven surface of the package. For instance, in case of system B₆, the concentration of carboxylic acid groups was lower for the inner layers of the package compared to the outside layer of the package for both H₂O and CO₂ RFGD treatments (Fig. 14). Consequently, to prevent

long treatment times and to prevent an inhomogeneously treated nonwoven surface, RFGD treatment of NW-PET should preferably be performed per single layer (system A₁).

CONCLUSIONS

It can be concluded that the facial and internal surface of a single NW-PET layer is modified during H₂O or CO₂ glow discharges using the experimental settings as described in this article. The surface of NW-PET is more oxidized by using a CO₂ RFGD treatment than by using a H₂O RFGD treatment. The higher surface concentration of oxygen for CO₂ RFGD-treated NW-PET is partly due to a higher surface concentration of carboxylic acid groups. H₂O and CO₂ RFGD treatments differ with respect to the type of (progressive) oxidation reactions that take place at the nonwoven surface.

The surface composition of the H₂O and CO₂ RFGD-treated NW-PET changes by washing with water. In spite of this, both 600-pulse RFGD-treated NW-PET-H₂O^w and 600-pulse RFGD-treated NW-PET-CO₂^w have a considerable surface concentration of carboxylic acid groups (one group per 95 and 37 Å², respectively) compared to NW-PET^w (one group per 440 Å²).

A large number of pulses (>6000) was needed to modify the internal nonwoven surface of a package of 20 layers (approximately 7 mm thick) of NW-PET compared to a single layer of NW-PET (<30 pulses). The surface composition of the inner layers differed from the surface composition of the outer layers. For example, RFGD treatment of a package of six layers of NW-PET (600 pulses) introduced a significant difference in the surface concentration of carboxylic acid groups between the inner and outer layers of the package. Alter-

ing the process conditions might decrease the number of pulses needed for complete modification of the internal nonwoven surface of a multi-layer package. However, under the given process conditions, it is recommended to treat only single layers of NW-PET instead of multilayer packages of NW-PET by means of H₂O or CO₂ glow-discharges to prevent long treatment times and to prevent differences in surface composition between the inner and outer layers of nonwoven.

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