Characterization of Nonwoven Poly(ethylene terephtalate) Devices Functionalized with Cationic Polymer

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ABSTRACT: A cationic functionalization was carried out on poly(ethylene terephtalate) (PET) nonwovens by the method of padding with a solution of polymer (P_1 and P_x). An atmospheric pressure plasma treatment was prior used to improve the hydrophilic property of the nonwoven surface before the functionalization with cationic agents. The zeta potential measurements of the nonwovens, based on streaming potential, show the presence of cationic groups at the PET surface depending on the pH value. The analysis of washing water showed that the PET nonwoven functionalized with cationic polymer P_x needed more washing cycles than with polymer P_1, to remove all the species non fixed at the surface. The cytotoxicity tests show that both of ammonium polymers are toxic toward endothelial cells. This means that it leaves many active chemicals on the surface of the functionalized materials, even after washing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3583–3590, 2012

Key words: padding; atmospheric air plasma treatment; zeta potential; cytotoxicity test; inhibition zone test; wettability characterization

INTRODUCTION

In recent years, much attention has been paid to creating more comfortable living conditions, especially for health and hygiene.[1] For example, nonwoven fabrics are the most commonly used textiles due to their physical properties and their versatility, especially in operating rooms, for surgical gowns, patient drapes, laboratory coats, coveralls, and other kinds of protective clothing.[2] Surface modification of textiles is usually performed to improve various functional properties, such as wetting, adhesion, antibacterial activity etc.[3] Functionalization of textiles can be obtained thanks to different techniques, such as physical vapor deposition (PVD), grafting, chemical vapor deposition (CVD), using enzymes or nanoparticles, sol–gel process, plasma treatments or using aqueous solutions.[3] In this study, polymers containing ammonium or amino groups were used to functionalized poly(ethylene terephtalate) (PET) nonwovens. Atmospheric plasma treatments are used to modify polymer surfaces using plasma gases made up of a mixture of charged particles (electrons and ions), excited atoms (free radicals, *meta*-stable molecules), and photons. Indeed, the plasma gases are formed when the gases between two electrodes are activated by applying an electrical potential difference to electrodes.[4] During plasma treatment, the polymer to be treated is exposed to the plasma gases which interact with the polymer surface and modify it. Surface modifications vary with the nature of the polymer substrate and the chemistry nature of plasma gases, as well as with the treatment operating parameters.[5] After the treatment, new functional groups are generated on the surface and can further be used, for instance, for improving the hydrophilic property of the PET nonwovens, when some polar groups are present at the surface.

The improvement of functional properties may be explained by modifications of thermodynamical surface properties, especially surface energy and nature of charge at surface, which can be quantified by zeta potential. Zeta potential[6] is the electrical potential at the shear plan between a charged surface and a liquid when moving with respect to each other. It originated from the dissociation of acidic or basic functional groups on the polymer surface and the preferential adsorption of cations or anions in competition with the adsorption of water molecules.

The purpose of this study was to investigate the evolution of PET surface modifications nonwovens

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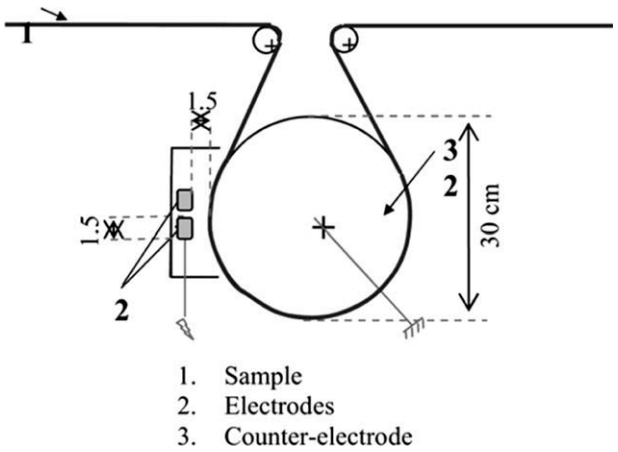

Figure 1 Schematic of plasma treatment under atmospheric pressure by means of dielectric barrier discharge, using "Coating Star" plasma machine manufactured by Ahlbrandt system.

functionalized with polymers containing cationic or amino groups. In our work, zeta potential, wettability, analysis of washwater, cytotoxicity tests, as well as inhibition zone test were used.

EXPERIMENTAL

Materials

A PET nonwoven fabric, which was free from spinning oil and other impurities, was manufactured by the CENT (European Center of nonwovens, France) with a basic weight of 207 g^{-2} and a thickness of 0.8 mm. This fabric was made of 0.9 dTex PET fibers according to a needlepunching and spunlacing, also known as hydroentanglement method.

Atmospheric air plasma treatments

PET nonwoven fabric was first treated by atmospheric air plasma. The atmospheric air plasma device used in this study was the "Coating Star" machine from Ahlbrandt Systems (Fig. 1), which has electrodes covered with ceramic to carry out the plasma treatments. When these electrodes are subjected to a difference of potential, a glow discharge called "dielectric barrier discharge" (DBD) was created. Atmospheric air was chosen as the gas during the treatment. The following machine parameters were kept constant during the functionalization: speed of 2 m min^{-1}, electrical power of 1000 W, frequency of 26 kHz, electrical voltage of 15 kV, two successive electrodes of 1.5 cm width and 0.5 m length, and an electrode/counter-electrode gap of 1.5 mm.

Each nonwoven sample was treated twice on one side. Those parameters were established on a previous study to get a nonwoven PET with optimized hydrophilic parameters.

Functional polymers

The polymers P_1 containing quaternary ammonium (Fig. 2) and polymer P_x containing amino groups (Fig. 3) were diluted in ethanol solution (2.5%). Ammonium derivatives were broad-spectrum disinfectant that can act on fungi, bacteria by inhibiting their growth, or by destroying the microorganisms included in their spectrum of activity when introduced into a formulation including detergent.[7]

Functionalization process

The cationic property of the nonwoven was carried out by the method of padding (Fig. 4) which is a traditional technique in textiles finishing. The fabric continuously passed into a bath containing the solution with active agents (Polymer P_1 or P_x), and then is squeezed between two rollers at a 4 bars pressure. The wet pick-up ratio of the padding is calculated using the following equation:

$$\text{Wet pick-up ratio } (\%) = [(\text{wet weight} - \text{dry weight})/\text{dry weight}] \times 100$$

where Wet weight, weight of sample after padding (g); Dry weight, weight of sample before padding (g).

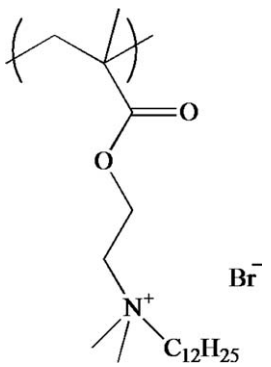

Figure 2 Chemical formula of polymer P_1.

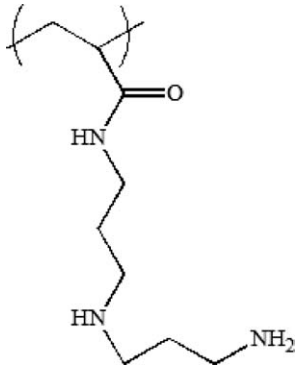

Figure 3 Chemical formula of polymer P_x.

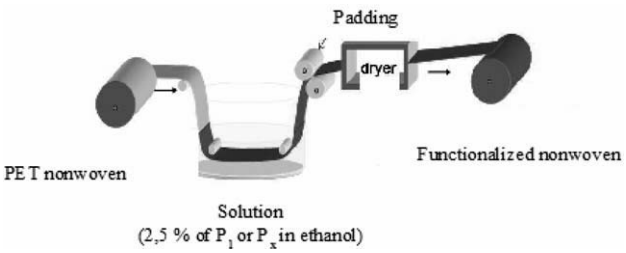

Figure 4 Schematic of the padding process.

The samples were immediately dried at 110°C for 2 min. Then, these samples were washed three times with distilled water at 37°C with a bath ratio of 1/100 (1 g of samples in 100 mL of distilled water) for 10 min for each cycle. The bath of washing is renewed at each cycle. The washing water is retrieved to be analyzed by an acido-basic dosage. The aim of the cleaning phase is to remove the excess of active ingredients (polymer P_1 or P_x) which were not fixed on the textile structure after the drying step.

MEASUREMENTS

Wettability

The surface of the PET nonwoven was modified by the atmospheric plasma treatment. Water contact angle measurements were carried out with water on a tensiometer 3S from GBX (Fig. 5) to quantify the surface treatment modifications. The contact angle[8] between water and solid was determined from the menicus weight Wm deduced from the liquid weight W_t in contact with the fabric.[4]

Contact angle was obtained by the following relation:

$$W_m = \gamma_{LV} \times p \times \cos\theta$$

where p is the sample perimeter in contact with the liquid, which was determined by measurement of a liquid decane ($\theta = 0$, $\cos\theta = 1$) to reduce the error in calculating the contact angle. [$P = (W_t g - W_c g)/\gamma_{LV}$].

γ_{LV}: surface tension of the liquid (mN/m).

$g = 9.81$ m s^{-2}.

W_t: the total weight (mg).

W_c: the capillary weight (mg).

Streaming potential measurements

The zeta potential measurements of nonwovens samples were determined with the streaming potential technique. The streaming potential[8] arises when an ionic solutions flows in contact with the stationary surface. The principle is based on the displacement of an electrolyte solution in a cell where the textile substrate is electrically charged. The electrostatic interaction between the charge of the interface and the ions in solution causes a concentration in counter ions and depletion of coions in the cell. The solution composition is changed slightly between the outlet and inlet of the cell, which depends on the quantity of charged sites on the surface of the textile substrate and the pressure between the entrance and the exit in the cell.

The zeta potential was measured by means of an apparatus provided by the company CAD Instruments (Fig. 6). The sample is maintained in the column (1) with filters of 70 microns (2). Electrodes of Ag/AgCl (3) are arranged on both sides of the filters. The electrolyte (1 L) is moved between the containers (4) under nitrogen pressure (0–500 mbar) through an admission valve (5). The direction of movement is controlled by a set of valves movement and venting (6 and 7). The reversal of direction is caused by level sensors in Ag immersed in the solution (8).

The potential difference E is measured at the extremities of the column under stages of increasing

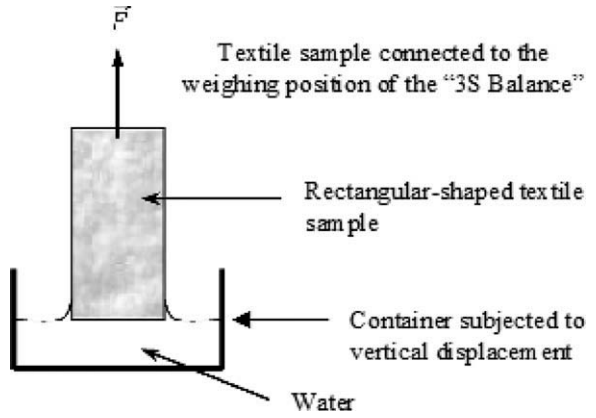

Figure 5 Wettability measurement with the "3S Balance" from GBX Instruments (France).

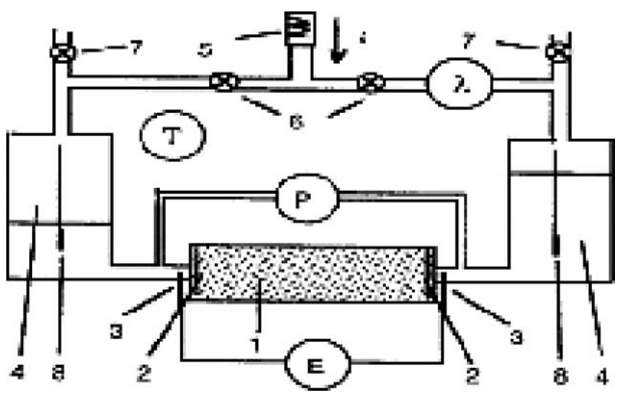

Figure 6 General diagram for the measurement of zeta potential of nonwoven surface.

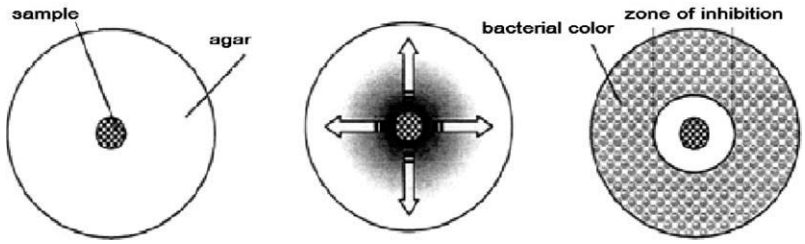

Figure 7 Schematic principle of the agar diffusion method (11-mm diameter disks).

pressure P applied during 1–10 min in the two directions of flow. The parameters acquired are the pressure (P) and voltage (E) at the extremities of the column, the solution conductivity (γ) and the device temperature (T).

Zeta potential is calculated by the following equation[8]:

$$\zeta = \frac{E}{\Delta p} \times 10000 \times 13.55 \times C \times \lambda$$

where ξ and E are expressed in mV, P in mbar, and γ in S cm^{-2}. Constant C gathers the medium permittivity and the solution viscosity, both dependent on temperature. The phenomenological law which determines C is:

$$C = 16.32 - 0.35197T + 0.00351T^2$$

The sample was introduced and maintained in the electrolyte solution (KCl 0.001 mol l^{-1}) during 24 h to reach equilibrium before the measurement. This solution passed through the sample located in a cylindrical tube made of glass under a pressure ranging between 20 and 500 mbar. The study of zeta potential as a function of pH was carried out while varying the pH of the KCl solution from 3 to 10 by adding drops of solutions of HCl or KOH (0.1 mol L^{-1}). For each pH value, the PET nonwovens to be analyzed were stabilized in the electrolyte solution by circulating until both pressure and voltage were stable.

Analysis of the washing water

The analysis of the washing water is used to determine the number of washing which is necessary to ensure that there is no more desorption of polymer. After each washing of the nonwoven functionalized with the polymer P_x, the water was analyzed by a potentiometric dosage thanks to catalyze laboratory in Marseille using the apparatus Titrino 716 DMS (Metrohm). This indirect dosage of the bromide counter ions gives information about the quantity of quaternary ammonium.

For the cationic polymer P_x, we use an acido-basic dosage of the washing water, by pH-metric method, to determine the quantity of $-NH_2$ groups.

Microbiological evaluation

Microbiological evaluation was performed according to the standardized Kirby-Bauer method (the agar disk-diffusion method)[9] following International Standards (ISO 20743). This study aimed at determining the antibacterial activity of ammonium compounds (P_1 and P_x) fixed on the nonwoven PET. Briefly, virgin and functionalized nonwoven PET disks were placed in a Petri dish containing Mueller-Hinton Agar inoculated with *Staphylococcus aureus* (CIP224, collection stain). After 24 h incubation at 37°C, the radius of the no-bacteria-growth area (zone of inhibition) was measured with a ruler and recorded in millimeters (Fig. 7).[10] These values represented the antimicrobial activity of the nonwoven PET.

Biological evaluation

Nonwoven PET were cut into disks (Ø11 mm) for cell proliferation assay and the powder of polymer P_1 and P_x were prepared for cell viability assay. All samples were sterilized by UV-light (UV lamp ref.) for 15 min. *In vitro* biological tests were performed with human epithelial cells line (L132, ATCC-CCL5) according to the International and European Standards (ISO 10993-5/EN 30993-5).[11] L132 cells were cultivated in minimum essential medium (MEM, Gibco) with glutamax (Gibco BRL), supplemented with 10% fetal calf serum (FCS) (Eurobio). All media contained fungizon (25 µg/mL, Gibco BRL) and gentamicin (50 µg/mL, Panpharma). Cells were incubated at 37°C in 5% CO_2 atmosphere and 100% relative humidity in a CO_2 incubator (CB 150/APT line/Binder).

Cell viability

The cell viability test allows evaluating the 50% lethal concentration LC50 by colony-forming method with the L132 epithelial cells. Cells were exposed to the increasing concentrations of P_1 and P_x (0, 3.125, 6.25, 12.5, 25, and 50 mg/L^{-1}), without renewal of

TABLE I
The Wet Pick-up Ratio of Padding for the Functionalized Nonwoven PET

Samples	PET-P_1	PET plasma-P_1	PET-P_x	PET plasma-P_x
Wet pick-up ratio (%)	90	96	91	93

the growth medium during the experiments. After 9 days, the medium was removed and the colonies were colored with crystal violet (0.2 wt %). The colonies were then counted using a binocular microscope. At least three repeated experiments were performed in triplicates for each concentration. Results are expressed as the mean percentage ± SD with respect to the control (medium without test sample, 100%), and are also compared with nickel powder as positive control.[12,13]

Cell vitality test

The growth period for cell vitality tests was 3 and 6 days with no renewal of the medium. Sample disks from virgin and functionalized nonwoven PET were placed in 48-well plates (Costar®, Starlab, France), and maintained onto the bottom of the well with a Viton® rings (Radiospares, France); the wells [tissue culture polystyrene (TCPS)] without PET sample were also tested as control. 4000 epithelial cells were then gently seeded in each well and placed in the CO_2 incubator.

Cell vitality was assessed with the Alamar Blue® (Interchim),[14,15] after respectively, 3 and 6 days of incubation, without renewal of the medium. The culture medium was removed from each well and 500 μL of a diluted solution of Alamar Blue® (10%), a nontoxic fluorescent dye, was deposited in each well. After 3 h of incubation, 150 μL solution of each well were transferred into 96-well plates (Nunc®, Polylabo, France) and the fluorescence intensity was measured by fluoremeter (Twinkle LB970™ Berthold, France) at an excitation wavelength of 560 nm and an emission wavelength of 590 nm. The cell vitality rate was calculated as the absorbance of living respiratory cells (indicative of the metabolic activity) on virgin and functionalized nonwoven PET samples divided by that of control (TCPS). A minimum of three separate experiments for each group were conducted in triplicate and final results were expressed as the mean percentage ± SD with respect to the control culture (100%).[16]

TABLE II
Cos θ, θ Values of Water on PET Nonwovens

	PET, 0W	PET plasma, 1000 W
Cos θ	−0.682	0.602
θ	133	53

RESULTS AND DISCUSSION

Wet pick-up ratio

The wet pick-up ratio were determined for the PET nonwoven functionalized with the polymer P_1 (PET-P_1) and P_x (PET-P_x) or with a preactivation with a plasma treatment (PET plasma; Table I). More polymer solution is picked up after a plasma treatment. Indeed, plasma treatment increases the hydrophilic property of the samples. So the wet pick-up of the PET plasma-P_1 and PET plasma-P_x are more important than for the PET-P_1 and PET-P_x.

Water contact angle

Table II shows cos θ and θ values of water on PET nonwovens before and after plasma treatment. The water contact angle decrease strongly from 133° for the PET to 53° after a plasma treatment on one side and realized twice time with electrical power of

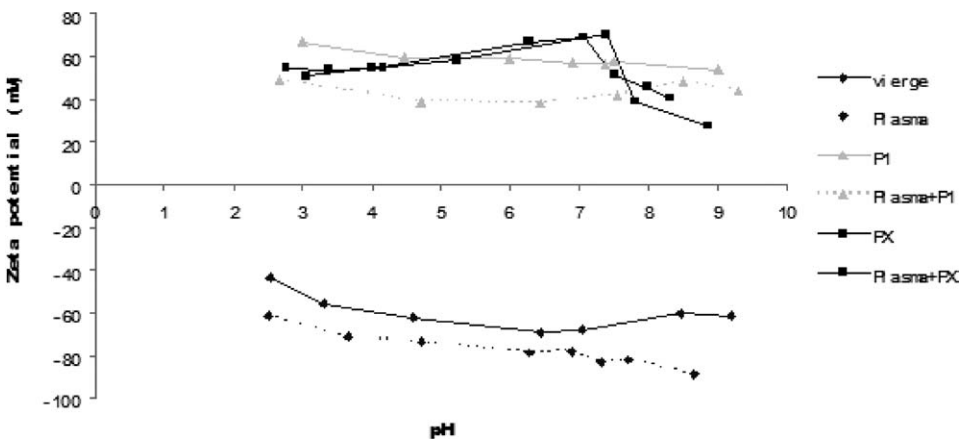

Figure 8 The ζ-pH plots of PET nonwovens.

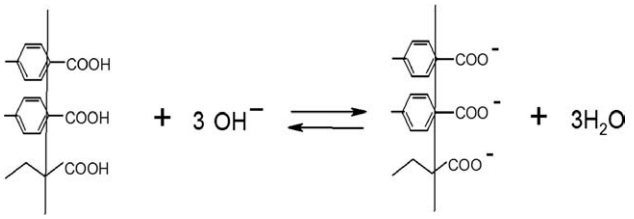

Figure 9 Carboxyl groups dissociation reaction at basic pH.

1000 W. It means that the oxidized species created during the treatment gave hydrophilic properties to the PET fabric surface. The excited species in the plasma has enough energy to activate and modify the PET surface.

Zeta potential

The zeta potential has become a useful parameter to determine electrokinetic behavior. Figure 8 presents zeta potential (ξ) versus pH plots for untreated and functionalized PET nonwovens. These curves showed an expected behavior for the surface of PET nonwovens, with (PET plasma) or without plasma treatment (PET). For the original PET nonwoven, the value of zeta potential was negative, meaning that the surface charge of PET was negative and its value increased with the pH until a maximum value. At basic pH, these negative charges were acidic species and resulted from carboxylic group dissociation of PET (Fig. 9). The plateau means that acidic groups are completely dissociated. The ξ negative value for the plasma-treated PET (PET plasma) curve is less than original PET nonwoven. For example, at pH = 8.4, ξ was -60.6 mV for the original PET and -88 mV for plasma-treated treatment. The more negative the zeta potential is, the higher is the carboxyl group density at the fiber surface. The atmospheric air plasma-treated fabrics, consequently, have more carboxyl groups at the surface. Indeed, plasma treatments[8] generate polymer chain scissions of the weakest bonds of the PET. These chains scission create a large amount of very reactive chain-ends, such as free radicals, which then react easily with the reactive species present in the plasma. These reactions will create some oxidized groups like carbonyl, carboxyl, and hydroxyl groups at the chain-end.

TABLE III
Quantity of Polymer *Px* or *P*1 in Washing Water for PET Nonwoven Functionalized

Samples	Quantity (ppm)
PET—P_x (one washing cycle)	1.2
PET—P_x-2 (two washing cycles)	0.87
PET—P_x-3 (three washing cycles)	0
PET plasma—P_x-1 (one washing cycle)	2.0
PET plasma—P_x-2 (two washing cycles)	2.4
Plasma—P_x-3 (three washing cycles)	2.07
PET—P_1 (one washing cycle)	0
PET—P_1-2 (two washing cycles)	0
PET—P_1-3 (three washing cycles)	0
PET plasma—P_1-1 (one washing cycle)	0
PET plasma—P_1-2 (two washing cycles)	0
Plasma—P_1-3 (three washing cycles)	0

TABLE IV
Viability of L132 Cells in the Presence of Increasing Concentrations of P_1 and P_x, and Nickel Power (Positive Control)

	Polymer			
[P] µg/mL	P_1	P_x	[Ni] µg/mL	Nickel
0	100 ± 0%	100 ± 0%	0	100 ± 0%
3.125	93 ± 4%	103 ± 8%	5	98 ± 3%
6.25	82 ± 9%	102 ± 1%	10	82 ± 5%
12.5	76 ± 7%	67 ± 9%	20	65 ± 5%
25	96 ± 2%	0 ± 0%	40	45 ± 5%
50	0 ± 0%	0 ± 0%	80	21 ± 2%

At the opposite, for nonwoven functionalized with the cationic polymer P_1, the zeta potential was positive for a pH between 2.5 and 9. That means that there are positive charges on the PET surface made by the quaternary ammonium of the polymer P_1. We can conclude that the cationic polymer P_1 remains at the surface of PET after water washing. For nonwoven functionalized with the polymer P_x, Figure 8 shows a positive zeta potential for PET-P_x until a pH = 9.5, explainable by protonization of amino end groups. Over a pH = 7.3, the positive zeta potential is going to decrease with the increasing alkaline pH until the IEP (isoelectric point) where there is no charge on shear plane of solid ($\xi = 0$).

For the same pH value, a sample functionalized with the polymer P_1 just after plasma treatment has a zeta potential lower than the sample functionalized directly with the polymer P_1. The decrease of zeta potential for the PET plasma-P_1 in comparison with PET-P_1 might be due to the interactions between some of the anionic groups, coming from the carboxylic groups of the PET, and the cationic groups, coming from the quaternary ammonium of the polymer P_1.

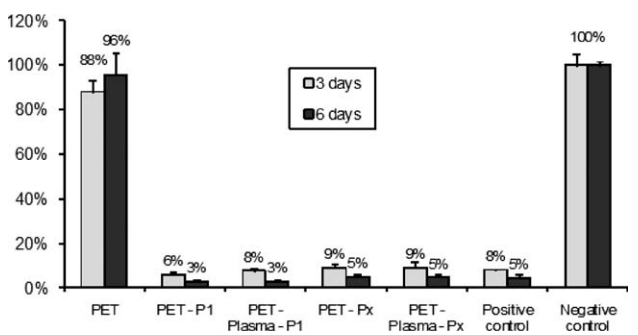

Figure 10 Proliferation rate of L132 cells growth after 3 and 6 days.

Figure 11 Pictures of bacteriological testing of the inhibition zone.

Analysis of the washing water

When the polymer amount in washing water is less than or equal to 5 ppm (part per million %), the fabric is assumed to be clean. After each washing of the nonwoven functionalized with the polymer P_x, the water was analyzed by a potentiometric dosage. For the cationic polymer P_x, we use an acido-basic dosage of the washing water, by pH-metric method, to determine the quantity of $-NH_2$ groups.

Table III presents the total quantity of cationic agent P_x and polymer P_1 present in the washing water for each cycle. The quantity of each polymer is very small, what can demonstrate that agent P_x was totally fixed to the surface of the PET nonwoven, and this fixation was very durable to washing. For agent P_1 we can observe a small desorption of this cationic polymer during the washing step. The plasma treatment didn't improve the fixation of the cationic agent on the PET nonwoven surface.

The polymer P_1 and P_x, have a good adsorption or physisorption with the PET nonwoven, because no significant desorption has been observed. The adhesion between the polymer and the PET surface is ensured by the existence of several points of hangs, implying the establishment of intermolecular interactions (Van der Waals or hydrogen bonds).

Biological evaluation

Table IV shows the viability test performed with L132 cells. Results have shown a toxicity of polymer P_1 and polymer P_x with lethal concentration of 25 and 50 mg/L, respectively. In the same way, positive control, i.e., nickel powder showed a lethal concentration of 35 mg/L. So the results reveal that both polymers are toxic toward L132 cells.

The fluorescence of the Alamar Blue dye in the presence of the cells that proliferated on the supports is proportional to the cell vitality. The fluorescence in the control wells was taken as the normalized cell vitality i.e., 100%. The average results of the proliferation tests of the L132 cells after 3- and 6-day cultures on the various functionalized samples are represented in Figure 10. The results revealed that, after 3-day culture, there were significant reduction in epithelial cells growth on the functionalized PET (below 10%) and a further decrease in the proliferation rate after 6 days (below 5%). Thus, whatever the concentration and the nature of the antibacterial agent, the functionalized and washed nonwoven PET show toxicity toward the epithelial cells. This implies that there remained much active chemicals on the surface of the functionalized materials, even after rigorous washing. Although the antimicrobial polymers are linked to the PET fibers, their cytotoxic or antimicrobial activities still maintained high.

Microbiologic evaluation

After incubation, the bacteria (*Staphylococcus aureus*) proliferate on the surface of an agar plate except where they meet a sufficient concentration of active molecules to inhibit their growth. Thus, a circular zone free from settlements, called inhibition zone, appears around the disks during the test. The larger the diameter of this area is, the greater the strain is susceptible to the active chemicals. The observation of the picture represented at Figure 11 showed that there was no inhibition zone for all kind of nonwoven PET, which implied that there was a good fixation for the polymers P_1 and P_x to the nonwoven PET after washing, which also confirmed the optimal cycles of washing process.

CONCLUSIONS

This study has shown the effective functionalization of PET nonwoven with polymers containing quaternary ammonium or amino groups. Atmospheric plasma treatment was used to activate the surface of PET nonwoven and increase the interaction with the polymers, but this preactivation has just improved the hydrophilic property of nonwoven. Data obtained from analysis of washing water of the functionalized PET reveals that one washing was sufficient for the nonwoven treated with the polymer P_1 and presents a good fixation with the PET nonwoven. However, the PET nonwoven treated with polymer P_x needed more

washing cycles than P_1 to limit the desorption. Measurements of zeta potential show the presence of cationic or amino groups on the functionalized surface. This technique is a very sensitive method to check the presence of functional groups at the PET surface. The cytotoxicity test carried out showed that these functional polymers present many active chemicals on the surface of the functionalized materials. No diffusion zone for all PET nonwovens was observed during the inhibition zone test. This result shows a good fixation for the polymers P_1 and P_x to the nonwoven.

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