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Study on the Effect of Plasma Treatment of Woven Polyester Fabrics with Respect to Nisin Adsorption and Antibacterial Activity

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ABSTRACT: The effect of plasma treatment of polyester (PET) fabric with respect to nisin adsorption and antibacterial activity was studied. Both cleaned untreated PET fabric and plasma-treated PET fabric were separately dipped in aqueous nisaplin solution with 0.5 and 1% of nisin, for 24 h under stirring, and then dried. With 1% of nisin, high and immediate antibacterial activity against *Staphylococcus aureus* was observed, and this activity was maintained even after 24 h. However, with 0.5% of nisin, no immediate bacterial reduction was observed, and only the untreated PET fabric exhibited antibacterial activity after 24 h. Only nisin molecules which can diffuse from the fabric can impart antibacterial activity, as demonstrated by the absence of bacterial inhibition zone after complete removal of releasable nisin in water. The desorption capacity of nisin from the fabric into water was monitored by tensiometry, while the presence of residual strongly sorbed nisin on the fabric was confirmed by wettability, zeta potential measurements, and wash durability test after nisin coloration by a protein dye. Plasma treatment, which increases the hydrophilic behavior of the PET fabric (WCA reduced from 80° to 42°), increases considerably the quantities of strongly and weakly sorbed nisin. However, it does not improve antibacterial activity compared to the PET fabric without plasma treatment. The reduced mobility of the nisin molecules due to chemisorption of the first layers of nisin on the plasma treated PET fabric can explain the reduced antibacterial activity with 0.5% nisin. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 866–873, 2013

KEYWORDS: textiles; adsorption; peptide; polyesters; functionalization of polymers

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INTRODUCTION

Textile materials are excellent media for growing microorganisms, especially those used in hospitals, infant wear, underwear, and sportswear.[1] Such infected fabrics could act as vectors for the spread of microbes, which, if pathogenic, may lead to cross infections and therefore pose a significant hazard to humans.[2] Polyester fabrics or Poly(ethylene terephthalate) (PET) which accounts for more than 50% of wordwide apparel production, are also widely used in several biomedical applications, such as ventricular assist devices, and prosthetic arterial grafts.[3]

Antibacterial textiles are considered to be a reliable alternative due to their importance in providing comfort, health and hygiene for humans and for combating pathogenic bacteria such as *Staphylococcus aureus* (*S. aureus*) which is one of the most common etiologic organisms of intensive care units acquired infections,[4] and its impact has increased as a result of the rising incidence of methicillin resistant strains (MRSA).[5]

Various antimicrobial agents have been applied to impart antimicrobial properties to textile.[6] The use of renewable and eco-friendly antimicrobial products, such as the bacteriocin nisin, presents an alternative for the development of antibacterial textile. Nisin is an antimicrobial peptide produced by some strains of *Lactococcus lactis* subsp *lactis*.[7–10] It can inhibit the growth of pathogenic Gram-positive bacteria such as *S. aureus*, *Listeria monocytogenes*, *Clostridium perfringens*, and *Bacillus cereus*.[8] Textile functionalization using nisin may provide a good tool for preventing microbial attachment, cross contamination and biofilm formation on textile.

Already surface adsorption method has been used to functionalize surfaces, mainly films.[11–14] However, porous materials such

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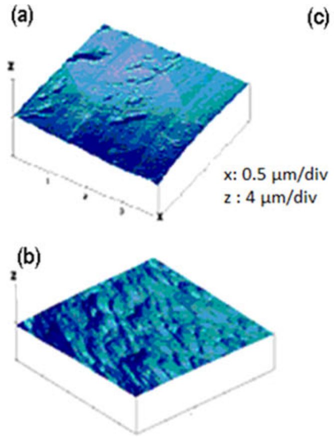

(c)

XPS analysis		PET	PET +plasma
Chemical group	Binding energy (eV)		
C-C	285.0	73.5	59
C-O	286.6	15.7	20.7
-(O=C)-O-	289.2	10.8	18.8
Average water contact angle(°)		80°	42°

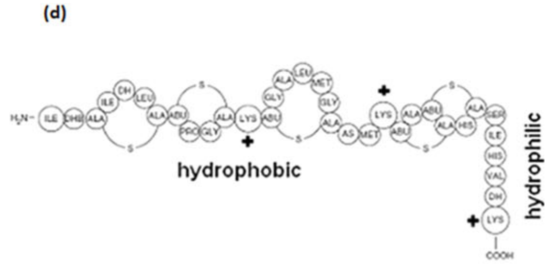

Figure 1. AFM images of untreated PET fiber surface (a), and air atmospheric plasma treated PET surface at 60 kJ/m^2 (b), and XPS and wettability results of untreated PET compared to plasma treated PET fabric (c), chemical structure of Nisin (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as textiles are readily prone to bacterial adhesion and rapid proliferation because of high surface area of contact for bacteria. Several authors confirm the adsorption and antibacterial activity of nisin on PET film.[14] Our previous work confirmed the sorption of a lipopeptide (surfactin) on PET nonwovens.[15] It would be interesting to see whether nisin adsorbed on porous PET textile can be an effective way to make an antibacterial textile. Moreover, contradictory results have been reported concerning the effect of surface properties (hydrophilic/hydrophobic) on the antibacterial activity of surface-sorbed nisin. Thus, the main objective of this work is to compare the antibacterial behavior of sorbed-nisin on hydrophobic untreated PET and plasma treated PET-hydrophilic surface. Indeed air-plasma treatment induces the creation of polar groups by PET chain scissions, making both the inner and the outer fabric surface hydrophilic.[17]

In the first part of the study, antibacterial activity against *S. aureus* and MRSA bacteria has been assessed. Then, physicochemical tests have been used to investigate the release ability of nisin in water from nisin-sorbed PET fabrics using tensiometry. Surface characterization of PET fabrics was carried using wettability, Zeta Potential, and Spectrophotometry, after complete removal of surface-sorbed releasable nisin.

MATERIALS AND METHODS

PET Fabric Preparation

Woven PET Fabric. A 100% PET woven fabric of density 284 g/m^2 with a thickness of 0.56 mm and 63.5% porosity was used for the study. The PET woven fabric was cleaned to be free from surface impurities and spinning oil. The cleanliness of the PET samples was checked by measuring the surface tension of final rinsing water (used to clean the PET samples), which remained constant and equal to 72.6 mN/m, which is indeed the surface tension of pure water.

Plasma Treatment of Woven PET Samples. All plasma treatments were carried out using an atmospheric plasma machine called "Coating Star" manufactured by Ahlbrandt System (Germany). The following machine parameters were kept constant: electrical power of 1 kW, frequency of 26 kHz, electrode length of 0.5 m and interelectrode distance of 1.5 mm. The outer layer surfaces of both electrodes were of ceramic (a dielectric material), so that when these electrodes were subjected to a potential difference, a glow discharge called the "Dielectric Barrier Discharge" was created.

As shown in our previous papers[16,17] air-atmospheric treatment can yield physical and/or chemical changes at the PET fabric fiber surface, depending on the plasma treatment power. At the treatment power used in this study (60 kJ/m^2), the plasma treatment creates uniform ordered scale-like structure (6 scales/µm) but also an increase in polarity due to an increase in both carbonyl(+5%) and carboxyl(+8%) groups as confirmed by X-ray photoelectron spectroscopy (XPS) measurements [Figure 1(a–c)], which also explains the decrease in water contact angle (WCA) from 80° to 42° after the plasma treatment.

Adsorption of Nisin on PET Fabrics. Nisaplin from Sigma-Aldrich (France) containing 2.5% of nisin was used in this study. The bacteriocin was solubilized in 2×10^{-2} mol/L of HCl. Two different aqueous solutions were prepared with 1%, 0.5% of nisin (w/v). PET textile samples (of diameter 2.5 cm) were immersed in the nisin solution and were placed on an agitator at 180 rpm and 25°C for 24 h. 40 mL solution was used for every gram of PET fabric. The textile samples were then placed on sterile Petri dishes and dried at 30°C for 24 h.

Antibacterial Tests

Bacteria. *S. aureus* ATCC 6538 and a methicillin-resistant *S. aureus* (MRSA) strain were used in this study to assess the antibacterial effect of nisin functionalized PET.

Antibacterial Characterization of the Nisin Treated PET Using a Diffusion Method. An overnight *S. aureus* culture was diluted 200 times in Müeller Hinton medium. 2 mL of this dilution was transferred to a Müeller Hinton medium agar Petri dish and spread evenly over the plate. The excess was removed. The textile sample was placed in the centre of the plates which were incubated at 30°C in a humid chamber overnight. The next day any zones of inhibition around the samples were measured.

Antibacterial Textile French Standard Method for Enumeration of Bacteria Transferred to a Textile Sample. The international standard ISO 20743:2007(F) was used. An overnight culture of *S. aureus* was first diluted to (1−3) × 10^6 CFU/mL, and 1 mL

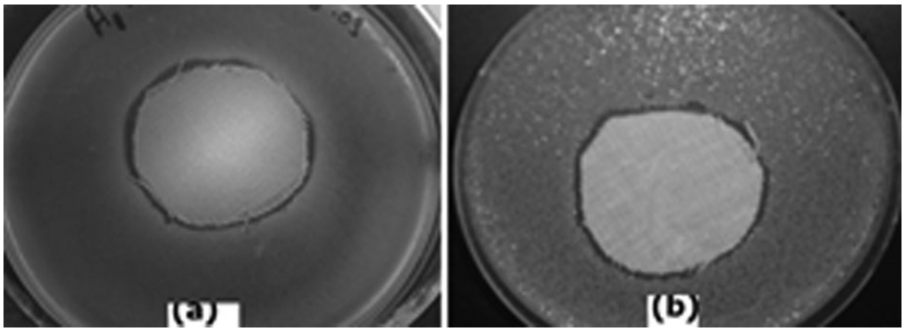

Figure 2. Results of qualitative antibacterial tests after 24 h carried out using the diffusion inhibition method, for the PET fabric treated with nisaplin solution containing 1% nisin, (a) against *S. aureus*, (b) against MRSA (Methillin resistant *S. aureus*).

of this cell suspension spread over the Müeller Hinton plate as described above. The textile discs were placed on the plate and a 200 g sterile metal load placed on the textile, for 5 min.

The antibacterial effect of the PET fabrics was assessed immediately after the contamination with *S. aureus* ($t = 0$ h) or after 24 h ($t = 24$ h) of incubation at 37°C. The samples were transferred to a sterile plastic bag with 20 mL of neutralising solution and placed in a Stomacher for 2 min to remove bacteria from the textile samples. Appropriate dilutions of the bacterial suspension were plated onto agar medium and the colony counts were determined after 24 h. The experiments were carried out at least four times.

Physicochemical Characterization of Nisin Adsorbed at PET Fabric Surface

Quantification of Releasable Surface-Sorbed Nisin in Water. To determine the quantity of surface-sorbed nisin released from the PET fabrics into water, three samples (4 × 2 cm) of each treated fabrics were immersed separately in 50 mL of distilled water with surface tension of 72.6 mN m^{-1}, for 2.5 h under agitation. The surface tension of water was controlled after each 30 min, and the experiment was stopped when there was no further decrease in surface tension. The amount of nisin, which is an amphiphilic surfactant, could be quantified since the water surface tension of varies linearly with the logarithm of nisin concentration [Figure 4(b)].

Characterization of PET Fabrics After Complete Removal of Releasable Surface-Sorbed Nisin in Water

WCA measurements using wicking test. Textile surface is a porous structure and for all WCA <90°, sessile drop method cannot be used to measure WCA since the water drop is readily absorbed by the textile structure. A tensiometer from GBX Instruments (France) was used to measure the "meniscus weight," when a rectangular-shaped fabric (fixed vertically to the tensiometer at the weighing position), was progressively brought into contact with water. On immediate contact with the water surface, a sudden increase in weight was detected, due to the water meniscus formation on the fabric surface (W_m).

The WCA at the textile sample surface could be determined from the "meniscus weight" (W_m) using eq. (1),[6] since both the surface tension of liquid water and the perimeter of the contacting surfaces were known.

$$W_m \times g = \gamma_L \times \cos\theta \times p \tag{1}$$

with: p = fabric perimeter in contact with water (mm); W_m = calculated meniscus weight (g); $g = 9.81$ g s^{-2}; γ_L= water surface tension (mN m^{-1}); θ = contact angle (°).

Streaming potential measurements. The surface zeta potential was measured by streaming potential measurement using a Zetacad equipment at 25°C. A 0.001mol L^{-1} of KCl electrolyte solution was used. One gram of PET fabric was maintained in a cell while the electrolyte was forced to flow through the fabric at varying pressures. Before any Zeta potential measurement, the sample was maintained in the electrolyte solution for 24 h to reach equilibrium before making measurements. Five measurements were carried out on each sample for pH values of the electrolyte solution varying from 3 to 10.

Coloration of PET bound nisin. Staining of proteins in adsorption studies has already been carried by Nejadnik et al.[18] In our study, to approximate any residual nisin strongly sorbed on the PET fabric (after complete removal of releasable nisin), the fabrics were colored with a fluorotriazine dye whose general formula is shown in Figure 7(a). Indeed this dye has a reactive fluorine group capable of binding to the free —NH_2 of proteins at room temperature and pressure, with the creation of covalent bonds by nucleophilic substitution reaction.[19] The treated fabrics were subjected to coloring by soaking in 200 mL of water containing 30 mg of the dye, at room temperature for 90 min, with agitation. The color intensity "*K*/*S*" of the fabrics was assessed using spectrophotometry.Indeed

$$K/S = \frac{(1-R)^2}{2R} = \frac{Ac}{S} \tag{2}$$

where ***K*** refers to coefficient of absorption, ***R*** reflectance at min. reflectance wavelength, ***S*** is coefficient of scatter, ***c*** = concentration of the absorbing species, ***A*** = absorbance of dyes.

The release ability of the any residual surface-sorbed nisin was also assessed by measuring the fabric color intensity before and after durability tests carried by washing at 60 and 90°C.

RESULTS

Antibacterial Characterization of the Nisin Treated PET

Qualitative Assessment. The qualitative antibacterial tests carried out with the diffusion method shows that when 1% nisin is used, the PET fabrics with sorbed nisin are active against both *S. aureus* ATCC 6538 and the MRSA strains, with an inhibition zone appearing after 24 h of incubation [Figure 2(a,b)]. However, without sorbed-nisin, there was no inhibition zone for the PET fabric (data not shown).

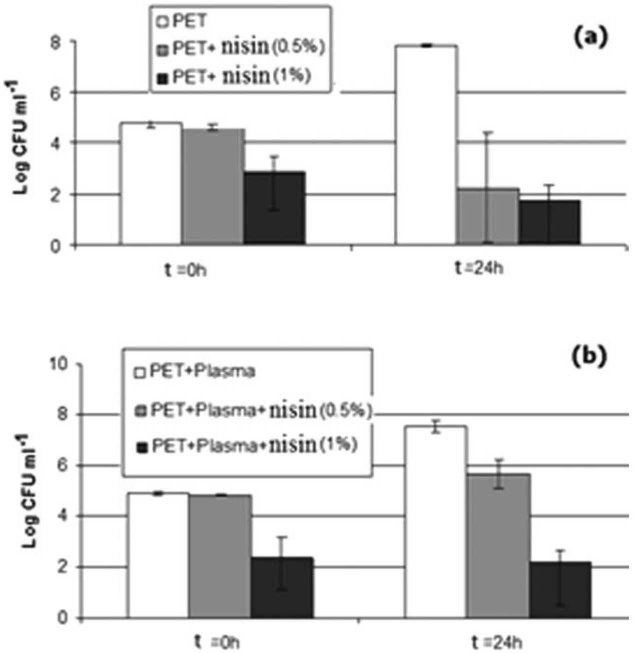

Figure 3. Quantitative assessment of the antibacterial effect against *S. aureus* of the PET fabrics functionalized with 0.5 and 1% of nisin: for the untreated PET fabric (a) and for the plasma treated PET fabric (b).

When qualitative test was carried out after complete removal of releasable nisin (by immersion of nisin-sorbed PET fabrics in water for 2 h), no inhibition zone against *S. aureus*, was detected. Bacterial growth occurred underneath the PET disc (data not shown). Indeed, nisin should impart antibacterial activity to the PET by its release or diffusion ability, as shown by Lins et al.[20]

Quantitative Assessment. Quantitative antibacterial assessment test was carried with nisin-sorbed on cleaned untreated PET and plasma treated PET fabric using nisaplin solution with 0.5 and 1% nisin.

For PET fabrics treated with 1% nisin, the *S. aureus* enumeration after immediate contact ($t = 0$ h), shows a significant bacterial reduction of 2.4 log CFU/mL compared to the PET fabric without sorbed nisin [Figure 3(a)]. After 24 h of incubation at 37°C, bacterial cell density decreases slightly to 1.8 log CFU/mL, while that of the PET fabric without sorbed-nisin, increases to 7.8 log CFU/mL. Indeed with 1% nisin, bacterial reductions at $t = 0$ h and $t = 24$ h, are similar for both untreated and plasma treated PET fabrics

Our findings show that for both cleaned and plasma treated PET fabric sorbed with 0.5% nisin solution, there was no significant effect against *S. aureus* after 1 min of contact (at $t = 0$) [Figure 3(b)]. However, after 24 h of incubation ($t = 24$ h), a bacterial reduction of 6 Log CFU (compared to PET fabric without nisin) was measured for the nisin-sorbed on PET fabric without plasma treatment, only.

Physicochemical Characterization of PET Fabrics with Sorbed Nisin

Quantification of Release Ability of Sorbed-Nisin, from Fabric Surface to Water, at RTP (Room Temperature and Pressure). Figure 4(b) shows the amounts of fabric-sorbed nisin released per gram of fabric, (in mmol/g) as a function of time, according to the procedure described in "Quantification of releasable surface-sorbed nisin in water" Section. For the PET fabrics without plasma treatment, whatever the concentration of nisin used (0.5 or 1%), the total amount and the rates of release of nisin in water are almost similar (gray curves).

For the plasma treated PET fabric sorbed with a high concentration of nisin (1%), the rate and the amount of nisin released over time is the highest (see black curve).

With 0.5% nisin, the total amount of nisin released is similar for both PET fabrics with or without plasma treatment. However, plasma treatment lowers the rate of release of surface-sorbed nisin, delaying the time taken for diffusion of all releasable nisin from the textile surface into water: 1.5 h compared to 1 h for the PET fabric without plasma treatment.

Comparing Results to Antibacterial Activity. Indeed after total release of weakly bound nisin (i.e., $t > 1.5$ h), there was complete loss of antibacterial activity (cf. section 3.1.1), while quantitative test shows that for both concentrations of nisin used, there was antibacterial activity after 24 h. So, the quantitative antibacterial results after 24 h can be compared to the rate and amount of nisin released in water during the first 30 min. Thus for PET fabric (without plasma treatment) with both 0.5 and 1% of nisin, similar rate and amount of nisin released during the first 30 min (see gray curves), would explain the similar bacterial population reduction after 24 h. In the case of the plasma treated sample with 0.5% nisin, the lower rate of nisin release (see dashed black curve) compared to the other fabrics would explain the low reduction in bacterial population even

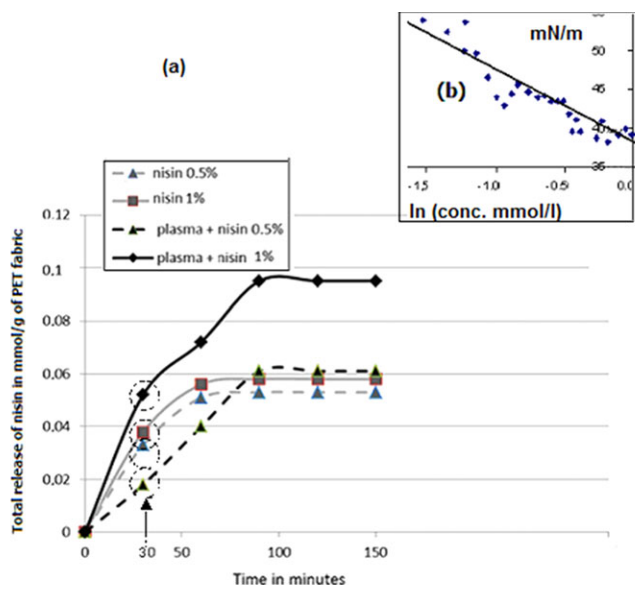

Figure 4. (a) Amounts of weakly bound nisin released from the PET fabric surface on immersion in water as a function of time, estimated by measuring surface tension of aqueous solutions and using the calibration curve (b) showing the variation of water surface tension as a function of concentrations of aqueous nisaplin solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

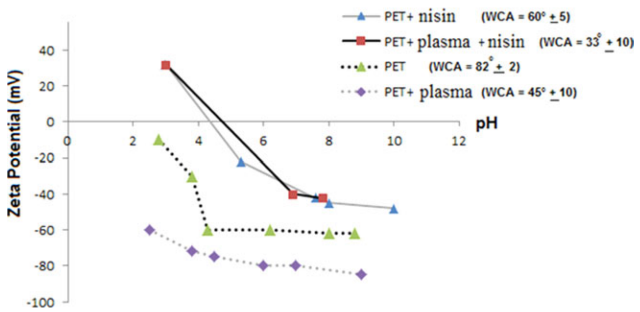

Figure 5. Variation of zeta potential plotted against pH, after total release of weakly bound nisin. The WCA of each PET treated sample with strongly-sorbed nisin, is also given. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after 24 h (2 log CFU reduction in colony count in comparison to the 6 log CFU reduction seen with the PET fabric without any plasma treatment treated with 0.5% nisin).

Fabric Surface Characterization After Removal of all Releasable Surface-Sorbed Nisin. Physicochemical tests were carried on fabrics after total diffusion in water of all releasable surface-sorbed nisin from the fabric surface.

WCA measurements using wicking test. The WCA values measured using the tensiometer described in "WCA measurements using wicking test" Section, are given in Figure 5 (together with the zeta potential values).

PET fabrics treated with nisin are more hydrophilic than those without nisin treatment.

For PET fabrics without plasma pretreatment, WCA decreases from 82° to 60° with 1% nisin.

For the plasma treated PET fabric having a WCA of 45°, a further decrease is observed after nisin treatment, reaching a WCA of 33°.

Furthermore, changing nisin solution concentration from 0.5 to 1% has no significant effect on the reduction of the fabric WCA.

Streaming potential measurements. Figure 5 shows the variation of zeta potential plotted against pH. An increase in zeta potential values of the fabric is observed at nearly all pH values even after removal of all releasable nisin in water. This phenomenon is observed for both PET fabrics, that is, with or without plasma treatment. This confirms the presence of strongly sorbed nisin, which cannot be released in water. Indeed, surface charges on the PET fabric are due to carboxylic groups present at the chain ends of the PET: the surface charge is nearly zero at pH 2 and potential zeta decreases with increasing pH, as the PET surface becomes more negatively charged due to the ionization of carboxylic acid groups into carboxylate ions. Air-atmospheric plasma treatment further decreases the zeta potential of PET due to increase in COO— groups formed as a result of PET polymer chain scissions, which are confirmed by XPS (Figure 1).

Increases in zeta potential confirm the presence of strongly sorbed nonreleasable nisin at the PET fabric surface. Thus, in acidic medium, the zeta potential is positive due to protonation of amino groups of nisin molecules into [sbond]NH_3^+. With increasing pH, these groups become neutral and more carboxylate ions are formed on both nisin and the PET polymer chains. Therefore, there is a reduction in zeta potential as pH increases, and it tends towards the zeta potential of untreated PET at very high pH (>10). Indeed, the isoelectric pH corresponding to a neutral structure of the PET bound nisin is reached at pH = 4.6.

Indeed a prior plasma treatment of the PET does not influence the Zeta potential of the fabric with sorbed-nisin.

Quantification of Surface Bound Unreleasable Nisin (After Coloration). Figure 6b shows the color intensity "*K*/*S*" values of the colored fabrics at its minimum reflectance wavelength.

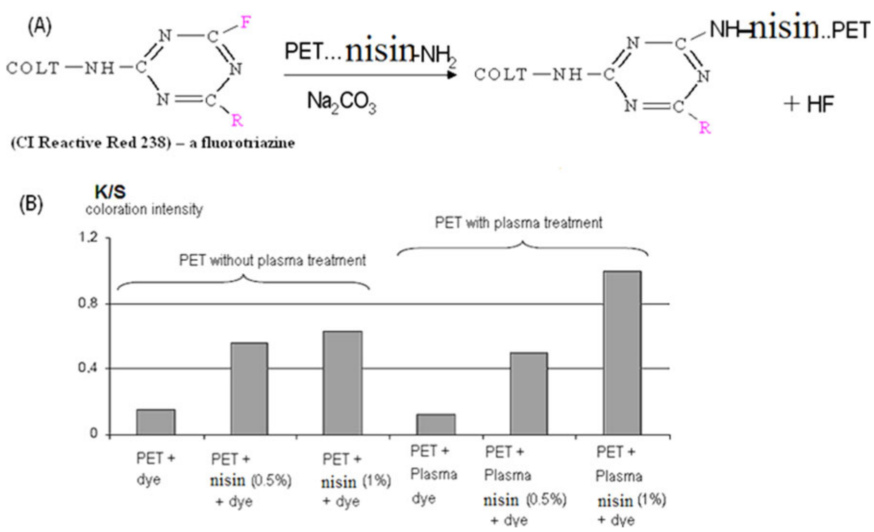

Figure 6. Color intensity "*K*/*S*" of PET fabrics with or without strongly surface-sorbed nisin, after coloration with a protein staining dye fluorotriazine. (a) illustrates the possible chemical reaction between the dye and the adsorbed nisin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. ΔK/S Values After Wash Fastness TEST at 60 and 90̊C During 30 min

Dyed fabrics	Before washing ΔK/S	After washing (30 min at 60̊C) ΔK/S	After washing (30 min at 60̊C) Nisin loss (%)	After washing (30 min at 90̊C) ΔK/S	After washing (30 min at 90̊C) Nisin loss (%)
PET + 1% nisin + dye	0.48	0.39	19	0.34	29
PET + 0.5% nisin +dye	0.40	0.36	10	0.27	32.5
Plasma treated PET+ 1% nisin + dye	0.88	0.75	15	0.58	34
Plasma treated PET+ 0.5% nisin + dye	0.39	0.32	18	0.25	35.9

Δ*K/S* is the coloration intensity measured due to adsorbed nisin only. It is the difference in color intensity between PET fabric with sorbed nisin and PET fabric without sorbed nisin.

Results show that without nisin treatment, the dye gets very slightly adsorbed at the PET fabric surface: the *K/S* value is small and similar (0.18) for both untreated cleaned and plasma treated PET fabrics. After treatment with nisin, the "*K/S*" value increases considerably confirming the presence of surface bound unreleasable nisin on the PET fabric surface. However, without plasma treatment, the "*K/S*" (~0.6) does not vary considerably with the increase in nisin concentration from 0.5 to 1%, while in the case of plasma treated PET, the color intensity "*K/S*" value with 1% nisin ($K/S = 1$) is twice of that with 0.5% nisin ($K/S = 0.5$).

Wash Durability Test at 60 and 90°C of the Colored PET Fabrics with Sorbed Nisin

To assess the degree of adherence of nisin on the PET, wash durability tests were performed by subjecting the colored fabrics (with sorbed nisin) to hot water washing at 60 and 90°C for 30 min (see paragraph "Coloration of PET bound nisin" Section). The amount of nisin that stayed bound to the PET sample was expressed in terms of $\Delta K/S$ where:

$\Delta K/S = K/S$ (of PET fabric with adsorbed nisin) — K/S (of PET without adsorbed nisin)

The difference between $\Delta K/S$ values before and after wash fastness test would represent the quantity of nisin lost during washing.

Results in Table I show that surface bound nisin are quite resistant to washing with hot water. Indeed, after immersion in water at 60°C, there was a loss of nisin estimated to about 10–19%. At 90°C, two third of the adsorbed nisin were still present on both the untreated and plasma treated PET fabric. This confirms that there is strong bonding between the nisin and the PET fabric and that, after removal of the weakly bound nisin, the immobilized nisin resistance to hot water is not significantly different on plasma treated PET surfaces.

DISCUSSION

The qualitative tests carried out with the diffusion method showed that when 1% nisin was used, both untreated and plasma treated PET fabrics were active against *S. aureus ATTC 6538* and *MRSA* strains, with an inhibition zone appearing after 24 h. However, no inhibition zone was observed after complete release of weakly bound nisin (during 2.5 h). This means that there is a direct relationship between the quantity of releasable weakly bound nisin, and antibacterial activity. Hence, the antibacterial property of the nisin treated fabric is given by the diffusion ability of the bacteriocin following its release since nisin kills susceptible bacteria through a multistep process that destabilizes the phospholipid bilayer of the cell and creates transient pores as described by Lins et al.[20]

Quantitative tests show that for PET fabrics with and without plasma activation, adsorption of 1% of nisin leads to high and immediate antibacterial activity against *S. aureus*, and this activity was maintained even after 24 h. However, with 0.5% of nisin, no immediate bacterial reduction was observed, and only the PET fabric without plasma treatment exhibited antibacterial activity after 24 h.

Only nisin molecules which can diffuse from the fabric can impart antibacterial activity. The desorption capacity of nisin from the fabric into water can be monitored by tensiometry, while the presence of residual strongly sorbed nisin on the fabric was confirmed by wettability, zeta potential measurements, and wash durability test after nisin coloration by a protein dye. Plasma treatment, which increases the hydrophilic behavior of the PET fabric (WCA reduced from 80° to 42°), increases considerably the quantities of strongly and weakly sorbed nisin. However, it does not improve antibacterial activity compared to the PET fabric without plasma treatment. The reduced mobility of the nisin molecules due to chemisorption of the first layers of nisin on the plasma treated PET fabric can explain the reduced antibacterial activity with 0.5% nisin.

The interactions of proteins at interfaces are well described in the literature; however, the adsorption of biologically active proteins such as nisin is less described and remains controversial. Many studies reported that the antibacterial activity of adsorbed nisin depends on the surface properties of the polymer mainly the hydrophilic or the hydrophobic properties of the support.[11–14] However, the results are controversial since some authors showed that when nisin was adsorbed on hydrophilic surfaces the antibacterial activity was strongest while other studies reported that the antibacterial activity of adsorbed nisin was better when the surface was hydrophobic. Our results demonstrated that plasma treatment which makes the PET fabric more hydrophilic, does not improve the antibacterial activity of the fabrics, though higher amounts of releasable nisin and strongly surface bound nisin are sorbed on the PET fabric when a higher nisin concentration (1%) is used. One possible explanation for

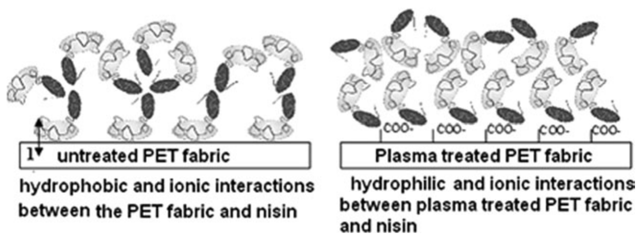

Figure 7. Possible spatial arrangement of nisin molecules at the PET surface without or with surface activation using air atmospheric plasma treatment.

the different results obtained is that the molecular and spatial arrangement of bound nisin at the PET surface is different when the PET fabric is subjected to a prior plasma treatment. Indeed the plasma treatment makes the PET surface more hydrophilic (WCA = 45°) which then attracts the hydrophilic part of nisin. Indeed due to its spatial configuration, each nisin molecule occupies less area on a hydrophilic surface than on a hydrophobic one. This explains why there are more nisin molecules adsorbed at the plasma treated PET fabric. Consequently, a multilayer arrangement of nisin molecules is different for the two different PET surfaces (without and with plasma treatment), since successive layers adsorb in a way that allows hydrophobic-hydrophobic or hydrophilic-hydrophilic interactions between two successive layers of nisin (Figure 7). This in agreement with what has been reported by previous authors who worked on the adsorption of nisin on silanized silica surfaces.[11] Moreover, at the immediate plasma treated PET surface, in addition to hydrophilic interaction, ionic interactions between COO[sbond] groups of the PET fabric surface and the cationic charges of nisin may occur. Moreover, the increased surface roughness of PET fiber due to plasma treatment (Figure 1b) increases the specific surface area on which nisin molecules may adsorb.

Strongly bound nisin on the plasma-treated surface after complete diffusion of releasable antibacterial nisin means that after the antibacterial activity of the textiles, the textile remains hydrophilic (WCA = 33°), and could be suited for applications where such property is a required feature, for example, in biomaterials.[21] On the contrary, sorbed-nisin on PET without plasma treatment, leads to antibacterial PET but is not very hydrophilic (WCA = 60°).

CONCLUSION

The effect of air-atmospheric plasma treatment of PET fabric with respect to nisin adsorption and antibacterial activity was studied.

Bioactive PET textile fabric can be developed using nisaplin solution containing nisin. Our results showed that nisin adsorbed to PET fabric surface (with or without plasma treatment) may have the potential to control pathogenic organisms such as *S. aureus* and the MRSA strains. However, the antibacterial effect on the initial load of the contamination or on bacterial colonization depends on the concentration of nisin used (1% or 0.5%). When lower concentration (0.5% of nisin) is used, the PET fabric without plasma has higher antibacterial efficiency on the initial load.

Results show that adsorption of nisin on plasma treated PET is different from that on untreated PET fabric. An increase in hydrophilicity by plasma treatment of the PET fabric increases the quantity of nisin adsorbed at the fabric surface. In both cases, part of the adsorbed nisin is strongly bound to the PET fabric surface, and the other part is easily released into the water and should be responsible for the antibacterial activity of the surface-sorbed nisin. However, the kinetics of release of nisin depends on the surface adsorption of nisin and thus on plasma preactivation of the surface. Wettability, Zeta potential measurements and coloration of surface-sorbed nisin seem to characterize successfully the unreleasable surface sorbed nisin on PET fiber surfaces.

Strongly bound nisin on the plasma-treated surface after complete diffusion of releasable nisin means that after the antibacterial activity of the textiles, the textile remains hydrophilic (WCA = 33°), and could be suited for applications where such property is a required feature. Adsorption of nisin on PET fabric surface is a possible way to functionalize PET fabrics, but other way should also be studied to have a more controlled release of the nisin and get antibacterial activity

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REFERENCES

1. Krein, S. L.; Olmsted, R. N.; Hofer, T. P.; Kowalski, C.; Forman, J. Banaszak-Holl, J.; Saint, S. *Am. J. Infect. Control* **2006**, *34*, 507.
2. Takai, K.; Ohtsuka, T.; Senda, Y.; Nakao, M.; Yamamoto, K.; Matsuoka, J.; Hirai, Y. *Microbiol. Immunol.* **2002**, *46*, 75.
3. Bide, M.; Phaneuf, M.; Brown, P.; McGonigle, G.; LoGerfo, F. In Modified Fibers with Medical and Specialty Applications; Edwards, J. et al., Ed.; Springer: The Netherlands, **2006**; *Vol. 94*, pp 91–124, 101-4020-3793-7.
4. Spencer, R. C. *Eur. J. Clin. Microbiol. Infect. Dis.* **1996**, *15*, 281.
5. Creech, C. B. II; Kernodle, D. S.; Alsentzer, A.; Wilson, C.; Edwards, K. M. *Pediatr. Infect. Dis. J.* **2005**, *24*, 617.
6. Simoncic, B.; Tomsic, B. *Text. Res. J.* **2010**, *80*, 1721.
7. Charlier, C.; Even, S.; Gautier, M.; Le Loir, Y. *Int. Dairy. J.* **2008**, *18*, 197.
8. Breukink, E.; De Kruf, B. *Biochim Biophys Acta (BBA): Biomembr* **1999**, *1462*, 223.
9. de Arauz, L. J.; Jozala, A. F.; Mazzola, P. G.; Penna, T. C. V.*Trends Food Sci. Technol.* **2009**, *20*, 146.
10. Hurst, A.; Hoover, E. N. In Food Antimicrobials; Davidson, 2nd ed.; P. M.; Branen, A. L., Eds.; Marcel Dekker, Inc., **1993**; pp 369–391.

11. Lakamraju, M.; McGuire, J.; Daeschel, M. A. *J. Colloid Interface Sci.* **1996**, *178*, 495.
12. Tai, Y.-C.; McGuire, J.; Neff, J. A. *J. Colloid Interface Sci.* **2008**, *322*, 104.
13. Patsy, P. L.; Yousef, E. A.; Shellhammer, T. H. *J. Food Safety* **2002**, *23*, 1.
14. Guerra, N. P.; Araujo, A. B.; Agrasar, A. T.; Macías, C. L.; Barrera, A. M.; Carballo J.; Pastrana, L. *J. Food Prot.* **2005**, *68*, 1012.
15. Behary, N.; Perwuelz, A.; Campagne, C.; Lecouturier, D.; Dhulster, P.; Mamede, A. S. *Colloids Surf. B: Biointerf.* **2012**, *1*, 137.
16. Leroux, F.; Perwuelz, A.; Campagne, C.; Behary, N. *J. Adhes. Sci. Technol.* **2006**, *20*, 939.
17. Takke, V.; Behary, N.; Perwuelz, A.; Campagne, C. *J. Appl. Polym. Sci.* **2009**, *114*, 348.
18. Nejadnik, M. R.; Garcia, C. D. *Colloids Surf. B: Biointerf.* **2011**, *82*, 253.
19. Shore, J. *J. Soc. Dyers Colourists* **1968**, *84*, 408.
20. Lins, L.; Ducame, P.; Breukink, E.; Brasseur, R. *Biochim. Biophys. Acta (BBA): Biomembr.* **1999**, *1420*, 111.
21. Pu, F. R.; Williams, R. L.; Markkula, T. K.; Hunt, J. A. *Biomaterials*, **2002**, *23*, 2411.