

# Chemical Grafting of Curcumin at Polyethylene Terephthalate Woven Fabric Surface Using a Prior Surface Activation with Ultraviolet Excimer Lamp

A. Kerkeni,<sup>1,2</sup> D. Gupta,<sup>3</sup> A. Perwuelz,<sup>1,2</sup> N. Behary<sup>1,2</sup>

<sup>1</sup>Université Lille Nord de France, Lille, France

<sup>2</sup>ENSAIT, GEMTEX, Roubaix, France

<sup>3</sup>Department of Textile Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India

Received 1 December 2009; accepted 12 August 2010

DOI 10.1002/app.33276

Published online 30 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Durable curcumin-treated antibacterial polyethylene terephthalate (PET) fabrics (against *Staphylococcus aureus*) were produced by dyeing with curcumin after surface activation using vacuum ultraviolet excimer lamp at 172 nm. Surface change properties of the exposed fabrics were characterized by surface analysis methods such as wettability, atomic force microscopy, and X-ray photoelectron spectroscopy. Results show an increase in surface hydrophilicity with a water contact angle of the PET fabric reaching 24° after 10 min excimer irradiation, which could be attributed to an increase in carboxyl group formation as confirmed by X-ray photoelectron spectroscopy measurements. Varying concentrations of curcumin

were immobilized onto untreated and vacuum ultraviolet-irradiated PET samples using diffusion method at 90°C, and the treated fabrics characterized using *K/S* (color strength) values at 440 nm. *K/S* values increased when the PET surface was subjected to a prior excimer irradiation, because of grafting of curcumin at the PET surface. Increased excimer irradiation time increased grafting of curcumin because the inner fabric fiber surfaces were also more thoroughly treated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1583–1590, 2011

**Key words:** antibacterial textile; curcumin; excimer lamp; PET (polyethylene terephthalate) surface modification

## INTRODUCTION

In the last few decades, antibacterial textiles have attracted a lot of attention because of their importance for combating pathogenic bacterial growth and providing comfort, health, and hygiene for humans. Several major classes of antimicrobial agents are currently used in the textile industry. Most of them are facing difficulties because of their toxicity, bacterial resistance, or water pollution.<sup>1</sup> Natural antimicrobial agents, which are renewable and biodegradable eco-friendly products, present an alternative for the development of very specific, antibacterial, and biologically functional textile, which would have a targeted efficacy on or inside the human body.<sup>2,3</sup>

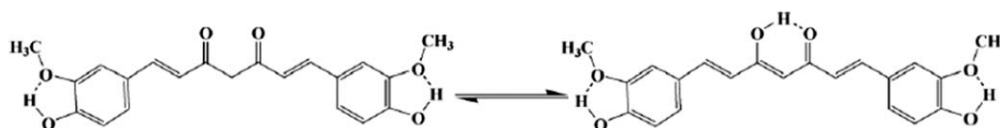
Curcumin (bis (4 hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5 dione) is a natural yellow-orange pigment extracted from *Curcuma longa* roots. In its chemical structure, curcumin has two aryl rings having *ortho*-methoxy phenolic OH groups, which are symmetrically linked in conjugation through the

diketone moiety (Fig. 1). The diketone functionality is also responsible for the intramolecular hydrogen atom transfer leading to the keto and enol tautomeric conformations.<sup>4</sup>

Curcumin is used as a spice and has attracted considerable attention because of its wide spectrum of biological and pharmacological activities. Extensive research on the medicinal applications of curcumin have shown its antioxidant, anti-inflammatory, anti-cancer, and wound-healing characteristics.<sup>4</sup> Studies using bacterial indicator systems have shown that curcumin also exhibits biological activity<sup>5</sup> and that it may find application in the phototherapy of psoriasis, cancer, and bacterial and viral diseases. Dahl et al.<sup>6,7</sup> have shown that curcumin is active against *Staphylococcus aureus* at low concentrations, but it is also active against *Escherichia coli* at higher concentrations and in the presence of light. Shinyoung and Yigi<sup>8</sup> showed that curcumin-dyed wool fabrics have antibacterial activity against both Gram-positive and Gram-negative bacteria, but the treatment is not resistant to washing and to light.

As far as polyester fiber (polyethylene terephthalate [PET]) is concerned, in addition to its wide use in apparel application, it is also a very useful non-biodegradable biomaterial. There are over millions of medical devices implanted annually in the United

Correspondence to: N. Behary (nmassika.behary@ensait.fr).  
Contract grant sponsors: Asia Link Project.



**Figure 1** Chemical structures of curcumin in keto-enol tautomeric equilibrium.

States, ranging from simple devices such as hernia repair mesh, wound dressings, and catheter cuffs to more complex devices such as the total implantable heart, left ventricular assist devices, and prosthetic arterial grafts.<sup>9</sup>

Polyester fiber surfaces are, however, more readily subjected to bacterial adhesion than other fibers such as polyamide and cotton fibers.<sup>10</sup> To prevent infection of the PET fabrics, several strategies are proposed and/or developed, and the purpose of this research was to use curcumin for the development of bioactive polyester, having antibacterial behavior.

Polyester PET is inert chemically, with no functional group to react with curcumin; it must, thus, undergo surface functionalization before attachment of a bioactive compound.<sup>9,11</sup> In a recent study we showed that UV lamp treatment modifies the surface of PET fibers without affecting the bulk properties,<sup>12</sup> enabling the grafting of acrylic acid. UV excimer treatment has also been carried out by Praschak et al.<sup>13</sup> and by Zhengmao and Kelley<sup>14</sup> who worked on surface modification of polyester followed by grafting, using respectively, a 222-nm and a 172-nm UV excimer irradiation, successfully grafted some specific chemical compounds.

Although there are studies reported on the functionalization of PET films and polyhydroxybutyrate bacterial polyester granules with curcumin using supercritical carbon dioxide,<sup>15</sup> there have been no studies on the use of excimer treatment on polyester fibers to graft curcumin molecules. Therefore, motivated by interesting aspects of these new excimer lamps, in this study, we have treated polyester with a 172-nm vacuum ultraviolet (VUV) excimer lamp to graft the bioactive curcumin to polyester fibers.

## EXPERIMENTAL

### Material

A 100% polyester (PET, density = 1.39 g/cm<sup>3</sup>) plain woven fabric from UTEXBEL (Belgium) of density 120 g/m<sup>2</sup> was used. The fabric was cleaned to remove all impurities and spinning oil, which adhere to PET fiber surface as a result of diverse processing steps of the PET fabric. Cleaning ensures excimer treatment of PET fabric and not of impurities.

PET fabric was washed with detergent and water at 60°C for 30 min, then rinsed twice in distilled

water and then boiled at high temperature (130°C) under pressure for 30 min in distilled water ( $\gamma = 72.3$  mN/m) and dried at 60°C for 20 min. Curcumin powder was purchased from Aldrich Chemicals (St. Louis, MO; with 97% of curcumin I).

### PET surface modification using excimer lamp

#### UV excimer treatment

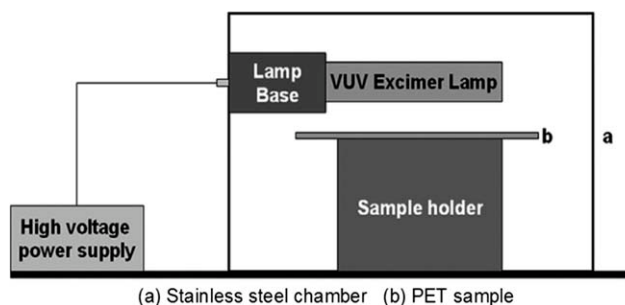
The Xenon excimer UV lamp (XERADEX 20W/L40/120/SB-SX46/KF50) and the high-voltage power supply (DBD 110 V/230 V 50 Hz/60 Hz) for the lamp were procured from Messrs Radium Lampenwerk Wipperfurth, Germany. A chamber was developed in-house for mounting the UV excimer lamp (Fig. 2). The lamp emits almost monochromatic light in VUV region ( $\lambda$ , 172 nm) with an irradiation power of 50 mW/cm<sup>2</sup>. Fabric samples can be exposed to the UV lamp radiation through a sample holder as shown in Figure 2. PET samples were treated under different exposure times (1, 5, 10, and 15 min), and on both sides of the PET fabric.

### PET surface change characterization

#### Atomic force microscopy analysis

Investigation using a "Nanoscope III" from Digital Instrument was carried out for atomic force microscopy (AFM) imaging in the tapping mode. Tapping mode tips "Budget sensor" from "Nanoandmore," of length 125  $\mu$ m, made of monolithic Silicon probe with aluminum reflex coating and with resonance frequency of 300 kHz were used.

Tapping mode was preferred to the AFM/LFM (contact mode AFM) because the tapping mode overcomes problems associated with friction, adhesion, and electrostatic forces, which may arise after an



**Figure 2** Excimer lamp irradiation chamber.

excimer treatment and which would distort image data. Tapping mode imaging was carried in ambient air.

The fiber surface roughness parameter  $Ra^{16}$  was calculated directly from AFM signals using the computer software-supplied Nanoscope III tool. AFM imaging was carried out on five different fiber samples selected randomly from the PET fabric sample having been subjected to different treatments.

#### Water contact angle and capillary measurements using wicking test

To quantify the surface treatment modifications, contact angle as well capillarity measurements were carried out on a tensiometer, 3S Balance from GBX Instruments (France). During measurements, a rectangular-shaped fabric sample of size  $2\text{ cm} \times 5\text{ cm}$  was connected to the "3S Balance" at the weighing position, and then it was progressively brought into contact with the surface of water placed in a container. The movement of the container was stopped when a sudden increase in weight ( $W_m$ ) was detected, which corresponded to a liquid meniscus formation on the fabric surface. A continuous increase of weight with time owing to liquid flow inside the fabric structure by capillarity was recorded. After 3 min, the fabric sample was separated from the water surface, and the weight of the liquid entrapped inside the fabric structure by capillarity: "the capillary weight ( $W_c$ )" read directly on the screen of the balance. More detailed description of this experiment can be found in our previous work.<sup>17</sup>

From the meniscus weight ( $W_m$ ), the water contact angle was calculated using eq. (1):

$$W_{m \times g} = \gamma_L x \cos \theta \quad (1)$$

where  $W_m$  is the meniscus weight (g),  $p$  is the sample perimeter in contact with the liquid (mm),  $g = 9.81\text{ g sec}^{-2}$ ,  $\gamma_L$  is the surface tension of water, and  $\theta$  is the water contact angle.

#### X-ray photoelectron spectroscopy

PET fiber surfaces before and after UV excimer treatment were analyzed by X-ray photoelectron spectroscopy (XPS). All XPS analyses were performed in a VG ESCALAB 220XL spectrometer (Thermo) by means of nonmonochromatic Mg  $K\alpha$  x-radiation (1253.6 eV) in the large area lens mode and in a vacuum atmosphere (around  $10^{-7}$  Pa). The surface composition was obtained from measurement of the areas of the C1s and O1s peaks, obtained at 30-eV pass energy.

#### Curcumin application and characterization of curcumin-treated PET fabrics

##### Curcumin application using diffusion method

First, 0.5 g of curcumin was dissolved in 20 mL of ethanol and then diluted using distilled water. The pH was adjusted to 5 using acetic acid. Indeed, curcumin is readily subjected to degradation in aqueous solution, and, in our study, we showed that best stability of curcumin at a dyeing temperature of  $90^\circ\text{C}$  is achieved at  $\text{pH} = 5$ .<sup>18</sup>

Different ratios of curcumin dyestuff to fabric weight (0.5, 1, 2, and 5%) were chosen, whereas the dye liquor ratio was always constant, 1 : 40, i.e.,  $40\text{ cm}^3$  of dye solution per gram of PET fabric. Dyeing of untreated and excimer-treated PET samples was carried out in accordance with general dyeing method using diffusion method in a HTHP (High Pressure and High Temperature/Beaker Dyeing Machines) at  $90^\circ\text{C}$ .

The temperature of the dye-bath was gradually raised (about  $1^\circ\text{C}/\text{min}$ ) from room temperature to  $90^\circ\text{C}$ , and was kept at this temperature for 30 min. The temperature of the dye-bath was then allowed to cool to  $60^\circ\text{C}$ ; then, dyed fabric was squeezed, rinsed thoroughly with distilled water, and air-dried.

##### Curcumin-treated PET characterization using spectrophotometer

Light diffusion reflectance measurements were carried out on the curcumin-dyed PET fabrics using Color-Eye® 7000A Spectrophotometer (GretagMacbeth), with D65 illuminant and  $10^\circ$  standard observer, at wavelength  $\lambda = 440\text{ nm}$ .

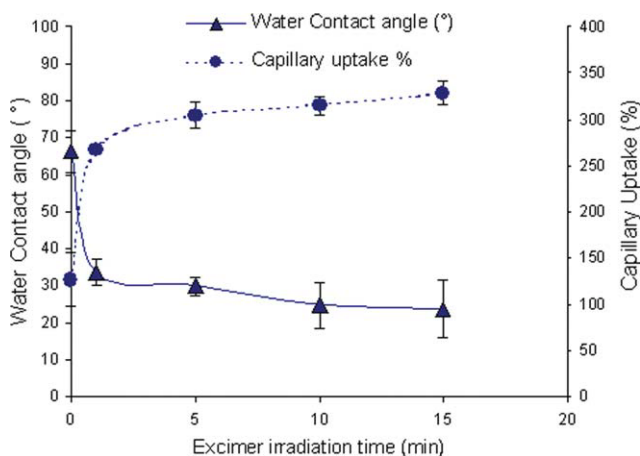
The color yield values were calculated according to Kubelka–Munk function ( $K/S$ ) by using eq. (2) before and after extraction of the physi-sorbed curcumin using ethanol.

$$K/S = (1 - R)^2/2R = Ac/S \quad (2)$$

where,  $K$  refers to coefficient of absorption,  $S$  is the coefficient of scatter,  $R$  is fractional reflectance,  $c$  is the concentration of the absorbing species, and  $A$  is the absorbance of dyes. It is assumed that the scattering coefficient " $S$ " depends on the properties of the fabric (substrate), and, thus, the  $K/S$  values are directly related to the concentration of dyes on the fabric.

##### Evaluation of antibacterial activity

The antibacterial activity against *S. aureus* of the treated and untreated samples was evaluated using a quantitative test method according to the



**Figure 3** Water contact angle (▲) and % capillary uptake (●) variations of PET fabric as a function of excimer lamp irradiation time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

American standard (AATCC Test Method 174-1998). Fabric swatch were cut and placed separately on sterile Petri dishes, and, using a microliter pipette, 1 mL of bacterial inoculum (230 colony forming units/mL) was distributed onto the fabric. Each swatch was then transferred aseptically to a jar, which was incubated for 24 h at 37°C. After incubation, 100 mL of a neutralizing agent was added, and the jar shaken vigorously to release the bacteria from the swatch. The number of colony forming units was then quantified by serial dilutions of the solution from the jar followed by its incubation on agar plates at 30°C for 24 h.

The percent reduction in number of colonies in curcumin-treated sample compared with the untreated sample gives the antibacterial activity of the fabric.

Antimicrobial Activity or % Reduction

$$= [(A - B)/A] * 100$$

where, *A* is the bacteria colonies of untreated fabric and *B* is the bacteria colonies of the treated fabric.

## RESULTS AND DISCUSSIONS

### Part I: Characterization of PET fiber surface change after VUV excimer lamp irradiation

Water contact angle and capillary uptake measurements

Results of water contact angle and capillary uptake (%) measurements carried out on PET fabric under different excimer exposure time (1, 5, 10, and 15

min) are presented in Figure 3. For each excimer irradiation time, four different samples were tested.

It can be seen clearly that the contact angle value was greatly decreased only after 1 min of exposure to excimer lamp, from 66° to 33°. The decrease in water contact angle continues slightly with increase in excimer exposure time.

In general, capillary uptake increases with increasing excimer irradiation time compared with untreated samples. After an excimer treatment of only 1 min, the capillary uptake is almost doubled (from 127.1% to 267%); highest capillary uptake (328%) is reached after 15 min of VUV irradiation time. Only 1-min UV excimer irradiation is indeed not enough to treat fibers inside the textile structure. Because the PET fabric stays a longer time inside the irradiation region, a more thorough treatment of fibers inside the textile structure takes place. Although an important increase in hydrophilicity of the outer PET fabric fiber surface is reached after 1 min of irradiation, treatment of inner PET fabric fiber surface is achieved after a 15-min UV excimer irradiation time.

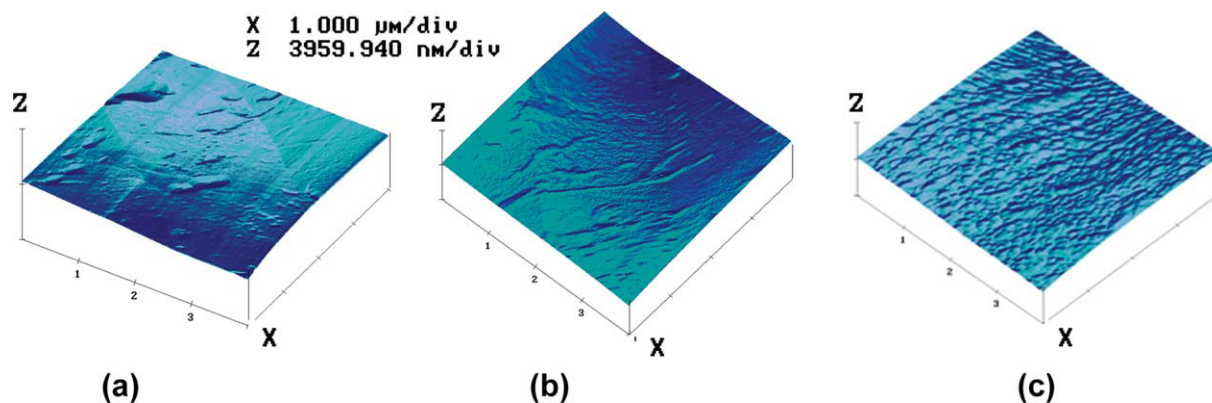
### AFM results

Figure 4(a–c) shows typical topographical images obtained in tapping mode of a cleaned-untreated PET fiber [Fig. 4(a)] and of a PET fiber with an excimer treatment after 1 min [Fig. 4(b)] and after 10 min [Fig. 4(c)], respectively.

The surface roughness of the PET surface before and after an excimer treatment of 1 min is almost the same ( $R_a = 19$  nm): the untreated PET fiber seems quite smooth with few bumps, which also appear after an excimer treatment of 1 min; nevertheless, the extreme upper surface layer of the PET fiber seems distorted [Fig. 4(b)] after the excimer treatment. However, after an excimer irradiation of 10 min, uniform scale-shaped bumps can be seen on the overall excimer-treated PET fiber surface [Fig. 4(c)], which has a higher surface roughness ( $R_a = 90$  nm) than the untreated PET fiber.

### XPS results

Table I and Figure 5 show an increase in the band at 289.2 eV, which corresponds to an increase in carboxyl groups  $-(O=C)-O^-$  at the PET surface from 10.8% to 19.3% after excimer treatment. There is only a very slight increase in content of C–O (0.3%) after the excimer treatment. Wetting measurements are thus correlated with the XPS analyses as an increase in surface carboxyl groups  $-(O=C)-O^-$  content after exposure to VUV excimer treatment.



**Figure 4** Typical topographical tapping-mode AFM images of cleaned PET fiber surface (a) and PET fiber subjected to UV excimer irradiation during 1 min (b) and during 10 min (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

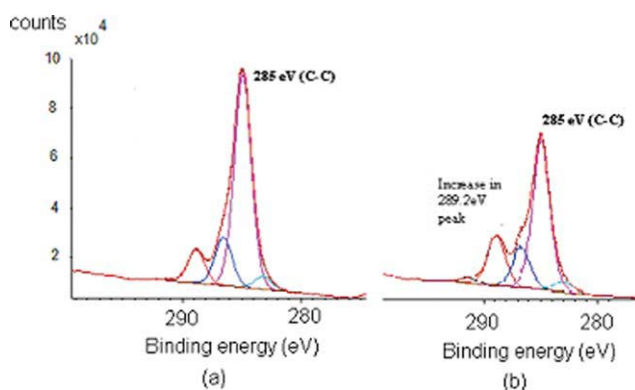
### Part I: Discussion

The increase in hydrophilicity of the PET fabric surface after the VUV excimer treatment is due to formation of polar groups when the PET surface is irradiated with the VUV excimer. Indeed, the polyester surface is hydrophobic with no chemical reactive group. The excimer lamp emits intense monochromatic light with high-energy UV photons at 172 nm capable of generating polymer chain scissions of the weakest bonds of the polyester surface, creating very reactive chain-end free radicals, which then react with the oxygen at the PET fiber surface, yielding oxidized carboxyl groups. XPS measurements show that there is an increase mainly in the band at 289.2 eV corresponding to polar carboxyl groups  $-(O=C)-O^-$  formation at the PET surface after an excimer lamp treatment. These carboxyl groups are polar species capable of increasing the surface energy of the polyester. Another explanation could be that the oxygen at the fiber surface would absorb the high-energy photon and form highly reactive

excited oxygen, which then reacts with the PET surface to form polar groups, which increase surface wettability.

Excimer treatment of a woven PET fabric depends on the excimer irradiation time. The outer surface of a PET fabric is readily treated to yield a very low water contact angle of  $33^\circ$  after 1 min irradiation only. The inner fabric fiber surface requires a longer treatment time to reach a maximum polarity determined by the capillary weight. A longer irradiation time is needed for a more thorough treatment of the PET fibers inside the PET fabric structure.

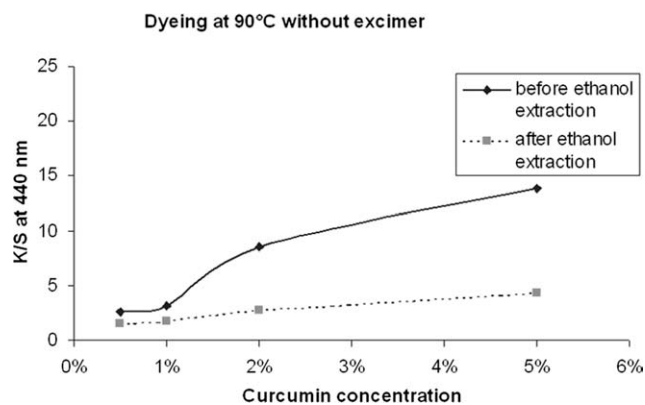
The excimer lamp treatment not only causes chemical structuring of the PET surface by adding polar groups but also morphological surface changes are observed by tapping mode AFM imaging. Although after 1-min treatment the water contact angle is divided by 2, no surface etching is observed. However, after a longer VUV irradiation time, further surface etching of the PET fiber surface takes place, yielding uniform scaly-shaped bumps on the overall PET fiber surface. Nanostructuring of the PET fiber surface takes place at higher irradiation time. We also observed this phenomenon when PET fibers are treated with atmospheric plasma treatment.<sup>17</sup>



**Figure 5** XPS spectra of untreated PET fabric (a) compared with UV excimer-treated PET fabric for an irradiation time of 10 min (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE I**  
The Binding Energy (in eV) and the Corresponding Quantification (%) of Each Chemical Group Present at the PET Surface without and with 10-min Excimer Treatment

Chemical group	Binding energy (eV)	Composition (%)	
		Without excimer	With 10 min excimer
C—C	285.0	73.5	62.5
C—O	286.6	15.7	16.0
$-(O=C)-O^-$	289.2	10.8	19.3



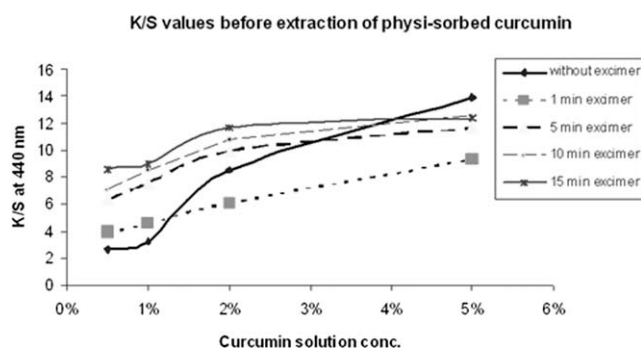
**Figure 6**  $K/S$  (440 nm) variation of PET fabrics dyed at 90°C as a function of curcumin solution concentration before and after extraction of surface physi-sorbed curcumin molecules using ethanol.

## Part II: Characterization of VUV-irradiated PET samples functionalized with curcumin

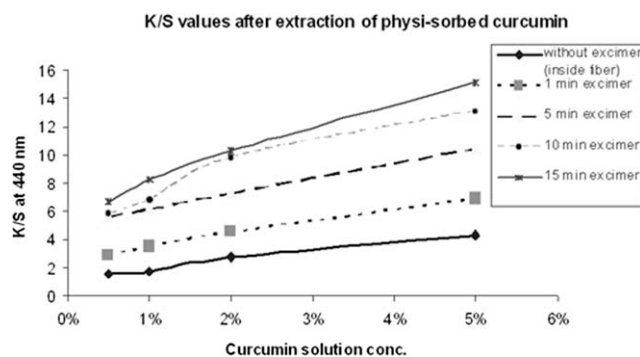
### $K/S$ values of treated fabrics

*Without excimer treatment.* Figure 6 shows the variation of  $K/S$  at 440 nm of PET fabrics dyed with varying concentration of curcumin at 90°C using diffusion method and without a prior UV excimer treatment of the PET fabric. Indeed, as curcumin concentration increases from 0.5% to 5%, the  $K/S$  values increases from 3 to 14. After the removal of surface physically sorbed curcumin by rinsing the fabric in ethanol, the  $K/S$  values are greatly reduced, especially at higher dye concentrations (2% and 5%). Thus, at a dye-bath of 5%, the  $K/S$  value is reduced from 14 to around 4.5. Indeed, at 90°C, a temperature below the glass-transition temperature of PET, dye diffusion inside the PET fiber is slow, and, as the concentration of curcumin increases, there is only a slight increase in dye diffusion inside the fiber: most of the curcumin molecules are physi-sorbed at the fiber surface.

*With a prior excimer treatment.* Figure 7 shows the variation of  $K/S$  of PET fabrics dyed with varying



**Figure 7**  $K/S$  (440 nm) variation of PET dyed fabrics as a function of curcumin concentration and as a function of excimer irradiation time.



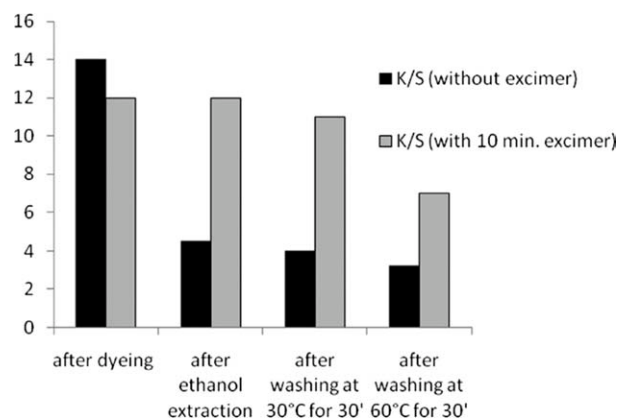
**Figure 8**  $K/S$  (440 nm) variation of PET dyed fabrics as a function of curcumin concentration and as a function of excimer exposure time, after extraction of surface physi-sorbed curcumin molecules using ethanol.

concentrations of curcumin at 90°C with a prior UV excimer treatment of the PET fabric at irradiation times 1, 5, 10, and 15 min, respectively. As it can be seen, without extraction of physi-sorbed curcumin and at lower concentrations (0.5% and 1%), as excimer irradiation time increases the  $K/S$  values increase too. However, at higher dye concentrations (2% and 5%), increasing excimer treatment time does not seem to increase the  $K/S$  values.

*After extraction with ethanol.* Figure 8 shows the variation of  $K/S$  values of curcumin-dyed PET fabrics with or without a prior excimer treatment, after extraction of physi-sorbed curcumin using ethanol. In general, before extraction with ethanol, the  $K/S$  values (Fig. 7) are only slightly higher than the  $K/S$  values after extraction with ethanol (Fig. 8) in the case of the excimer-treated samples. At higher concentration (5%) and excimer treatment time of 10 and 15 min, the  $K/S$  values are even smaller before extraction of physi-sorbed curcumin. This would mean that as the concentration of curcumin increases, the physically adsorbed curcumin would form an ordered monolayer to multilayer films at the PET surface, which would reflect light, reducing the  $K/S$  (absorption) values. Indeed, Warken et al.<sup>19</sup> and Proehl et al.,<sup>20</sup> who worked on the light absorption of dye molecules deposited on fibers, confirm that there is absorption reduction because of agglomeration of molecules on fiber surface in an ordered monolayer or multilayer form. Figure 8 shows that after extraction of physi-sorbed molecules, the  $K/S$  increases with excimer irradiation time and with dye concentration.

## Part II: Discussion

Indeed, without excimer treatment, the  $K/S$  values after ethanol extraction are directly related to the quantity of curcumin inside the PET fiber only. The increase in the  $K/S$  values with excimer treatment



**Figure 9**  $K/S$  (440 nm) variation of PET fabric dyed with 5% curcumin without excimer treatment (black) and with a 10-min excimer treatment (gray), after extraction of surface physisorbed curcumin with ethanol, and after washing in water at 30°C and 60°C during 30 min.

time cannot be explained by an increase in dye migration inside the fiber because, in a previous study,<sup>12</sup> we already showed that PET fiber's crystallinity remained unchanged with excimer treatment time. Indeed, the increase in the  $K/S$  with treatment time is due to the surface-chemically bound curcumin molecules, which are strongly bound to PET surface and could not be removed by ethanol. Grafting of curcumin to PET surface would take place with the phenol group of the curcumin group reacting with the carboxylic group on the PET fiber, through ester bond formation.

The excimer irradiation time of the woven PET fabric has a direct effect on the quantity of curcumin grafted. Indeed, as it was discussed in the first part, the minimum water contact angle of the outer surface of a PET fabric is reached after 1 min UV irradiation only. However, maximum capillarity, that is maximum polarity, is reached at longer excimer treatment (15 min), which allows a more thorough treatment of the PET fibers inside the PET fabric structure, and this would explain a higher rate of grafting of curcumin molecules as the excimer irradiation time increases.

A further washfastness test and a light fastness test (xenotest) were carried out to confirm the stability of curcumin grafting. Figure 9 shows the  $K/S$  variation of PET fabric dyed with 5% curcumin without excimer treatment (black) and with a 10-min. excimer treatment (gray) when subjected to washing in water at 30°C and 60°C during 30 min. The washing test confirms that, with a prior UV excimer treatment, the surface-sorbed curcumin adheres better to the PET, whereas in the absence of PET surface activation, the surface physisorbed curcumin are easily washed out with water or removed by ethanol.

The results also show that the grafting of the curcumin to excimer-treated PET is less stable to washing at 60°C. Most probably, the excimer treatment of PET produces at the fiber outer core surface, a zone with shorter polymer chains because of chain scissions of the PET. This zone would have a lower glass-transition temperature than the PET, and, combined with hydrophilic  $-(O=C)-O-$  groups, it allows an easier access to hot water (60°C), provoking hydrolysis of the bond between curcumin and hydrophilic group.

Moreover, the degradation of curcumin by heat would also explain the great reduction in  $K/S$  by washing at 60°C of the untreated and excimer-treated PET fibers. Chemically grafted curcumin molecules are, thus, partially lost by washing at 60°C, but are resistant to ethanol and washing at 30°C.

Light fastness test shows that with and without excimer treatment, the rate of photodegradation is similar (not shown here): curcumin degrades readily in light whether grafted or not to the PET. Compared with the work carried out by Shinyoung and Yigi,<sup>8</sup> our work shows that a prior UV excimer irradiation of PET improves washfastness (at 30°C) of PET dyed with curcumin, but there is no improvement in light fastness.

#### Antibacterial test results

The antibacterial activity presented in Table II are average values of three tests carried out on the PET

**TABLE II**  
Antibacterial Activity (%) against *S. aureus* of PET Fabrics Dyed with 1% and 5% Curcumin with and without a 10-min Excimer Treatment, Compared with  $K/S$  Values of the Dyed Fabrics before and after Ethanol Extraction

Curcumin concentration (%)	UV-excimer irradiation time (min)	Antibacterial activity (reduction) %	$K/S$ (after dyeing)	$K/S$ (after extraction with ethanol)	$\Delta K/S$ (physi-sorbed curcumin)
5	0	90	14	4.5	9.5
5	0	0 <sup>a</sup>	14	4.5	9.5
5	10	70	12	12	0
1	0	50	2.5	1	1.5
1	0	0 <sup>a</sup>	2.5	1	1.5
1	10	40	8	5	3

<sup>a</sup> Antibacterial test carried out after removal of physisorbed curcumin from dyed samples without excimer treatment.

dyed with curcumin. The antibacterial activity against *S. aureus* of curcumin-treated PET fabrics seems to depend on the concentration of curcumin: this activity increases from 40–50% to around 70–90% when the curcumin concentration is increased from 1% to 5% (Table II). The excimer treatment, i.e., chemical grafting of curcumin, decreases slightly the antibacterial activity of curcumin-treated PET fabrics.

Without excimer treatment and after removal of the physi-sorbed curcumin using ethanol, the PET dyed with 1% or 5% curcumin seem to have no antibacterial activity (see values with superscript “a”). Indeed, curcumin immobilized in the inner fiber core seem to have no antibacterial activity against *S. aureus*.

With a prior excimer treatment, there is no physi-sorbed curcumin when PET is dyed with 5% curcumin ( $K/S = 12$  before and after ethanol extraction): the antibacterial activity is, however, maintained up to 70% because of the chemically grafted curcumin. Without excimer treatment, the physi-sorbed curcumin molecules are responsible for antibacterial activity but are easily lost during further treatments ( $K/S = 14$  reduces to 4.5 after extraction with ethanol and washing at 30°C).

### CONCLUSIONS

UV excimer lamp is a valuable tool to modify surface properties of the PET fabric before grafting of bioactive curcumin molecules. Indeed, excimer treatment induces chemical modification of the PET surface with the creation of polar carboxyl group as confirmed by XPS, though at higher excimer irradiation time surface etching is also observed. During dyeing at 90°C, curcumin molecules adsorbed at the PET surface diffuse inside the fiber to a very low extent, and, in presence of polar groups at the PET surface created by excimer irradiation, grafting of curcumin takes place. The quantity of curcumin grafted at the PET fabric surface increases with excimer irradiation time because a longer excimer irradiation time is necessary to activate the PET fiber surface and generate polar species at the fiber surfaces of the inner fabric structure.

Finally, the antibacterial results show that the treated fabrics with curcumin are bioactive against

*S. aureus*. The antibacterial activity seems to be more related to the activity of surface-sorbed curcumin. With the excimer treatment, though a slight decrease in antibacterial activity is observed, it provides a more wash-durable antibacterial finish because of chemical grafting of the curcumin molecule instead of mere physi-sorption.

The authors acknowledge UTEXBEL (Belgium) for providing them with woven fabric sample used in this work. They thank Mr. Dassonville and Mr. C. Catel for their precious help.

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