Surface Treatments on Tencel Fabric: Grafting with β-Cyclodextrin

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ABSTRACT: Tencel is a cellulosic fabric obtained from wood pulp that is very similar to natural cotton. For its potential performances to be expanded, Tencel needs to be processed in different ways. The ability of cyclodextrins to include hydrophobic molecules, such as fragrances, antimicrobial agents, and other chemicals, can be exploited to produce new grafted textiles with peculiar performances. We report studies on the grafting of acrylamidomethylated β-cyclodextrin and monochlorotriazinyl-β-cyclodextrin to Tencel and on the inclusion of different molecules in the free cavities of cyclodextrins. The physicochemical properties and performances of the untreated and treated fabric have been determined with differential scanning calorimetry, ultraviolet–visible spectra, X-ray diffractometry, and breaking load loss, aroma, and antimicrobial finishing tests. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 706–715, 2003

Key words: host–guest systems; inclusion chemistry; fibers

INTRODUCTION

The toroidal shape and the presence of internal hydrophobic hollow cavities in cyclodextrins (CDs) produce the extraordinary capability of these hosting species to include a very wide variety of different molecules and ions and to form stable inclusion compounds (ICs).[1] According to the number of glucose units in the CD ring, we distinguish α-, β-, and γ-CDs, which contain six, seven, and eight monosaccharide moieties, respectively (see Fig. 1). Besides the inclusion of ionic species, such as I_3^-, and small or large organic molecules (aromatic acids, amines, aldehydes, ketones, etc.),[1,2] CDs produce a large number of other supramolecular adducts, such as polyrotaxanes, molecular necklaces, molecular tubes, and molecular trains, in which several cyclic molecules are threaded around a single long polymeric chain.[2,3] These IC usually can be crystallized and purified; they possess the same hosting properties as their originating ligands; and they are successfully exploited in different fields, such as food manufacturing, cosmetics, pharmaceuticals, and analytical and organic chemistry.[4–14]

The powerful capability of CDs to include hydrophobic molecules can be used in textile finishing as well. Several articles and patents report relevant applications of CDs for antimicrobial, insect-free, aroma finishing and in textile dyeing through the formation of physical bonds to different fibers.[15–18] The permanent grafting of different chemicals results in specific performances and new properties in fabrics. Vinyl-based monomers, epoxides, and acid anhydrides can be successfully used to modify cotton or wool fibers[19,20] and to improve their chemical resistance, crease recovery, dye affinity, and shrink-resist properties.

The grafting of different monomers onto cellulose usually requires the formation of free radicals on the fabric surface with oxidizing species such as $S_2O_8^{2-}$, Ce(IV), and Mn(III). Ceric ions generate reactive sites on the cellulosic backbone, without the formation of intermediate free radicals in the bulk solution.[21] Lee et al[15]. already reported the grafting of acrylamidomethylated β-cyclodextrin (CDNMA) onto cotton fibers initiated by Ce(IV) and confirmed the formation of a permanent chemical bonding of β-CD with the textile material by means of the double-bond content, Fourier transform infrared, high-performance liquid chromatography, and acid hydrolysis analyses (see Fig. 2).

Monochlorotriazinyl-β-cyclodextrin (CDMCT), which contains two to three reactive groups per ring, is another great tool for the surface modification of natural and synthetic fibers (polyester, polyamides, and polyacrylics) because the reactive chlorine atoms of the triazinyl groups can react with nucleophilic residues such as —NHR, —OH, or —SH (see Fig. 3). Once chemically grafted onto cellulosic substrates,[22] these materials can be used for fragrance release (odorizing in laundry cycles), odor adsorption (sheets and personal clothing), controlled release (antibacterial, fungicide, or insect repellent finishing), ultraviolet (UV)

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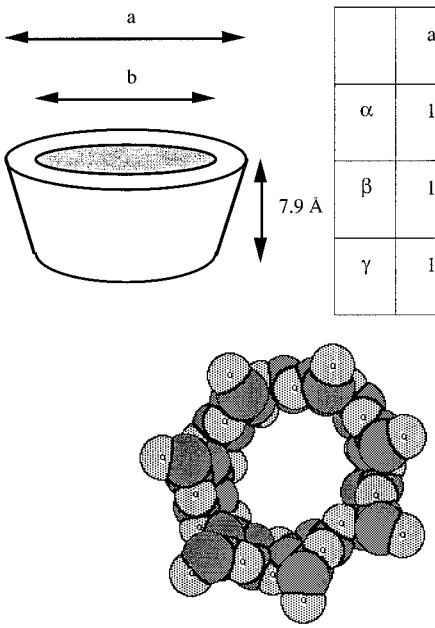

	a, Å	b, Å
α	14.6	4.9
β	15.4	6.2
γ	17.5	7.9

Figure 1 Structural parameters and CPK model of β-CD.

protection, and stabilization of active ingredients. CDMCT has no irritating or sensitizing effects, and so textiles treated with this chemical are expected to be toxicologically safe.[23]

Tencel is a lyocell fabric obtained through a spinning procedure from harvested tree pulp dispersed in *N*-methyl-morpholine oxide, and it shows very interesting properties from technological and environmental points of view.[24] Tencel looks like cotton, but it possesses a higher crystalline/amorphous cellulose ratio[25] and, therefore, a higher breaking load, enhanced tenacity, better dry elongation, higher resistance to laundry cycles, a more precious "hand," and a greater homogeneity with respect to other fibers.[26] From a structural point of view, Tencel is formed by elementary fibrils (with a diameter of ca. 80 Å) composed of crystalline cellulose and separated in the fiber-axis direction by highly oriented amorphous regions.[27]

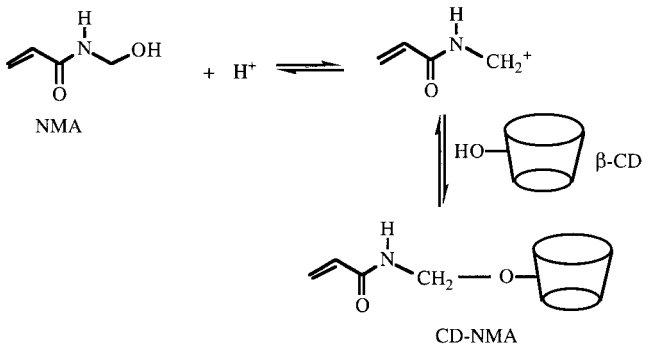

Figure 2 Synthesis of CDNMA.

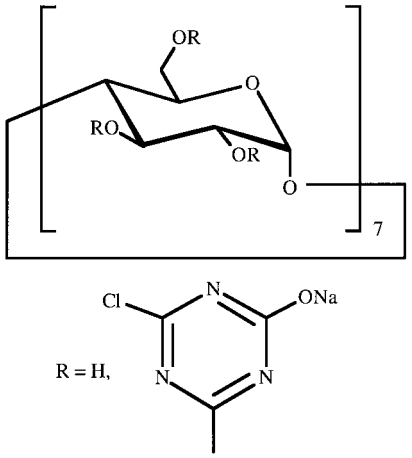

Figure 3 Structure of CDMCT.

Worldwide, the fashion industry is more and more interested in new and versatile fabrics, characterized by specific mechanical and physicochemical properties, for the production of textiles with highly specific properties, such as hand effect, drape effect, flame retardancy, water and oil repellency, shrink resistance, and antibacterial properties. Besides commercial interests, there are other valuable properties that need to be taken into account in the formulation, production, and development of new textiles. One of these is the protection given by clothing from solar UV radiation[28] or electromagnetic fields[29] to the human body; these issues in recent years have become more and more dramatic because of ozone layer depletion and so-called electrosmog.

The possibility of performing grafting treatments in fabrics is very important, and some data are already available.[22,23] This opportunity would ensure less damage to the strength of fabrics and a higher level of surface treatment.

In this article, we report our study on the chemical grafting of two β-CD derivatives onto Tencel fabric (CDNMA and CDMCT) and on the inclusion of some probe chemicals [vanillin (VAN), benzoic acid, iodine, *N*,*N*-diethyl-*m*-toluamide (DEET), and dimethylphthalate (DMP); see Fig. 4] in the grafted CD cavities. Our results indicate that Tencel can be efficiently modified, with no significant change in its structural and surface properties, and that the probe molecules remain on the fabric surface.

EXPERIMENTAL

Tencel, kindly provided by Tecnotessile Srl (Prato, Italy), was boiled in aqueous Na_2CO_3 for 3 h and then dried to ambient conditions before any chemical treatment or test. β-CD and Cavasol W7 MCT (called CDMCT throughout the article) were obtained from Wacker-Chemie Italia SpA (Milan, Italy) and used as

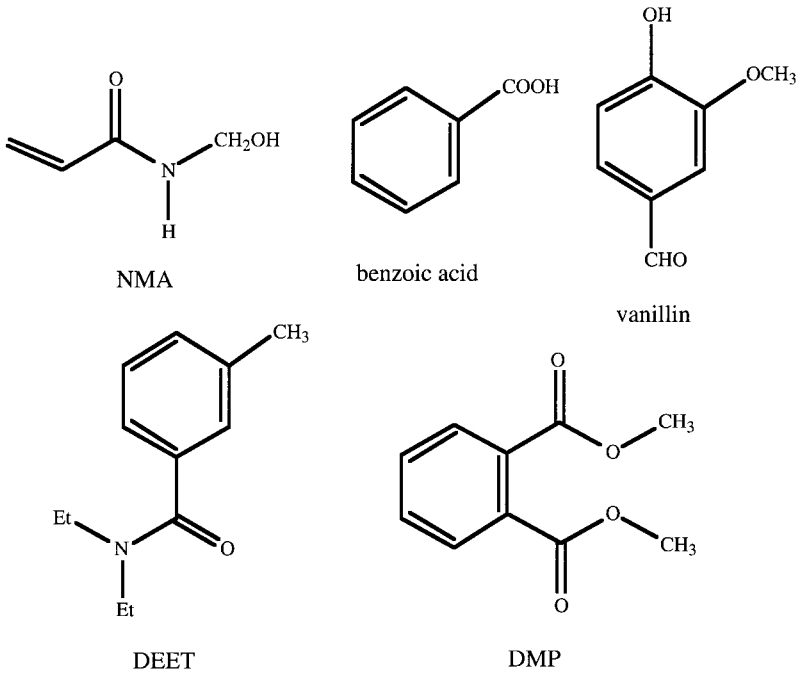

Figure 4 Probe guest molecules included in β-CD-free cavities.

received. Hydrochloric acid, formic acid, nitric acid, ceric ammonium nitrate, benzoic acid, VAN, iodine, DEET, and DMP were purchased from Fluka (Milan, Italy). *N*-Methylol-acrylamide (NMA) was obtained from Aldrich (Milan, Italy). All chemicals were used without further purification.

Synthesis of CDNMA

β-CD (25 g), 50% aqueous NMA (6.7 g), and 99% HCOOH (catalyst, 1.6 g) were added to 120 mL of water in a two-necked, round-bottom flask equipped with a thermometer and a condenser.

The reaction was carried out at 80°C for 30 min under magnetic stirring, 300 mL of acetone was added, and the mixture was stored in a refrigerator (5°C) overnight for the complete precipitation of CD-NMA. After filtration and washing with cold acetone, the product was vacuum-dried and kept in a desiccator. The final yield was 23.1 g.

Grafting of tencel with CDNMA

The permanent grafting of CDNMA onto Tencel was carried out in a two-necked, round-bottom flask equipped with a condenser and an argon inlet. Tencel fabric (0.5 g, 4 cm × 4 cm, reinforced edges) was added to 200 mL of a 0.012*M* ceric ammonium nitrate solution in 1% aqueous HNO_3, and it was left for 20 min with an argon purge and magnetic stirring. CD-NMA (10 g) was added, and the mixture was stirred under an argon atmosphere for 1 h at 40°C. The fabric was washed carefully with running water for the removal of any unreacted chemicals, neutralized with 1% aqueous sodium carbonate, washed again with running water and finally in boiling water for 30 min, and dried at 110°C for 1 h. Because the reaction in Ce(IV)/HNO_3 resulted in some loss of fibers from the external borders of the sample, the evaluation of the grafting yield through weight measurements was not possible.

Grafting of tencel with CDMCT

The permanent grafting of CDMCT was carried out by the dipping of Tencel samples (4 cm × 4 cm) for 5 min at room temperature in a water solution of CDMCT (20 g/L) and sodium carbonate (20 g/L) under magnetic stirring, and then they were carefully squeezed. To minimize the reaction of CDMCT with air moisture, the impregnated sample was treated in two different ways:

1. In an oven at 130°C for 15 min at atmospheric pressure (dry heat).
2. At 80°C for 4 h *in vacuo*.

The grafting yield was evaluated by the weighing of the samples before and after the treatment, with a weight increment of about 5%. CDMCT was easily detected on the treated fabric surfaces by UV spectroscopy.

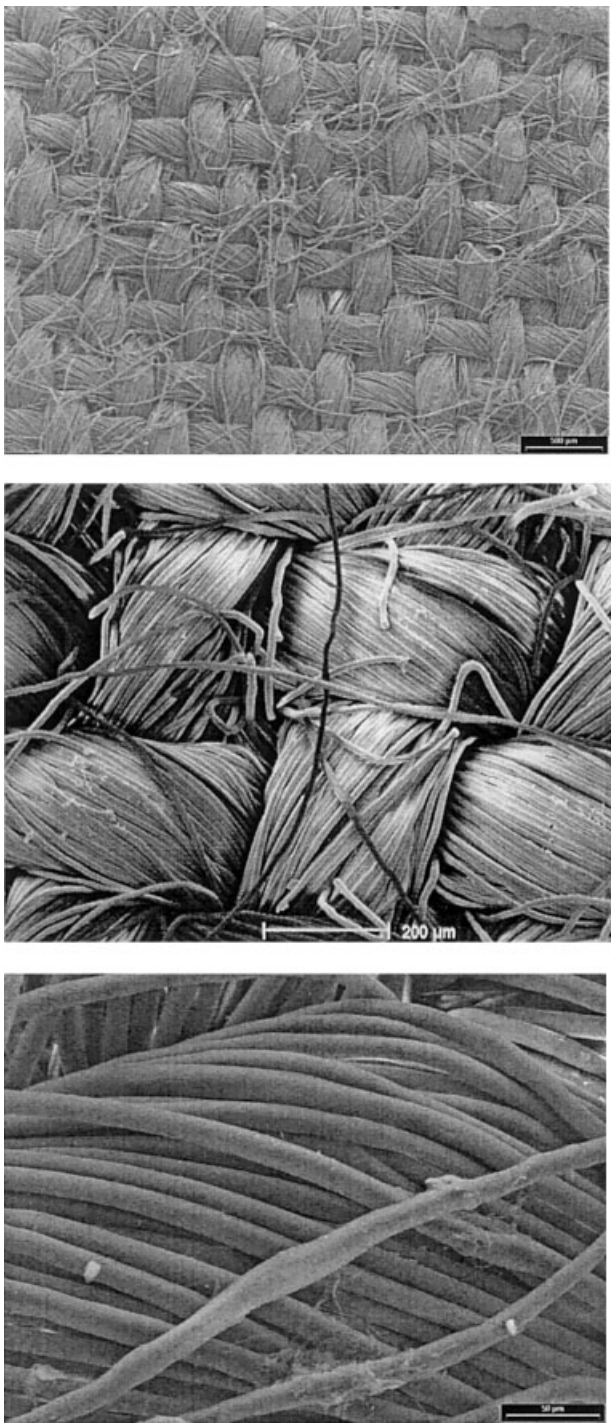

Figure 5 SEM pictures of untreated Tencel. The bars indicate the magnification.

Formation of CDNMA ICs

CDNMA and the guest chemical (benzoic acid) were mixed in a homogenizer with distilled water at room temperature for 30 min and were vigorously stirred. The IC was precipitated by the addition of acetone, filtered, washed, dried *in vacuo*, and eventually grafted onto Tencel according to the same procedure. In another case, the IC was obtained directly on the grafted textile surface: a 10% ethanol solution of VAN was added to a CDNMA-grafted Tencel sample and stirred at room temperature for 24 h. The sample was washed with hot water for the careful removal of the nonincluded chemical from the surface, and then it was dried.

Spraying

The different chemicals were dissolved in water or in a water/methanol mixture and then were sprayed on the fabric surface, dried at room temperature, washed with running and distilled water for the removal of any nonincluded product, and dried again.

Water absorbency (A_w)

A_w was evaluated according to the filtration method:[20] 0.1 g of a dry sample was immersed in distilled water or in a salt solution for 30 min at 25°C, and then water was allowed to drain for 1 h through a calibrated sieve (diameter = 100 mm, aperture = 4 mm). A_w was obtained as follows:

$$A_w = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}}$$

where m_{dry} and m_{wet} are the weights of the dry and wet samples, respectively.

Ultraviolet–visible (UV–vis)

Absorbance spectra were collected with a PerkinElmer Lambda 5 spectrophotometer for solutions of chemicals and with a PerkinElmer Lambda 35, equipped with a 60-mm integrating sphere, for fabrics.

Differential scanning calorimetry (DSC)

DSC curves were created with a PerkinElmer DSC 7 power compensation instrument equipped with PE PC Pyris 3.52 software. The measurements were performed in both isothermal and dynamic modes with a dry nitrogen flow of 16 cm^3/min. The scanning rate β was 10°C/min for each sample after isothermal conditioning at −30°C for 1 min. The calorimeter was calibrated with indium. About 10 mg of the sample

TABLE I
A_w for the Different Fabric Samples in Water and in 1 *M* aqueous NaCl at 25°C

Sample	A_w (water)	A_w (NaCl)
Tencel	1.54	1.67
Tencel + CDNMA	2.74	1.58
Tencel + CDMCT	1.91	1.87

TABLE II
Breaking Load and Elongation for the Untreated and Treated Tencel Samples

Sample	Breaking load (weft; kg)	Breaking load (warp; kg)	Elongation (weft; %)	Elongation (warp; %)
Tencel (untreated)	71	116	15	13
Tencel (treated with Ce^{IV})	62 (−13%)	115 (−1%)	20	20
Tencel + CDMCT (130°C)	50 (−29%)	89 (−23%)	18	26
Tencel + CDMCT (80°C)	43 (−39%)	73 (−37%)	14	14

was weighed in a standard aluminum sample pan and sealed.

Scanning electron microscopy (SEM)

SEM micrographs were taken with a Philips XL 20 instrument. The samples were placed on an aluminum holder and covered with either gold or graphite.

X-ray diffractometry

A Philips PW 10-5-/25 X-ray diffractometer was used, equipped with a copper cathode.

Antimicrobial and aroma activity

The antimicrobial activity was checked on *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Candida albicans* ATCC strains, according to the method reported in the literature.[30] The aroma activity was evaluated by sensory testing of different samples of fabrics.

Breaking load

The breaking load and elongation (both in the weft and warp directions) were determined with an Instron 1122 CRE dynamometer for textiles on samples 30 mm long at a speed of 50 mm/min.

RESULTS AND DISCUSSION

Figure 5 shows three SEM micrographs for a sample of untreated Tencel. The microscopic structure of the fabric can be seen at three magnifications; the diameter of a single fiber is about 10 μ.

A_w was measured for untreated Tencel and for the CDNMA- and CDMCT-grafted fabrics in water and in a 1*M* aqueous NaCl solution. The values are reported in Table I. The data show that the hydrophilicity of the fabric surface remains almost unaltered, except when Tencel is grafted with CDNMA; this results in a quite higher A_w value.

The breaking load and elongation parameters were determined in the weft and warp directions for the untreated fabric, after treatment with Ce(IV)/HNO_3, and after grafting with CDMCT (at 130 and 80°C). The values, reported in Table II, show that the treatment with Ce(IV)/HNO_3 does not significantly damage the fabric structure, whereas the chemical grafting of CDMCT leads to a breaking load loss of about 30–40% in the weft direction and of about 23–37% along the warp.

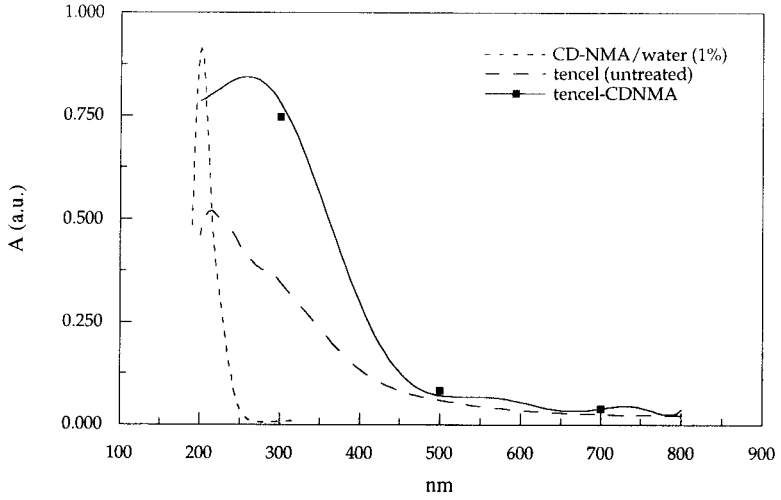

Figure 6 Absorption spectra of CDNMA in water and untreated and CDNMA-grafted Tencel.

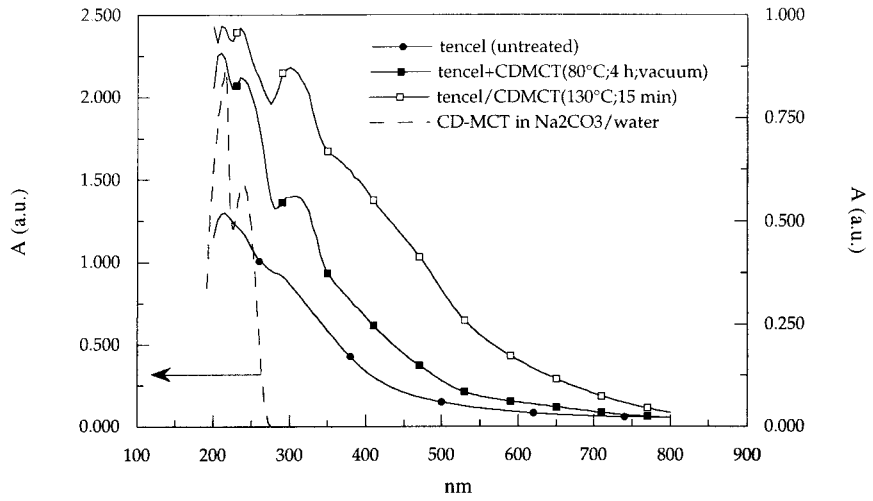

Figure 7 Absorption spectra of CDMCT in aqueous Na_2CO_3 and CDMCT-grafted fabric according to the two reported methods.

VAN was chosen as a fragrance tool molecule for the study of the aroma finishing of the treated Tencel. One fabric sample was simply immersed in an ethanol solution of VAN (0.6 g of VAN in 100 mL of 10% aqueous ethanol), and another piece of cloth was grafted with a previously prepared VAN/CDNMA IC.[16] The aroma activities were evaluated by sensory testing for 2 weeks, with the samples stored at room temperature in a closed vessel. The fragrance on the immersed sample lasted 7 days, whereas for the grafted sample, VAN aroma was still persistent 2 weeks after the treatment.

The inclusion capability of grafted Tencel fabrics was evaluated through UV–vis spectra. For each chemical, we obtained the absorption spectra on different Tencel samples: untreated, immersed or sprayed with a solution of the chemical, and grafted with CDNMA or CDMCT and sprayed with a solution of the guest molecule.

A set of five probe molecules was chosen to verify the inclusion capacity of the grafted fabrics. VAN was selected for its aroma, as a representative fragrance molecule. Benzoic acid and iodine were chosen for their relevant antimicrobial activity and because they are among the most common probes used for evaluating the hosting capability of a given acceptor. DEET and DMP are known to be powerful repellent agents for ticks and insects.

Figure 6 shows the UV–vis spectra of CDNMA in water (1%) and untreated and grafted Tencel. Grafting results in a new peak at about 260 nm, which is not seen in the untreated sample. Figure 7 shows the spectra of CDMCT in solution and grafted onto Tencel: the grafted fabrics show the typical peaks of tria-

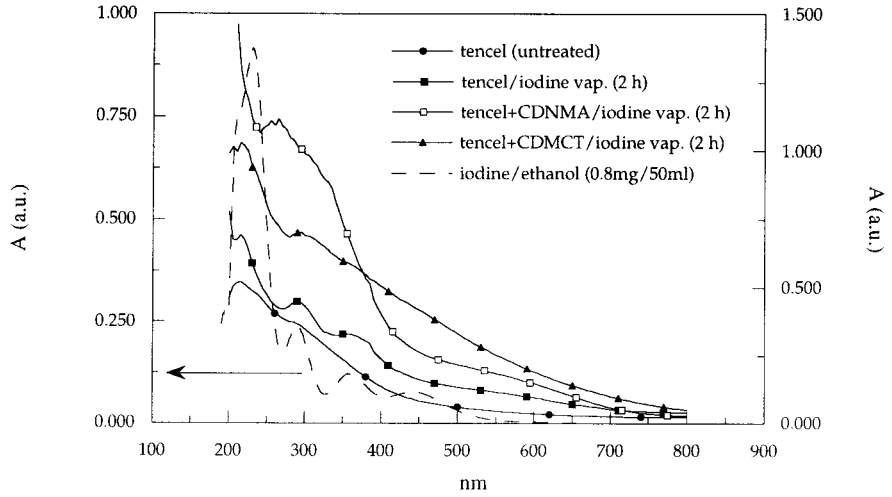

Figure 8 Absorption spectra of iodine in ethanol and untreated and grafted Tencel samples exposed to I_2 vapors (with CDNMA or CDMCT).

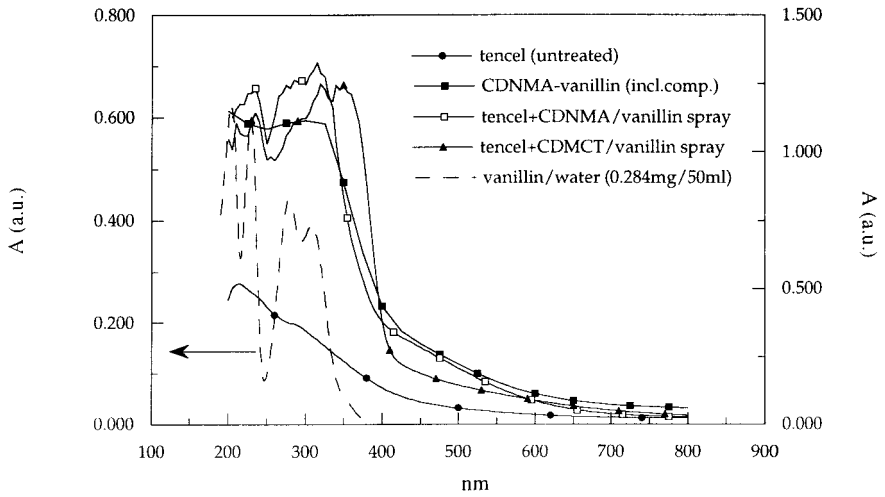

Figure 9 Absorption spectra of VAN in water, CDNMA/VAN IC, and grafted Tencel (with CDNMA or CDMCT) sprayed with aqueous solutions of VAN.

zinyl rings at about 210 and 240 nm. Figure 8 reports the spectra of I_2/ethanol, along with the data for untreated fabric and Tencel grafted with CDNMA and CDMCT, all exposed to iodine vapors for 2 h in a closed vessel. The curves show the same peaks of the alcoholic solution of iodine and indicate that iodine is better included by CDNMA than by CDMCT. Figure 9 provides the UV spectra for fabrics treated or grafted with VAN, indicating that the inclusion of VAN in the CD cavities successfully occurs on the fabric surface. Figures 10–12 provide the spectra for benzoic acid, DEET, and DMP, respectively. In all cases, the findings indicate that the guest molecule is present in the grafted fabric (with CDNMA and CDMCT) even after prolonged washing of the textile material.

In particular, for DEET, which is a well-known active ingredient in several commercial formulations for tick and insect repellents, we treated the fabric in three different ways:

1. The fabric was simply immersed in a water/alcohol solution of DEET (sample immersion in Fig. 11).
2. Tencel was first grafted with CDNMA, and then DEET was sprayed on the fabric with a water/alcohol solution (Fig. 11).
3. The DEET/CDNMA IC was first prepared by the mixing of a water solution of CDNMA and an alcohol solution of DEET under magnetic stirring at room temperature, and then the white powder that precipitated was filtered. The DEET/CDNMA system was then grafted onto Tencel according to the aforementioned procedure (Fig. 11.).

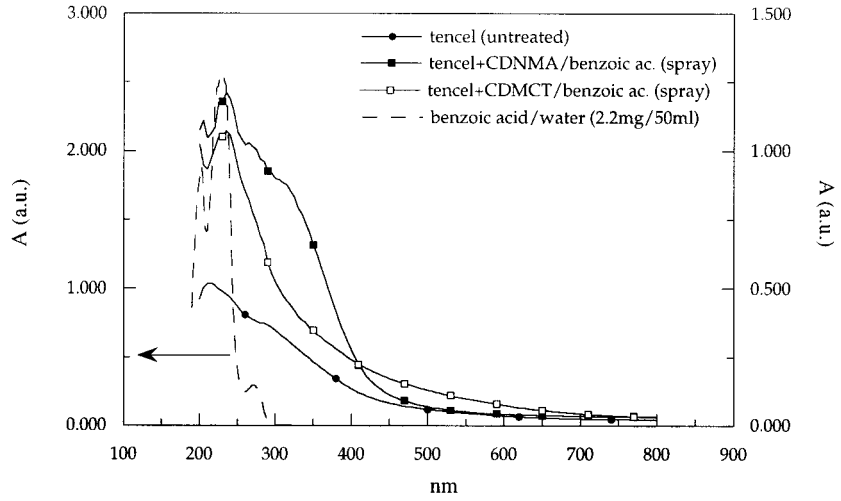

Figure 10 Absorption spectra of benzoic acid in water and grafted Tencel (with CDNMA or CDMCT) sprayed with aqueous solutions of benzoic acid.

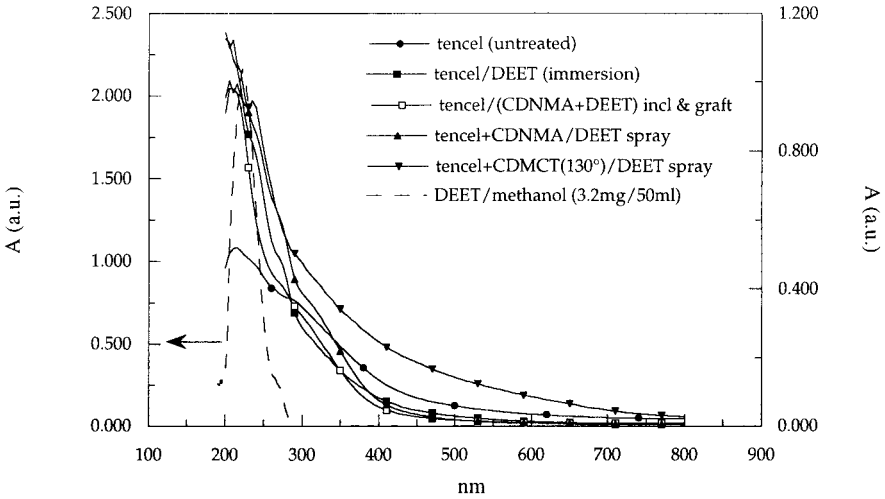

Figure 11 Absorption spectra of DEET in methanol, fabric immersed in a DEET solution, fabric grafted with CDNMA/DEET IC, and grafted Tencel (with CDNMA or CDMCT) sprayed with a solution of DEET.

According to our data, the spraying method (2) leads to a larger amount of DEET on the fabric surface than both the immersion method (1) and the grafting of the previously synthesized DEET/CDNMA compound (3). Repellency tests will be performed against different insects to assess the different capabilities of the three samples for protective clothing.

As for DSC experiments, CDNMA runs indicate the presence of endothermic and exothermic peaks, whereas Tencel shows no transition but only the loss of water vapor. Although DSC curves of pure benzoic acid, VAN, DEET, and DMP and their ICs with CDNMA or CDMCT reveal the presence of endothermal and exothermal signals, when they are grafted to the textile surface, all peaks disappear, probably because of the low amount of bound ICs with respect to the total mass of the fabric sample.

An X-ray diffractometry study was performed on untreated Tencel, Tencel heated up at 200°C in an oven (for the removal of all water), and CDNMA-grafted fabric. Diffractograms were then analyzed to obtain the crystallinity index,[31] which was defined as follows (see Fig. 13, inset):

$$\text{crystallinity index} = \frac{A + B}{A + B + C}$$

where *A* and *B* are the areas related to the crystalline part of cellulose and *C* refers to the amorphous region of the fiber. The calculation of the crystallinity indices for the three samples (see Fig. 13) provided the data given in Table III; the results indicate that this parameter does not significantly change and that CDNMA-

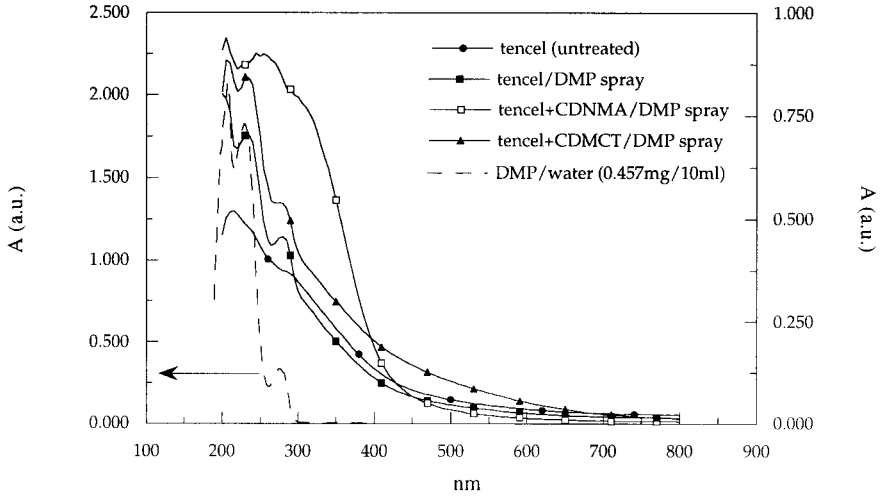

Figure 12 Absorption spectra of DMP in water, fabric sprayed with a DEET solution, and grafted Tencel (with CDNMA or CDMCT) sprayed with a solution of DMP.

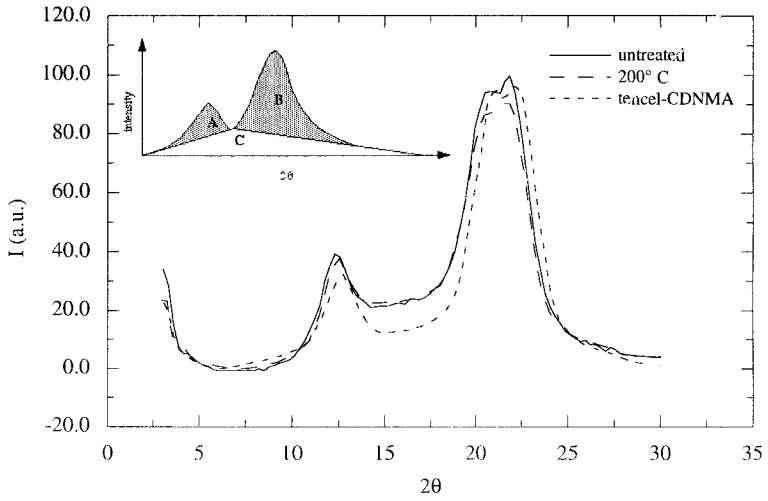

Figure 13 X-ray diffractograms for untreated Tencel, Tencel heated to 200°C, and CDNMA–Tencel. The inset shows the definition of the crystallinity index as the ratio between the areas of the crystalline phase ($A + B$) over the total area ($A + B + C$). C represents the amorphous region of the cellulosic fiber.

grafted Tencel keeps the same high order of crystallinity that is typical of this cellulosic fabric.

Benzoic acid was selected as an antimicrobial agent; its IC with CDNMA ICs was prepared as described and then grafted onto Tencel before the antimicrobial activity was tested. We chose four different strains of bacteria: *S. aureus*, *E. coli*, *P. aeruginosa*, and *C. albicans*. The first two kinds of microorganisms are of human origin (cutaneous or intestinal), *P. aeruginosa* is an environmental bacterium (air, water, plants, and land), and *C. albicans* is a yeast of human origin. All of them are pathogenic and/or opportunistic microorganisms.

Our results (see Table IV) show that for *S. aureus* and *C. albicans*, the bacterial growth is totally inhibited underneath the fabric; the effect is reduced for *E. coli*, and it is ineffective against *P. aeruginosa*.

TABLE III
Crystallinity Index of Untreated and Grafted Tencel Samples

Sample	Crystallinity index
Tencel (untreated)	70%
Tencel (200°C)	66%
Tencel + CDNMA	74.5%

TABLE IV
Antimicrobial Activity of Tencel Grafted with Benzoic Acid/CDNMA IC Against Different Bacterial Strains

Strain	Antimicrobial activity
S. aureus	++
E. coli	+
P. aeruginosa	−
C. albicans	++

CONCLUSIONS

Tencel, a versatile and resistant cellulosic fabric, was grafted with CDNMA and CDMCT so that free hosting CD cavities would be available for the direct formation of ICs with suitable hydrophobic species on the textile surface. SEM, breaking load loss, X-ray diffractometry, DSC, and water absorbency tests were performed to assess that the structure and surface properties of the fabric were not changed after the grafting process.

VAN (as a fragrance molecule), benzoic acid and iodine (as antimicrobial agents), and DEET and DMP (as insect repellents) were included in the β-CD cavities at the textile surface, as the UV–vis absorbance spectra showed. The inclusion of the probe molecules was carried out in different ways (immersion or spraying).

VAN was slowly released by the grafted fabric, as fragrance activity tests showed, whereas benzoic acid, included in a CDNMA–Tencel cloth, possessed antimicrobial activity, particularly against *S. aureus* and *C. albicans*.

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