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Modification of a Cellulosic Fabric with β-Cyclodextrin for Textile Finishing Applications

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Abstract

Grafting of cyclodextrin (CD) molecules on suitable fabrics provides hosting cavities that can include a large variety of chemicals for specific textile finishing. In this study we permanently grafted β-CD onto the surface of a cellulosic fabric, namely Tencel® according to different procedures. After the treatment, benzoic acid, vanillin, iodine, *N*,*N*-diethyl-m-toluamide, and dimethyl-phthalate were loaded, by either spraying their solutions on the CD-grafted fabric, or by grafting the previously prepared inclusion compound on Tencel®. The untreated and treated fabrics were evaluated through scanning electron microscopy, differential scanning calorimetry, UV-vis spectra, X-ray diffractometry, water absorbency, breaking load loss, aroma and antimicrobial finishing tests. Our results indicate that the included compounds are efficiently hosted in the CD cavities, and the fabric's surface properties are not significantly modified by the chemical treatments.

Introduction

The peculiar shape, and the presence of a hydrophobic cavity in cyclodextrins (CD) produce the extraordinary capability of these hosting species to include a large variety of different molecules, and form stable inclusion compounds (IC) and supramolecular adducts [1–3]. Usually these IC can be crystallized and purified, and are successfully exploited in different fields such as food manufacturing, cosmetics, pharmaceuticals, analytical and organic chemistry [4–14]. Several papers and patents report relevant applications of CD for antimicrobial, insect-free, aroma finishing, and in textile dyeing [12–15].

The grafting of CD derivatives onto cotton fibers have already been reported in the literature [12, 16] (Figure 1). Once grafted with cyclodextrins [17], these textile materials can be used for fragrance release (odoring in laundry cycles), odor adsorption (sheets and personal clothing), controlled release (antibacterial, fungicide, or insect repellent finishing), UV protection, and stabilization of active ingredients. Tencel® is a lyocell fabric, obtained from harvested trees' pulp dispersed in *N*-methyl-morpholine oxide, it looks like cotton, but it possesses a higher crystalline/amorphous cellulose ratio [18], and therefore more precious qualities.

In this paper we report our study on the chemical grafting of two β-cyclodextrin derivatives on Tencel® fabric – namely acrylamidomethylated-β-cyclodextrin (CDNMA) and monochlorotriazinyl-β-cyclodextrin (CDMCT) –, and on the inclusion of some probe chemicals (Figure 2) 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's surface.

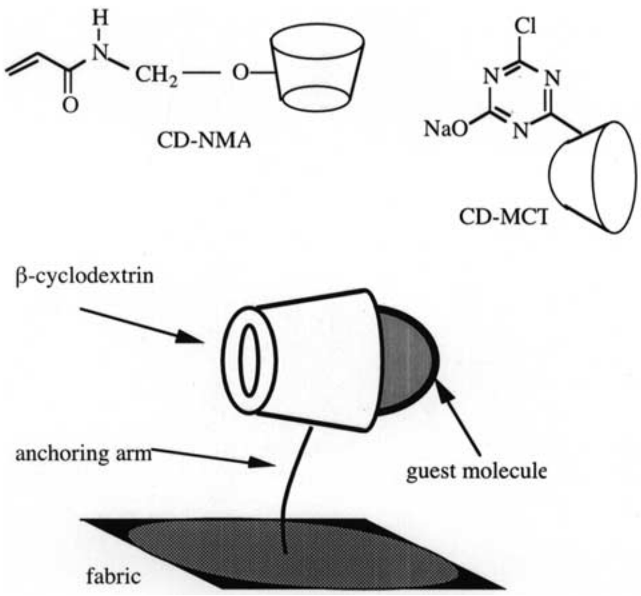

Figure 1. Structure of CDNMA, CDMCT, and schematic picture of an inclusion compound formed on the fabric's surface.

Experimental

Tencel®, provided by Tecnotessile Srl (Prato, Italy), was washed with boiling aqueous Na_2CO_3 for 3 h and then dried to ambient conditions. β-CD and Cavasol® W7 MCT (CDMCT) were obtained from Wacker-Chemie Italia SpA

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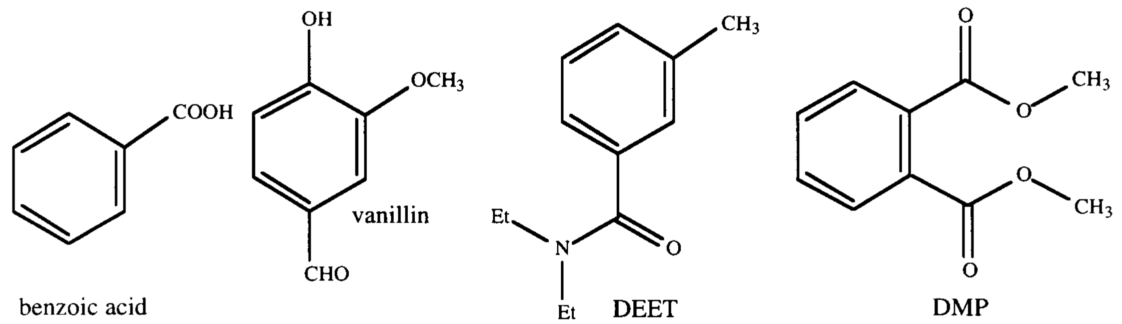

Figure 2. Chemicals used for inclusion compounds on the fabric's surface.

(Milan, Italy) and used as received. CDNMA was synthesized and grafted according to the literature [12]. Permanent grafting of CDMCT was carried out by dipping Tencel® samples for 5 min at room temperature in a water solution of CDMCT and Na_2CO_3, under magnetic stirring, and squeezed. The impregnated sample was either treated at 130 °C for 15 min (dry heat), or at 80 °C for 4 h under vacuum. The different chemicals were dissolved in water or in a water/methanol mixture, and then sprayed on the fabric's surface, dried at room temperature, washed with running and distilled water, in order to remove any non-included product, and then dried again.

Water absorbency (A_w) was evaluated according to the filtration method [19]: 0.1 g of dry sample were 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 $(m_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}}$, where m_{dry} and m_{wet} are the weights of the dry and of the wet samples, respectively. Absorbance spectra were collected with a Perkin Elmer Lambda 5 spectrophotometer for solutions, and with a Perkin Elmer Lambda 35, equipped with a 60 mm integrating sphere, for fabrics. Differential scanning calorimetry curves were carried out with a Perkin-Elmer DSC 7 (dry nitrogen flow of 16 cm^3/min, scanning rate of 10 °C/min). Scanning electron micrographs were taken with a Philips XL 20 instrument. A Philips PW 10-5-/25 X-ray diffractometer was used, equipped with a copper cathode. The antimicrobial activity of treated fabrics was checked on *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Candida albicans* ATCC strains, according to the method reported in the literature [20]. Aroma activity was evaluated by sensory test on different samples of fabrics. Breaking load and elongation (both in the weft and warp directions) were determined with a 1122 Instron CRE dynamometer for textiles on samples with a length of 30 mm at a speed of 50 mm/min.

Results and discussion

Figure 3 reports a scanning electron micrograph on a sample of untreated Tencel® and shows the microscopic structure of the fabric; the diameter of a single fiber is about 10 μm.

The water absorbency parameter, A_w, was measured for all fabric samples, in water and in 1 M NaCl, and the values are reported in Table 1. The data show that the hydrophilicity of the fabric surface remains almost unaltered, except when Tencel® is grafted with CDNMA that results in a quite higher water absorbency.

Table 1. Water absorbency parameter (A_w) for the different fabric's 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

The breaking load values, reported in Table 2, show that the treatment with Ce(IV)/HNO_3 does not significantly damage the Tencel® structure, whilst 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.

Vanillin (VAN) was chosen as a probe to study the aroma finishing of the treated fabric. One sample of fabric was simply immersed in an ethanol solution of vanillin (0.6% of vanillin in 10% aqueous ethanol), and another piece of cloth was grafted with a previously prepared VAN/CDNMA inclusion compound [13]. Aroma activities were evaluated by sensory test for two weeks, storing the samples at room temperature in a closed vessel. The fragrance in the immersed sample lasted 7 days, while in the case of the grafted sample VAN aroma was still persistent after 2 weeks from the treatment. The inclusion capability of CD-grafted Tencel® fabrics was evaluated through UV-vis spectra. For each chemical we obtained the absorption spectrum on different Tencel® samples: untreated, immersed or sprayed with a solution of the chemical, grafted with CDNMA or CDMCT and then sprayed with a solution of the guest molecule.

Figures 4a–e show the UV-vis spectra of the treated grafted fabrics. All profiles indicate that the guest molecule is present in the grafted fabric even after prolonged washing of the textile material.

Mosquitoes repellency tests are currently being performed in order to assess the different capability of the treated samples for protective clothing.

Regarding DSC experiments (not shown), the pure guest molecules (benzoic acid, vanillin, DEET, and DMP) and their IC with CDNMA or CDMCT reveal the presence of

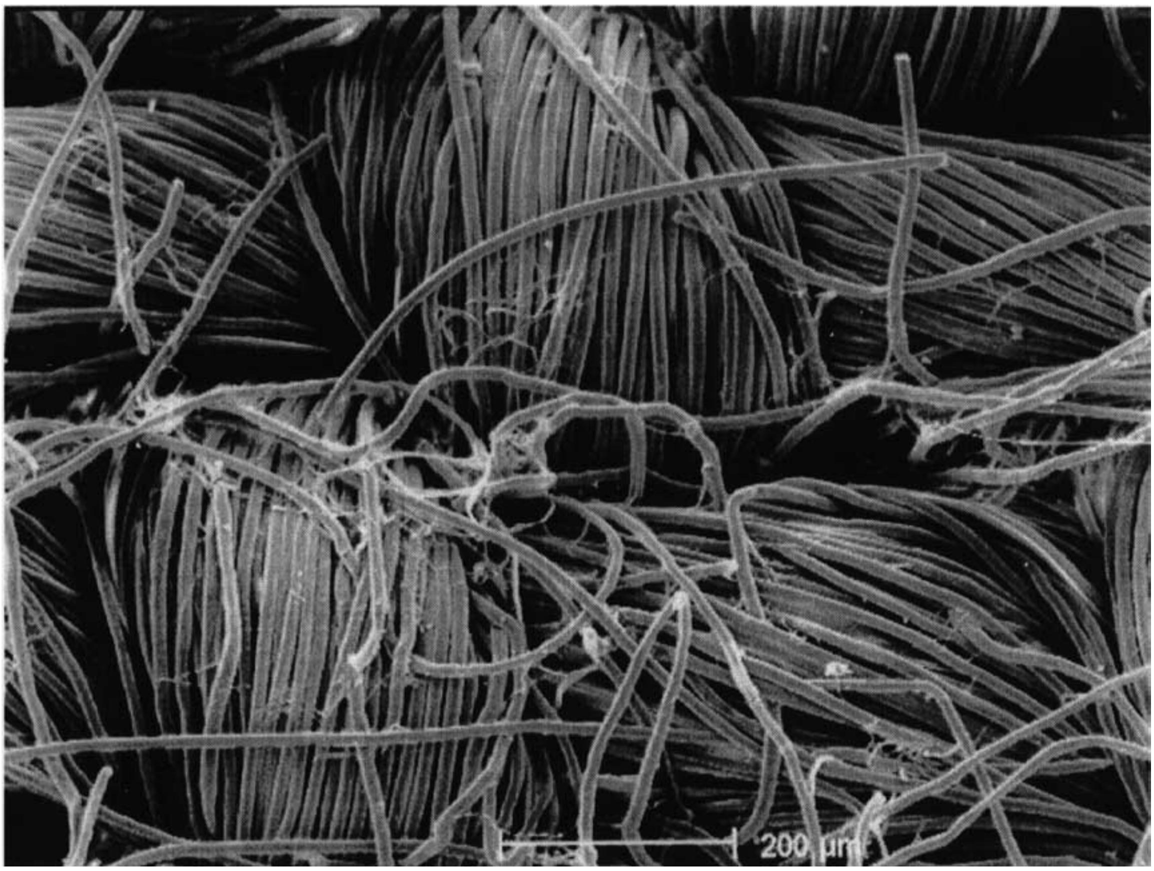

Figure 3. Scanning electron micrograph of an untreated Tencel® sample.

Table 2. Breaking load (kg) and elongation (%) for the untreated and treated Tencel® samples

Sample	Breaking load (weft)	Breaking load (warp)	Elongation (weft)	Elongation (warp)
Tencel® (untreated)	71	116	15	13
Tencel® (treated with CeIV)	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

endo- and/or exothermal signals, that disappear when they are grafted to the textile surface.

X-Ray diffractometry profiles are shown in Figure 5 for untreated Tencel®, Tencel® heated up at 200 °C in an oven (to remove all the water content), and CDNMA-grafted fabric. The crystallinity index can be calculated as $(A+B)/(A+B+C)$, according to the literature [21], 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 results (see Table 3) indicate that CDNMA-grafted Tencel® keeps the same high order of crystallinity that is typical of the untreated fabric.

Table 3. Crystallinity index of untreated and grafted Tencel® samples

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

Benzoic acid was selected as antimicrobial agent; its inclusion compound with CDNMA was prepared, and then grafted onto Tencel®, before testing the antimicrobial activity. We chose four different strains of pathogenic and/or opportunistic bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Candida albicans*. Our results (Table 4) show that in the case of *S. aureus* and *C. albicans* the bacteria growth is totally inhibited underneath the fabric.

Conclusion

Tencel®, a resistant cellulosic fabric, was grafted with acrylamidomethyl-β-cyclodextrin (CDNMA) and with

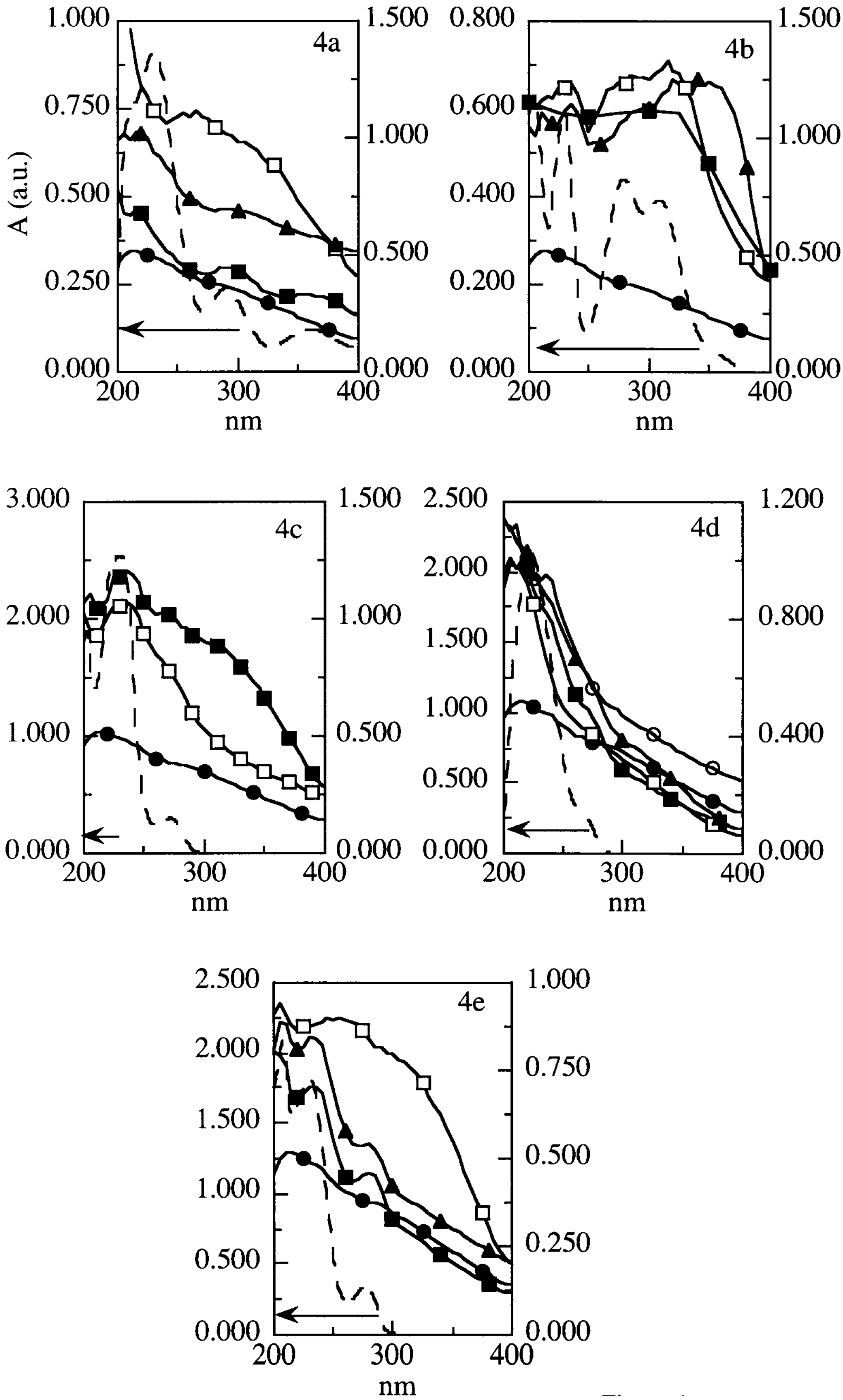

Figure 4. UV-vis spectra of the treated samples. 4a: ● untreated, ■ I_2 vapours, □ tencel + CDNMA+ I_2 vapours, ▲ tencel + CDMCT + I_2 vapours, - - - - I_2/ethanol (0.8 mg/50 mL). 4b: ● untreated, ■ CDNMA/VAN inclusion compound, □ tencel + CDNMA/VAN spray, ▲ tencel + CDMCT/VAN spray, - - - - VAN/H_2O (0.28 mg/50 mL). 4c: ● untreated, ■ tencel + CDNMA/BEN spray, □ tencel + CDMCT/BEN spray, - - - - BEN/H_2O (2.2 mg/50 mL). 4d: ● untreated, ■ tencel/DEET (immersion), □ tencel grafted with the (CDNMA/DEET inclusion compound), ▲ tencel + CDNMA/DEET spray, ○ tencel + CDMCT(130 °C)/DEET spray, - - - - DEET/CH3OH (3.2 mg/50 mL). 4e: ● untreated, ■ tencel/DMP spray, □ tencel + CDNMA/DMP spray, ▲ tencel + CDMCT/DMP spray, - - - - DMP/H_2O (0.46 mg/10 mL).

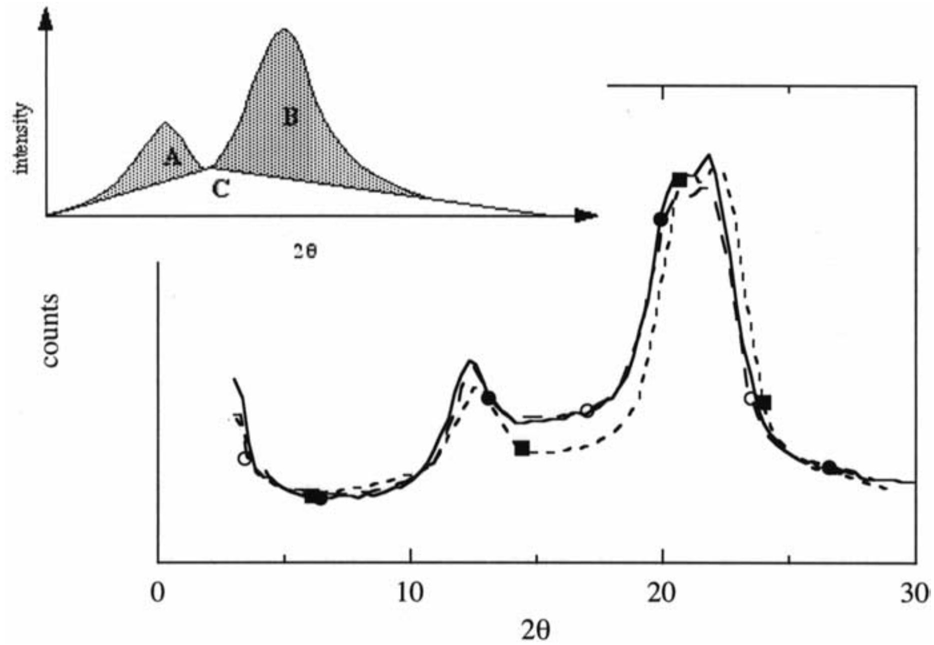

Figure 5. X-ray diffractogram of untreated (●), heated (○) and CDNMA-treated Tencel® samples (■). The areas denoted as A, B, and C are used for the calculation of the crystallinity index.

Table 4. Antimicrobial activity of Tencel® grafted with benzoic acid/CDNMA IC against different bacterial strains

Strain	Antimicrobial activity
Staphylococcus aureus	++
Escherichia coli	+
Pseudomonas aeruginosa	−
Candida albicans	++

monochlorotriazinyl-β-cyclodextrin (CDMCT), in order to obtain inclusion compounds with suitable hydrophobic species directly on the textile material. SEM, breaking load loss, X ray diffractometry, DSC, and water absorbency tests showed that no surface properties' modification occurred after the chemical treatments of the fabric.

Vanillin (as a fragrance molecule), benzoic acid and iodine (as antimicrobial agents), *N*,*N*-diethyl-m-toluamide (DEET) and dimethyl-phthalate (DMP) (as insect repellents) were included in the β-cyclodextrin's cavities at the textile's surface, as the UV-vis absorbance spectra showed. Vanillin was slowly released by the grafted fabric, as fragrance activity tests showed, while benzoic acid included in a CDNMA-Tencel® cloth possessed antimicrobial activity, particularly against *S. aureus* and *C. albicans*.

Acknowledgments

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References

1. T. Loftsson and M. Masson: *Int. J. Pharm.* **225**, 15 (2001).
2. C.R. Rusa, C. Luca, and A.E. Tonelli: *Macromolecules* **34**, 1318, (2001).
3. A. Harada: *Acc. Chem. Res.* **34**, 456 (2001).
4. P. Lo Nostro, J.R. Lopes, and C. Cardelli: *Langmuir* **17**, 4610 (2001).
5. J. Szejtli and T. Osa: *Cyclodextrins (Comprehensive Supramolecular Chemistry)*, Vol. 3, Elsevier (1996).
6. J.K. Ong V.B. Sunderland, and C. McDonald: *J. Pharm. Pharmacol.* **49**, 617 (1997).
7. T. Loftsson and M.E. Brewster: *J. Pharm. Sci.* **85**, 1017 (1996).
8. L. Huang, M. Gerber, J. Lu, and A.E. Tonelli: *Polymer Degr. Stabil.* **71**, 279 (2001).
9. A. Chisvert, M.C. Pascual-Martí, and A. Salvador: *J. Chromat. A* **921**, 207 (2001).
10. E. Junquera, J.C. Romero, and E. Aicart: *Langmuir* **17**, 1826 (2001).
11. K.A. Connors: *Chem. Rev.* **97**, 1325 (1997).
12. M.H. Lee, K.J. Yoon, and S.-W. Ko: *J. Appl. Polym. Sci.* **80**, 438 (2001).
13. M.H. Lee, K.J. Yoon, and S.-W. Ko: *J. Appl. Polym. Sci.* **78**, 1986 (2000).
14. P. Savarino, G. Viscardi, P. Quagliotto, E. Montoneri, and E. Barni: *Dyes & Pigments* **43**, 143 (1999).
15. P. Le Thuaut, B. Martel, G. Crini, U. Maschke, X. Coqueret, and M. Morcellet: *J. Appl. Polym. Sci.* **77**, 2118 (2000).
16. H. Reuscher and R. Hinsenkorn: *J. Incl. Phenom. Mol. Recogn. Chem.* **25**, 191 (1996).
17. A. Hebeish and Z.H. El-Hilw: *Coloration Technology* **117**, 104 (2001).
18. J. Crawshaw, M.E. Vickers, N.P. Briggs, R.K. Heenan, and R.E. Cameron: *Polymer* **41**, 1873 (2000).
19. H.T. Deo and V.D. Gotmare: *J. Appl. Polym. Sci.* **72**, 887 (1999).
20. P. Dolara, B. Corte, C. Ghelardini, A.M. Pugliese, E. Cerbai, S. Menichetti, and A. Lo Nostro: *Planta Medica* **66**, 356 (2000).
21. N.E. Marcovich, M.M. Reboredo, and M.I. Araguren: *Thermochimica Acta* **372**, 45 (2001).