

Corona discharge treatment route for the grafting of modified β -cyclodextrin molecules onto cellulose

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Abstract Corona discharge treatment (CDT) was implemented to attempt to graft a modified β -cyclodextrin (β -CD) onto cellulose. The occurrence of grafting was indirectly proven by gravimetric analyses, X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). Besides, the effect of CDT onto cellulosic substrate was studied using SEM and XPS. It appeared that surface roughness increased with the treatment time as a consequence of an etching effect and that surface oxidation took place as evidenced by the creation of hydroxyl and carboxyl groups. These functional groups are not responsible for chemical link between modified β -CD and substrate. It was assumed that the grafting results from the reaction of double-bonds of modified β -CD and radicals formed on treated surface, these ones being evidenced by DPPH radical trapping. Moreover the inclusion of a guest molecule is still possible in grafted modified β -CD giving a new proof of grafting.

Keywords Corona discharge treatment · Cellulose · Modified cyclodextrins · Grafting

Introduction

Cellulose is one of the most attractive biopolymer because of its excellent characteristics (hydrophilicity, low density, high crystallinity, high modulus...). Moreover, this renewable resource and its derivatives belong to the most important family of sustainable materials which is continuously gaining growing interest [1, 2]. For industrial uses, cellulose is mainly obtained from wood pulp and cotton. Cotton is a product found in different applications as clothing, furnishing, building industries, medical dressings, and composites. The cellulosic hydroxyl groups in cotton can be partially or fully reacted with various molecules (via esterification, etherification, oxidation [3–5]) to afford derivatives with useful novel properties. For other applications, cotton fibres are submitted to a specific treatment in order to increase their affinity towards reactants. However, the aqueous and/or non aqueous reactive medium sometimes may lower the degree of polymerization on which many properties of cellulose depend, especially mechanical ones.

Compared to chemical routes, polymer activation by Corona discharge treatment (CDT) proffers many advantages. This particular treatment (i) only acts on the surface of the fabric without modifying bulk properties [6], (ii) is an eco-friendly solvent free process, (iii) allows a large range of species to be grafted [7–10], (iv) can be applied as a continuous process, (v) can be performed under different atmospheres. Moreover, CDT, as well as cold atmospheric plasma, can be carried out to improve adhesion, wettability, hydrophilic properties [11–14] or to graft molecules on polymeric surfaces [15, 16].

To the best of our knowledge, literature does not report the grafting of cage molecules on cellulose by Corona activation so far. This paper reports the use of CDT to graft cyclodextrins derivatives. Cyclodextrins (CDs) are well

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known guest molecules with current applications for example in chemistry, pharmacy or food industry [17]. These molecules are simple and naturally occurring oligosaccharides with a torus-shaped structure, hydrophobic inside and hydrophilic outside [18]. As a consequence, many hydrophobic chemicals or active substances can be effectively encapsulated by CDs. Due to the chemical structure of both components, the grafting of CDs onto cellulose generally requires crosslinking agents [19]. Thus, the main objectives of this work were to achieve the grafting of an allyl-cyclodextrin onto cellulose by Corona discharge activation in order to develop new eco-friendly poly functional materials for encapsulation of small molecules (i.e. perfumes, antiseptics, drugs...).

It is noteworthy that the term “grafting” used here means a linkage between entities. We supposed but we had not the proof that this linkage is covalent insofar as the techniques we implemented have no direct access to bonding.

Experimental

Materials

Cellulose sample

In this study, a 100% white cotton fabric was used for all the experiments. It was thoroughly unsized at 90 °C and rinsed with distilled water before drying in order to remove the most finishes. Its weight according to the norm NF G07150 is 236.1 g/m² and its pattern is a 2/2 reps.

Corona discharge treatment (CDT)

The system consists of an horizontal cylindrically shaped glass reactor 10 cm in diameter and 30 cm length. Two planar rectangular electrodes (10 × 8 cm²) are disposed in the center of the reaction chamber (distance between electrodes: 5.5 mm). The Corona discharge is assured by a

low frequency high voltage generator (typically 15 kV, 50 Hz). Two glass plates (130 × 110 mm²) are used as dielectric barriers to avoid arc discharge (Fig. 1). The samples are laid between the electrodes and treated for various times (from 5 to 30 min).

Synthesis of tetradecakis-(2,6-O-allyl)- β -CD

Tetradecakis-(2,6-O-allyl)- β -CD was synthesized from stoichiometric amounts of β -CD and allyl bromide (Fig. 2) conforming to the protocol proposed by Bergeron et al. [20] and developed by Fulton and Stoddart [21]. The reaction yield was 82% after crystallization and the pale yellow crystals were characterized by ¹H NMR and FT-IR. Moreover the expected formula C₈₄H₁₂₆O₃₅ was confirmed by elemental analysis.

2,2-diphenyl-1-picrylhydrazyl radical, DPPH

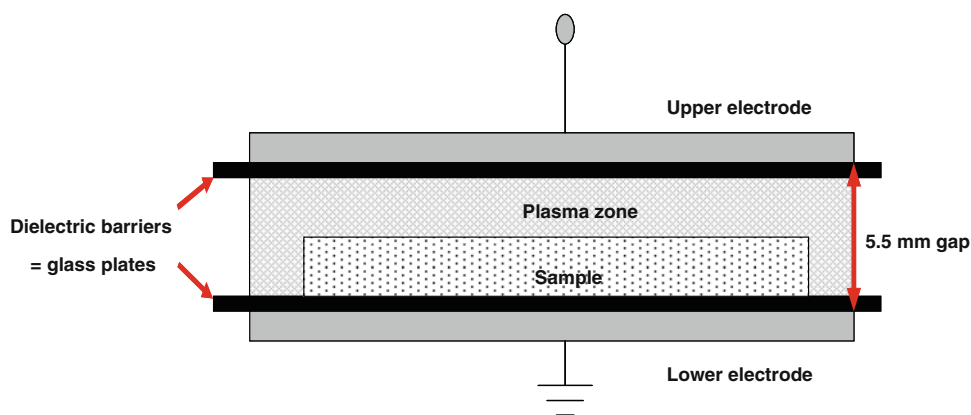
DPPH (95%) furnished by SIGMA was used without further purification to trap free radicals formed on the Corona activated surface. It presents a characteristic purple colour which fades easily in presence of antioxidants.

Methods

Surface characterization after CDT

Surface chemical modifications were characterized by X-ray photoelectron spectroscopy (XPS). The analyses were carried out with a KRATOS Axis Ultra (KRATOS Analytical, UK) spectrometer using a monochromatic AlK α source. Samples were introduced into XPS chamber which was immediately set under vacuum in three steps (10⁻⁹ Torr) overnight. For our experiments, charge neutralisation was provided by the Kratos charge neutralisation system. The resolution of spectra was 0.5 eV. The binding energy axis has been calibrated to give a BE = 83.96 eV for metallic gold Au 4f_{7/2} and a BE = 932.62 eV for

Fig. 1 Principle of Corona discharge treatment



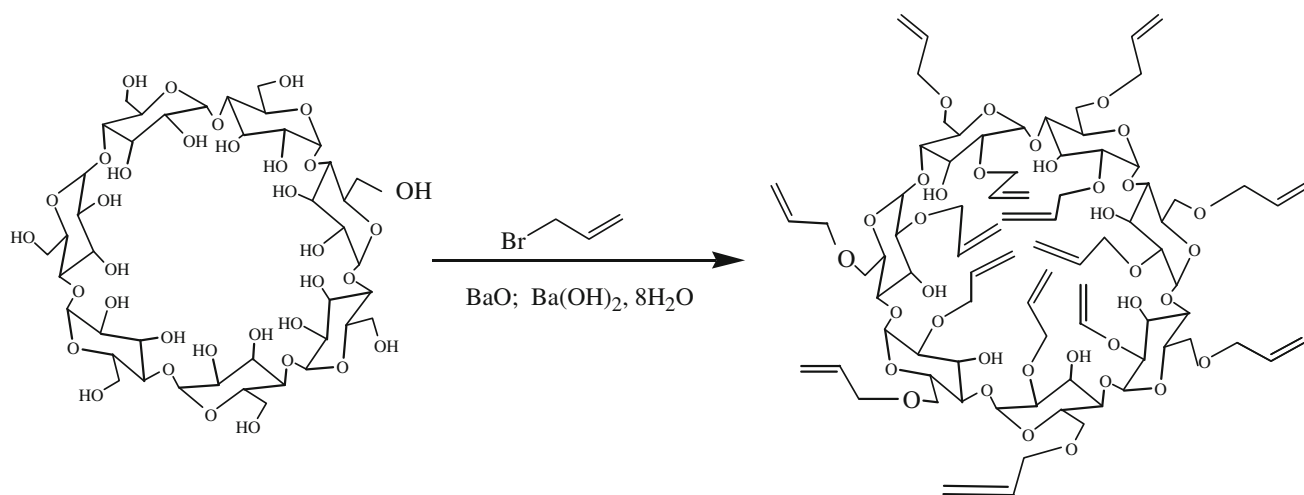


Fig. 2 Synthesis of *per*-(2,6-*O*-allyl)- β -CD

metallic copper Cu $2p_{3/2}$. The binding energy scale was then shifted to place the main hydrocarbons C1 s feature present at 284.8 eV. Spectra were analysed using the Vision software from KRATOS. A Shirley base line allows the subtraction of the background whereas Gaussian (70%) Lorentzian (30%) peaks were used for spectral decomposition. Quantification was performed using the photoemission cross sections and the transmission coefficients given in the Vision package.

Surface physical modifications were evidenced by Scanning Electron Microscopy (SEM). Observations were performed using a HITACHI S 4800 model microscope. Dry samples were coated with a thin layer of carbon before observations under the microscope mark, in order to increase the sample conductivity.

Free radicals trapping

$2 \times 2 \text{ cm}^2$ cotton samples were exposed to Corona treatment at fixed discharge 15 kV voltage and immersed immediately after treatment in a DPPH ethanolic solution ($6.10^{-5} \text{ mol.L}^{-1}$) for 8 min. The concentration of the resulting solution was determined using UV spectroscopy. The absorption spectra were recorded with a spectrometer Lambda 16 Perkin Elmer and the decrease of intensity for the absorption peak at 517 nm was measured.

Grafting protocol

Two kinds of protocols were used in order to graft the modified β -CD:

Firstly, cellulose samples (weight around 810 mg) were impregnated with 2 mL of a solution of 2,6-*per*-allyl- β -CD

in dichloromethane (25 g/L) at room temperature, dried and exposed to Corona treatment under fixed discharge 15 kV for several processing times.

Regarding the second protocol, the steps are inverted: after CDT, cotton samples were immediately immersed in 20 mL of the graft reaction medium (2.5 g/L) at room temperature for 30 min.

Whatever the protocol used, samples were extracted with a mixture of deionized water/ethanol (50:50%-vol) in a Soxhlet (five cycles) to remove any adsorbed residual modified cyclodextrin molecules and/or dust collected from environment.

Gravimetric analysis

An accurate balance Sartorius R160P F1 class 1 with a precision of 10 μg was used to weigh the samples. Before weighing, each sample was carefully washed using Soxhlet extractor in conditions detailed above and then oven dried for an hour at 100 $^{\circ}\text{C}$.

Samples were then conditioned for 24 h in a room with controlled temperature and humidity (i.e. 21 $^{\circ}\text{C}$ and 65% HR) and weighed under these conditions. The weight gain or loss of the fabrics (symbolized by %wt) was measured to evaluate the yield of the grafting reaction and determined using the following equation:

$$\% - wt = \left(\frac{m_f - m_i}{m_i} \right) \times 100 \quad (1)$$

where m_i and m_f are the sample weights before and after experiments, respectively. Most of the experiments were performed in triplicate (or more) and the accuracy of %wt values was estimated as $\pm 0.8\%$.

Other analyses

To evidence the presence of modified cyclodextrin on cotton, XPS, SEM (conditions mentioned above) were also performed.

A study of inclusion complexation was carried out by UV–Vis using the same device as previously mentioned. Control and grafted cotton samples ($2 \times 2 \text{ cm}^2$) by both protocols were immersed in an aqueous buffer solution (pH 11) of phenolphthalein ($10^{-5} \text{ mol.L}^{-1}$) for 1 h at room temperature. The absorption spectra were recorded and the decrease of intensity for the absorption peak at 557 nm was measured.

Results and discussion

Effect of treatment upon surface chemical composition

Figure 3 displays the XPS patterns of the cellulose before (A) and after 30 min treatment (B). This figure shows the presence of two main peaks common for both substrates and corresponding to carbon (C_{1s} : 284.8 eV) and oxygen (O_{1s} : 532.6 eV) atoms. The traces of K and Ba are likely associated with crystalline parts of cellulose during plant growth and cannot be removed by usual techniques. After Corona treatment, oxygen O_{1s} content increases while that of carbon C_{1s} decreases. In both spectra (pure and treated cotton), the deconvolution (Fig. 4) of the signal attributed to carbon atoms (C_{1s}) reveals four peaks corresponding to

$\text{C}-\text{C}$ and/or $\text{C}-\text{H}$ (284.8 eV), $\text{C}-\text{OH}$ (286.5 eV), $\text{O}-\text{C}-\text{O}$ and/or $\text{C}=\text{O}$ (288.0 eV) and $\text{O}-\text{C}=\text{O}$ (289.3 eV) bonds. The pure cotton XPS spectrum should normally present three peaks. In our case we observe a contamination which appears as a supplementary small peak at 289.3 eV ($\text{O}-\text{C}=\text{O}$ bonds) and contributes to an enhancement of the peak at 288.0 eV as $\text{O}-\text{C}-\text{O}$ and $\text{C}=\text{O}$ can not be separated by XPS.

In case of oxygen, three peaks were obtained and attributed to $\text{O}-\text{C}-\text{O}$ (533 eV), $\text{O}-\text{H}$ or $\text{O}-\text{C}$ (532.5 eV) and $\text{O}=\text{C}$ (531.5 eV) as displayed on Fig. 4.

All the characteristic values of these analyses are summarized in Table 1. The theoretical surface O/C ratio in pure cellulose is 0.83. For raw cellulose, this ratio was found to be slightly lower (0.80) but in close agreement with the theoretical value. When comparing untreated and treated cellulose samples, we observed significant changes of carbon bonds distribution and a rising O/C ratio (Table 1). A large increase from about 41 to 64% of $\text{C}-\text{OH}$ bond is observed between raw and 30 min treated cellulose. In parallel, $\text{C}-\text{C}$ or $\text{C}-\text{H}$ peaks contribution decreases from nearly 45 to 11%. The interpretation of the variations of $\text{C}=\text{O}/\text{O}-\text{C}-\text{O}$ and $\text{O}-\text{C}=\text{O}$ contributions is rather questionable given the presence of contaminant species evidenced in raw cotton spectrum. Nevertheless, we can assume the formation of oxygen-containing functional groups such as esters, carboxyl and carbonyl, by reaction of carbon present in cellulose surface and oxygen atmosphere as reported by Belgacem et al. [22]. These results were confirmed by contact angle measurements (not reported

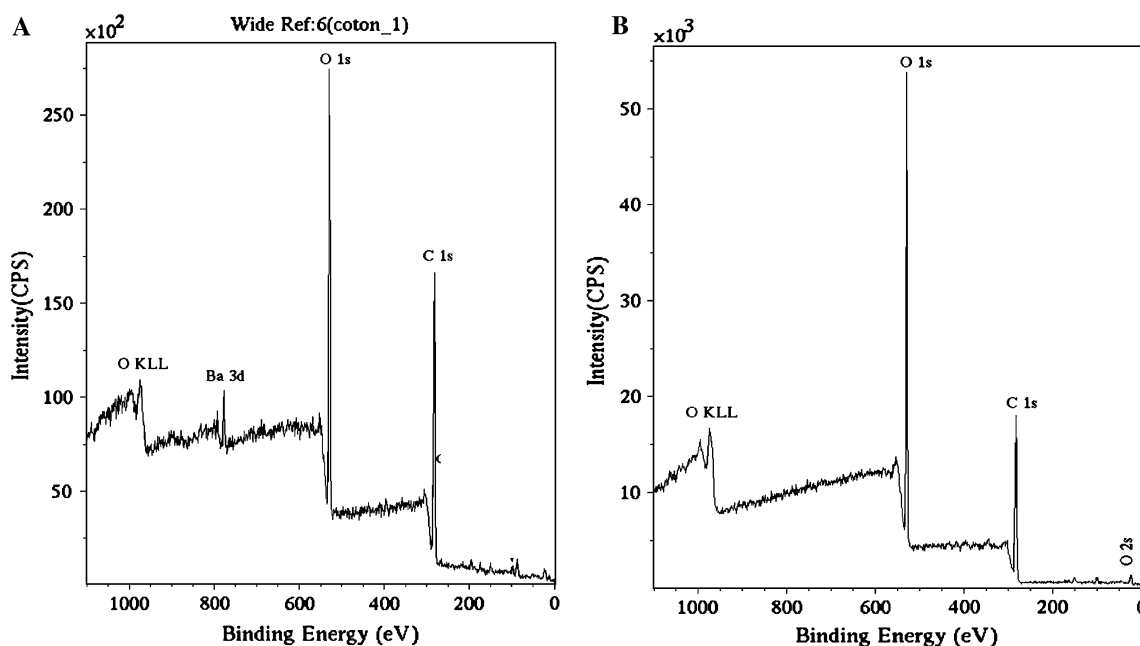


Fig. 3 Wide spectra of cotton substrate **a** untreated and **b** after 30 min treatment

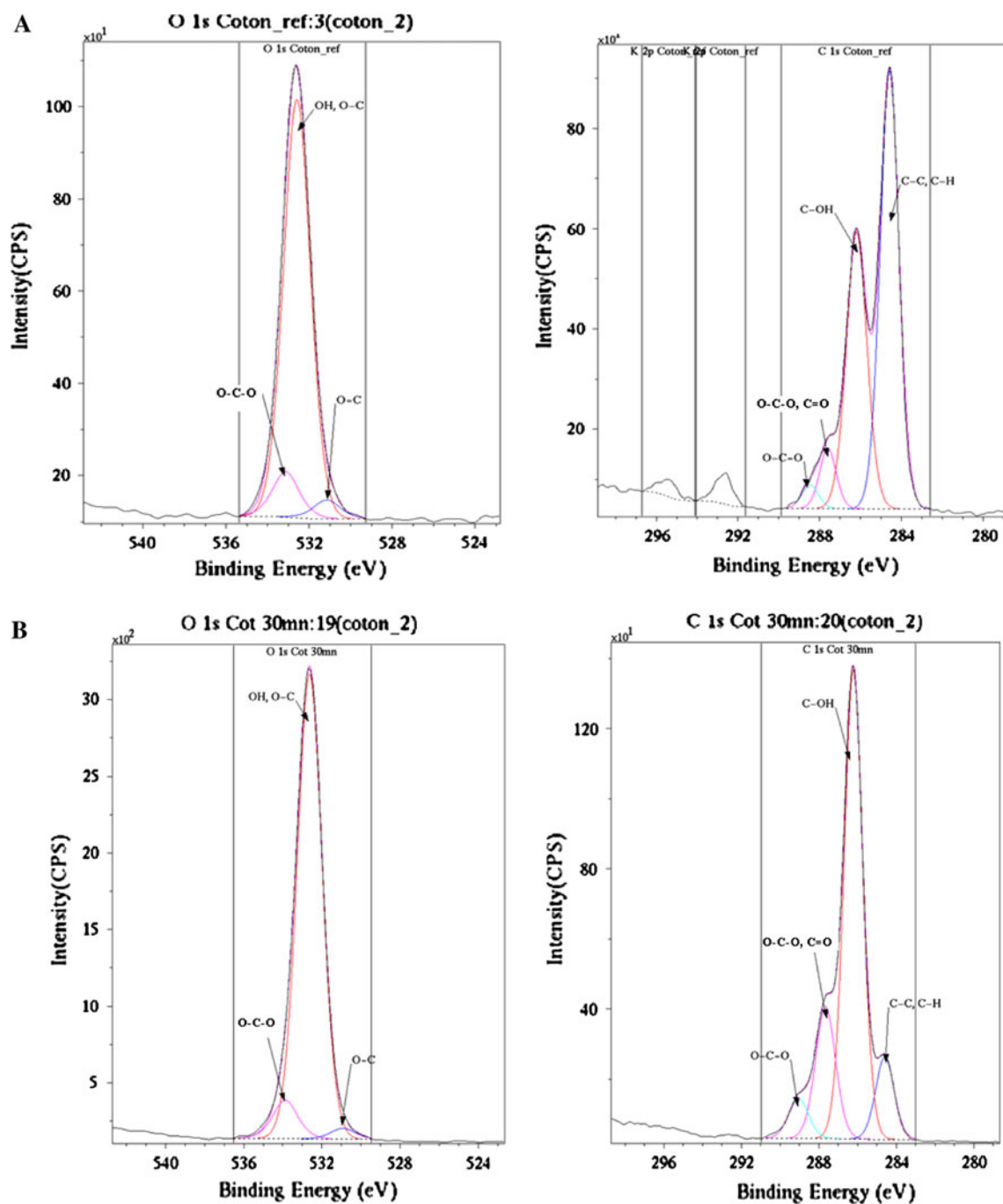


Fig. 4 Oxygen O1 s and carbon C1 s peaks of cotton fibres **a** untreated and **b** after 30 min treatment

Table 1 Contribution of chemical bonds (%) for untreated and treated cotton sample

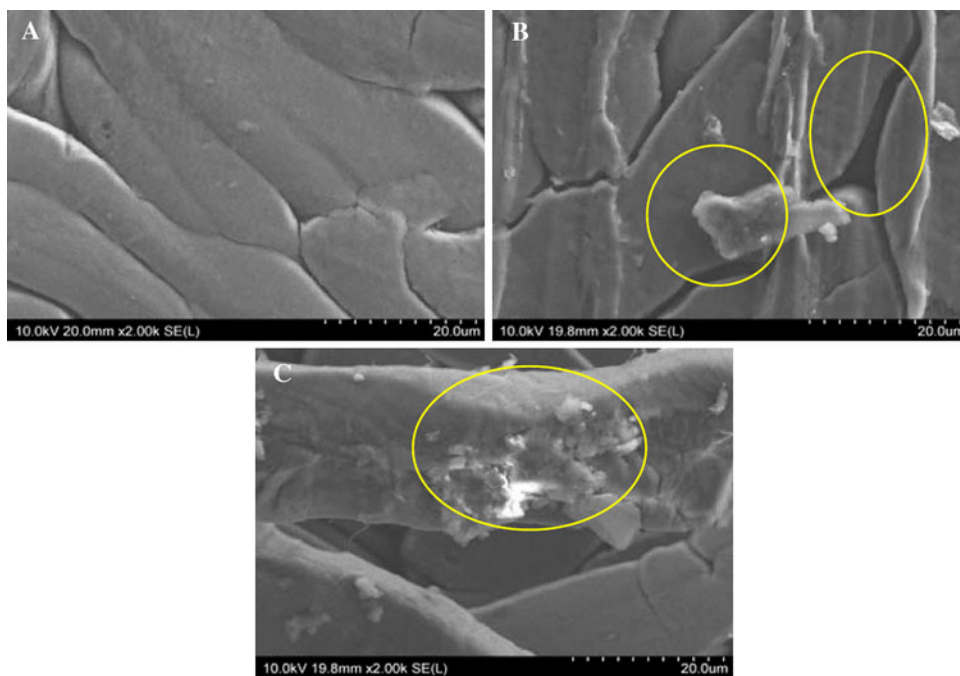
	Raw cellulose	Treated 15 min	Treated 30 min
O/C ratio	0.80	1.39	1.38
C–C or C–H	44.91	9.12	11.17
C–OH	40.74	64.77	63.61
O–C–O or C=O	12.01	19.77	19.37
O=C=O	2.34	6.34	5.85

here) that showed an increase of the wettability versus treatment time.

Surface physical modification after treatment

SEM images of Corona treated and untreated cotton fibers are shown in Fig. 5. Surface appears smoother for the untreated sample. As the treatment time increases, holes appeared in the cellulose surface. According to Zhang et al.

Fig. 5 SEM micrographs of cotton samples **a** untreated, **b** after 15 min treatment, **c** 30 min treatment



[23], this result can be attributed to ablation effect caused by the bombardment of the polymer surface by the oxygen-containing plasma species. Corona discharge treatment is thought to activate the molecules at the surface: it can be assumed that CDT produces many activated sites along polymeric chains, able to react with oxygen to give etching. The size and number of micro-pits increased with treatment time. Thus, the roughness tends to increase whereas the raw fibre surface remains smooth. This phenomenon has already been reported by Zheng et al. [24] on polymeric materials.

Evidence of the formation of free radicals

The absorption spectra of DPPH solutions in contact with Corona treated cotton were collected. It appears that the absorbance at 517 nm hence the concentration of DPPH decreases as the treatment time increases. From an original concentration (6.10^{-5} mol/L) of the ethanolic solution of DPPH and by subtraction, the concentration of free radicals formed at different CDT times was evaluated. These results are summarized in Fig. 6. These experiments highlight on one hand that radical species are generated at the sample surface and that, on the other hand, their concentration increases with treatment duration as previously mentioned in the case of polyolefin substrates [23].

According to Ward et al. [25], and as shown in Fig. 7, cellulose radicals generated by plasma treatment can be a result of one of the following mechanisms: (i) bond breakage between C_1 and ring oxygen, (ii) bond breakage between C_1 and glycosidic bond oxygen.

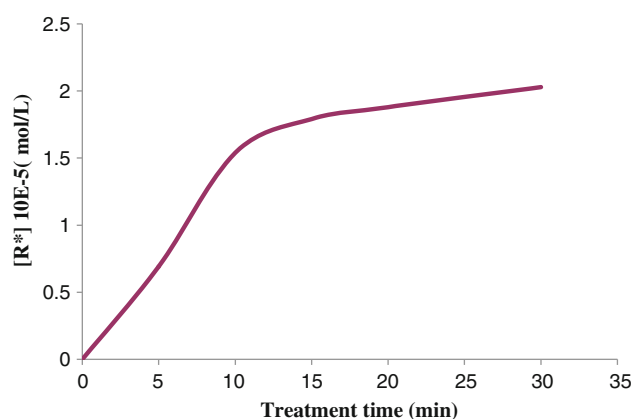


Fig. 6 Concentration of free radicals trapped versus treatment time (samples weight = 94.4 mg)

Grafting evidence

The grafting of chemical species on cellulose has already been evidenced by analytical techniques such as elemental microanalysis or XPS [26]. In our case, gravimetry, SEM and XPS analyses were implemented in order to prove the effectiveness of grafting. But presently, we can not assert that a covalent bond has really formed between CD and cotton.

Gravimetric analysis

The weight gains or losses of our samples after different treatments are given in Table 2. The Corona treatment induces a weight loss of 4.56 mg (i.e. 0.56%). This result is

Fig. 7 Free radicals formed by bond cleavage between **a** C1 and ring oxygen or **b** C1 and glycosidic oxygen bond (according to Ward et al. [22])

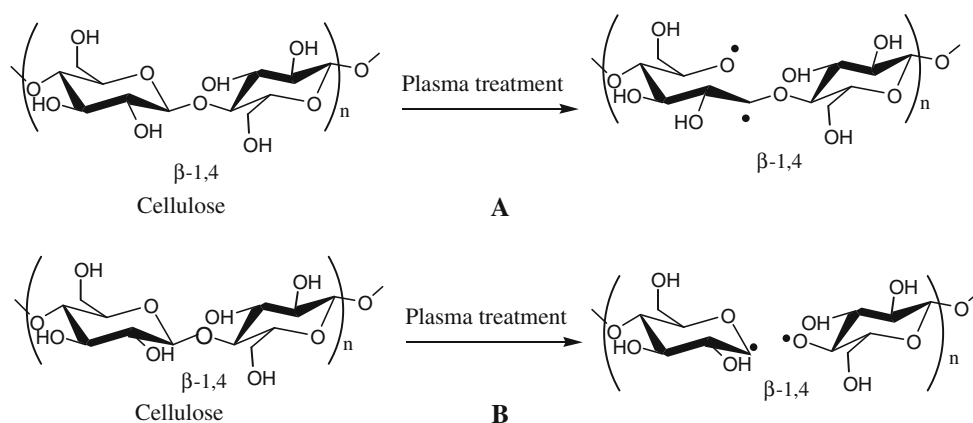


Table 2 Weight variations of cotton samples measured for different conditions (initial mass of samples \cong 810 mg, each sample washed and dried before measurement)

Cotton sample after	Δm (mg)
CDT (30 min)	-4.56
Immersion in CD	+0.02
First grafting protocol	+49.26
Second grafting protocol	+48.28

not surprising and is in fair agreement with those of Gassan et Gutowski [27] who observed that under high level treatment conditions (long time and high current), mechanical properties of fibers are lowered because the removal of low molecular weight species. Whatever the grafting protocol used (immersion/treatment or treatment/immersion), we observed a significant weight gain (around 6%) which can only be interpreted in terms of grafting since, in absence of Corona treatment, the Δm tends to zero and belongs to the experimental error domain.

The results of grafted mass of tetradecakis-(2,6-*O*-allyl)- β -CD on cotton (first protocol) as a function of Corona treatment time are reported in Fig. 8.

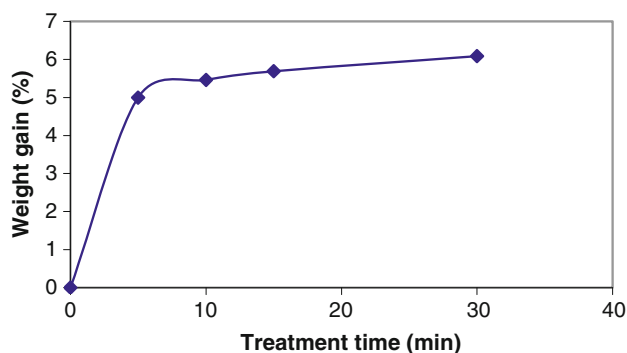
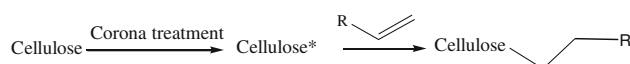


Fig. 8 Weight gain for cotton fabrics in the case of first protocol (immersion in solution of modified CD and treatment under Corona discharge for different times)

It appears that the amount of cyclodextrin grafted on cellulose increases with Corona treatment time to reach a constant value. As the samples underwent a Soxhlet extraction with deionized water/ethanol (50:50%-vol) before being dried and weighed, we can assume that covalent bonds were formed between treated cellulosic substrate and the modified cyclodextrin. To explain the reasons of this strong chemical effect, a new experiment was carried out. Three samples of cotton were Corona-treated for 30 min under atmosphere and 15 kV and then left at ambient atmosphere during 24 h. The first one was then analyzed by XPS and gave evidence of the surface oxidation. The second one was immersed in a 6.10^{-5} mol/L DPPH alcoholic solution but no variation in concentration was observed indicating that radical species were no more present at the surface. The third sample was impregnated with a solution of allyl-cyclodextrin but no mass gain occurred. Indeed, we obtained a mass variation of 4.47 mg in agreement with previously discussed results. Thus, we concluded that the creation of oxidized functions at the surface was not responsible of the linking. Actually, it can be assumed that the free radicals generated by CDT onto the cotton surface likely react with the unsaturated groups of the tetradecakis-(2,6-*O*-allyl)- β -CD. In the case of second protocol i.e. CDT/immersion, our results lead us to propose a hypothetical mechanism (even if some other mechanisms could be considered given the potential radicals resulting from treatment) for surface activation and grafting process via double bonds as displayed in Scheme 1.

In the case of first protocol (immersion/CDT), a high number of different pathways could be proposed because some fragments of CD molecule formed after treatment could also interfere with denaturated cellulose.



Scheme 1 Hypothetical mechanism for surface activation and grafting process

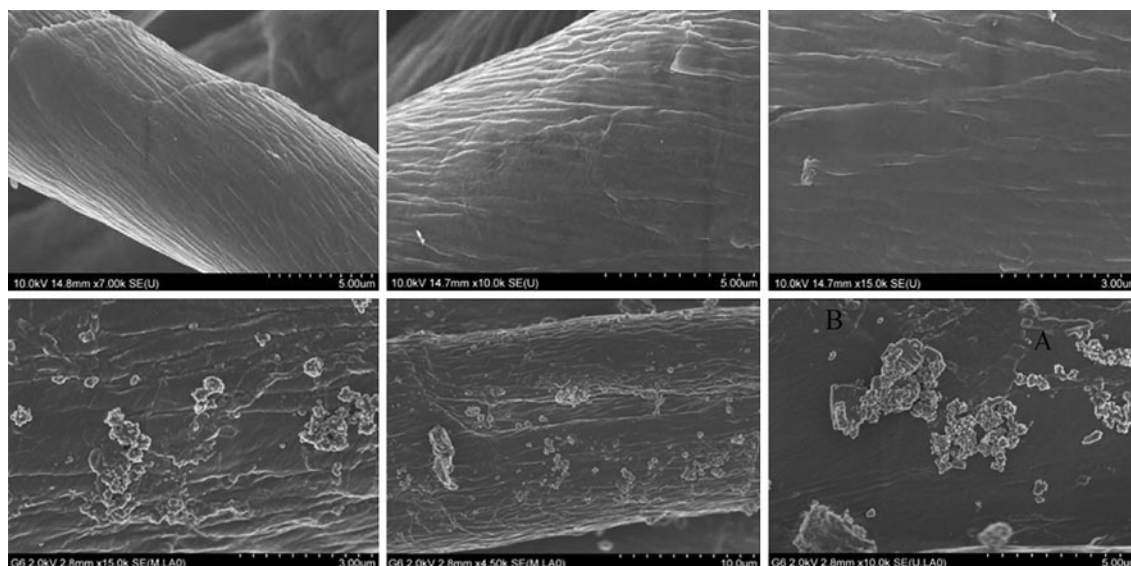


Fig. 9 SEM of cotton before and after grafting tetradecakis-(2, 6-*O*-allyl)- β -CD using CDT

Scanning electron microscopy observation

SEM was used to observe the fibre surface after grafting. The micrographs obtained are shown in Fig. 9 and confirm that tetradecakis-(2,6-*O*-allyl)- β -CD was successfully grafted on cellulose fibres. Indeed, the visible particles can not be assimilated to dust since samples were washed in a Soxhlet before analysis. It appears that the modified β -cyclodextrin is not regularly dispersed on the surface. These findings are in good agreement with previous microscopic observations insofar as the CDT creates preferential activated sites on macromolecules. Moreover, it seems that particles tend to form aggregates resulting from a possible self-polymerization of modified CD induced by CDT.

XPS analysis

XPS experiments were carried out to characterize surface samples after grafting protocols. The results—compared with those of cotton *before* and *after* treatment—are summarized in Table 3 and presented in Fig. 10.

After both protocols (immersion/CDT or CDT/immersion), different observations can be made. On one hand, the

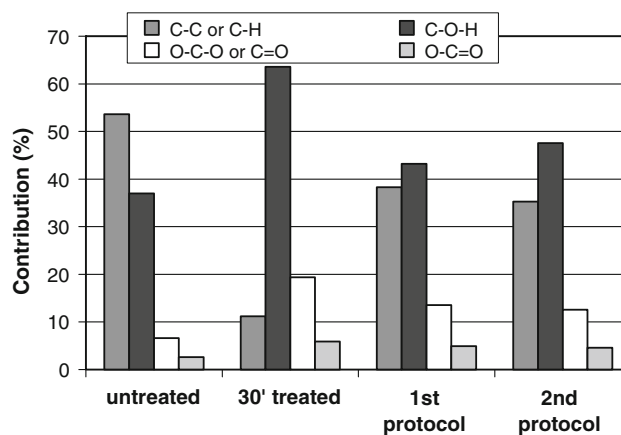


Fig. 10 Confirmation of grafting by XPS analysis from the decomposition of C1 s peak. The contribution of different bonds is reported as a function of applied conditions

amount of C–C and/or C–H bonds increases compared to that obtained with CDT sample. This tends to prove grafting since the supposed grafted molecules have the same chemical structure as that of the substrate and the spacer (allyl moieties is 100% C1-type molecule), the contribution C–C and/or C–H is expected to increase. On the other hand, the proportion of C–OH decreases. In the

Table 3 Contribution of chemical bonds (%) for cotton samples in different conditions

Cotton	Untreated	30 min treated	After first protocol	After second protocol
\underline{C}_{1s}	44.91	11.17	38.32	35.26
$\underline{C-C}$ and/or $\underline{C-H}$ $\underline{C-O-H}$	40.74	63.61	43.23	47.57
$\underline{O-C-O}$ or $\underline{C=O}$	12.01	19.37	13.55	12.58
$\underline{O-C=O}$	2.34	5.85	4.90	4.59

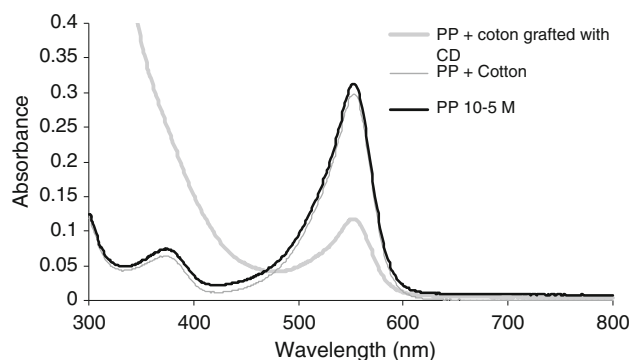


Fig. 11 UV-Vis spectra of phenolphthalein (PP) buffer solution in contact or not with control and grafted cotton after 1 h immersion

modified CD, 14 hydroxyl groups are substituted by allyl moiety (see Fig. 2) and consequently this molecule possesses less C–OH bonds than the treated substrate.

Inclusion potential of grafted cotton

Some experiments were carried out to check the potential of the modified cyclodextrin to include guest molecule after grafting on cotton according to both protocols. The Fig. 11 shows the absorbance of a solution of phenolphthalein (initial concentration 10^{-5} mol.L $^{-1}$) in contact with untreated cotton and grafted one. Spectra exhibit a peak with maximum absorption wavelength at 557 nm. In the case of grafted cotton sample, the absorbance is significantly decreased about three times indicating that phenolphthalein still form a great quantity of inclusion complex with grafted cyclodextrin. The most important findings of this experiment are that (i) host molecule was not damaged (or only partially) during the grafting process which was not obvious given the conditions of the second protocol (impregnation followed by corona treatment) and (ii) the anchored cyclodextrin still possesses complexation properties.

Gravimetry, SEM and XPS gave evidence that grafting was achieved without direct proof of covalent bonding. Moreover, it was checked that modified molecule was not totally degraded during the grafting process given the severe experimental conditions since inclusion of a guest molecule as phenolphthalein is still possible. Besides this last experiment constitutes an independent result of grafting.

Conclusion

This paper clearly shows that Corona discharge treatment can be used to achieve grafting of an allyl-ether modified β -cyclodextrin on cellulose fibres at room temperature. It

constitutes an interesting and promising route to functionalize biopolymers materials. As a matter of fact, Corona discharge treatment presents many advantages and is particularly a solvent-free thus eco-friendly technique. Moreover, it can be applied as a continuous process, which is the common route in textile or paper finishing.

XPS shows that Corona discharge significantly changed the chemical composition of the cellulose surface by increasing the O/C ratio and creating carbonyl and carboxyl functions. The study on treated surface with the radical quencher DPPH showed that the Corona treatment of cotton samples generates some free radicals that were evidenced to be responsible of the present grafting.

Work is in progress to determine the nature of the linkage between CD and cotton and to check the possible inclusion of active entities such as flavors or antibacterial substances in such modified cyclodextrins after grafting.

It would also be interesting to study the kinetics of inclusion and release of these guest molecules in various conditions.

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