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Biotreatment on Cellulose Fluff Pulp: Quaternary Ammonium Salts Finish and Grafting with β-cyclodextrin

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Abstract For its potential performances to be expanded, cellulose needs to be processed in different ways. Therefore, an object of the present work was to provide a chemical modification of cellulose through: a specific finish with two quaternary ammonium salts (namely Aliquat 336 and Aliquat 1529, respectively). Chemical grafting of β-cyclodextrin derivative (β-CD) onto fibers followed by the inclusion of benzoic acid in the grafted CD cavities as a probe chemical. Physicochemical properties and performances of the untreated and treated fibers have been determined with infrared spectra, microscopy, swelling measurements, antimicrobial finishing tests, and dye adsorption. Our results show that cellulose fibers can be efficiently modified with no significant changes in its structural and surface properties; the treated fibers show an attractive behavior in swelling, dye adsorption and antibacterial activity.

Keywords Cellulose fluff pulp · Quaternary ammonium salts · Grafting · β-cyclodextrin · Fiber swelling · Antimicrobial activity · Dye adsorption

Introduction

Nowadays, applications of fibrous polymers as raw materials in non-traditional sectors have a strong dynamics of growth. Among these new opportunities, the practical application in

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the biomedical fields or in membranes has benefited from contribution of cellulose fibrous materials noticed under generic term of "biotextiles". By offering a large specific area associated with an infinite possibility of forming, cellulose takes a place of great exchange. Several ways are possible to give an additional function to cellulose: new fibers, modification of the fibrous structure, physical, or chemical treatment with specific finish. These new functionalities can give either a risks protection ("anti" function), or a positive effects contribution ("pro" function) [1]. Hence, by the functions contribution, the formerly passive cellulose becomes active.

Textile goods, especially those made from natural fibers can provide an excellent environment for microorganisms to grow and thereby reducing its exhaustion property, because of their large surface area and ability to retain moisture. Consequently, to impart a high antimicrobial activity to fibers, its chemical modification has been found to be a highly effective method. Much attention has been given in the last two decades to develop fibers with strong antimicrobial activity; a number of chemicals might be employed to impart antimicrobial activity to fibrous polymers [2–4]. The quaternary ammonium salts has been proved to be an excellent antimicrobial agent for cotton [5], the major problem encountered with the cotton cellulose is its lack of attractive sites, i.e., anionic sites for cationic compound like quaternary ammonium salts. Among the various techniques of chemical modification, grafting is the suitable way to functionalize cellulose. Grafting onto cellulose is possible by the growing of a polymer chain on the actives sites of the cellulose backbone. It is a heterogeneous reaction in which the physical structure and state of aggregation of the cellulose plays an important role [6].

Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as hydrophilic character, improved water absorption, dye absorption, and ion-exchange capability [7–9]. The powerful capability of cyclodextrin to include hydrophobic molecules can be used in textile finishing as well. Several articles report relevant applications of cyclodextrin for antimicrobial finishing and in textile dyeing through the formation of physical bonds to different fibers [10, 11]. The toroidal shape and the presence of internal hydrophobic hollow cavities in cyclodextrins produce the capability of these hosting species to include a wide variety of different molecules and to form stable inclusion compounds [12].

The aim of this work is to increase the importance of the chemical modification of cellulose supports in order to get a material with improved absorbency and antibacterial activity. A first attempt has been made through a chemical treatment by a specific finish using Aliquat 1529 and Aliquat 336 quaternary ammonium salts. Afterward, acrylamidomethylated β-cyclodextrin was followed by the inclusion of benzoic acid in the free cavities of cyclodextrin, as a probe chemical for antimicrobial activity.

Fibrous cellulose, thus functionalized, was characterized in microscopy and infrared analysis (FTIR); the treated cellulose showed interesting behavior in swelling and antibacterial activity. The ability of cyclodextrin to include a wide variety of chemicals was also exploited for the dye adsorption to show the potentialities of the grafted cellulose in the textile liquid waste processing. Adsorption of reactive dye on grafted fibers was consequently studied.

Our results indicate that cellulose fluff pulp can be efficiently modified, with no significant changes in its structural and surface properties, and that the probe molecule (including compound) remain on the fiber surface.

Materials and Methods

Chemicals and Materials

- *N*-methylol acrylamide (Aldrich) was distilled at 60 °C under reduced pressure.
- β-cyclodextrin hydrated, $C_{42}H_{72}O_{36}$ H_2O (Aldrich), benzoic acid (Panreac), formic acid, nitric acid, sodium hydroxide, acetone (all Merck) and ceric ammonium nitrate (Aldrich) were reagent grade and used as received.
- Deionized water and physiological saline solution (0.9% NaCl) were used for swelling measurements. Physiological solution is usually used to characterize the absorption of hygienic products [13].
- Surfactants for impregnation are quaternary ammonium salts provided by Aldrich and were used as received.

First was hexadecyltrimethylammonium chloride; Aliquat 1529, with a formula of $(CH_3(CH_2)_{15}N(CH_3)_3Cl)$, and molecular mass: 320 g/mole (Fig. 1).

Followed by 1-octanaminium, *N*-methyl, *N*, *N*-dioctyl chloride; Aliquat 336, with a formula of $C_{25}H_{54}NCl$, and molecular mass: 404.17 g/mole (Fig. 2).

- Reactive dyes are used to dye cotton and cellulosic fibers. The dyes contain a reactive group, either a haloheterocycle or an activated double bond, that, when applied to a fiber in an alkaline dye bath, forms a chemical bond with an hydroxyl group on the cellulosic fiber. In this study the dye used for adsorption measurements was a commercial reactive dye based on vinyl sulfone functional group, kindly provided by Bezema CHT (Switzerland).
- The fibrous cellulosic support used was a treated Kraft pulp, based on a mixture of maritime pine and sawmill waste (Biofluff TD), kindly provided by Tartas S.A., a French company.

Physical form: white short fibers, population, 4.10^6 fibers/g; fibers length, 2.2 mm; linear mass, 30 mg/100 m; moisture content, 7%; α-cellulose content, >85%. Product density (cellulose), 1.50 g/cm^3.

- Bacterial cultures of *Bacillus subtilis* (Gram$^+$), *Escherichia coli*, and *Pseudomonas aeruginosa* (Gram$^-$) were from Algerian Pasteur Institute culture collection.

Finish Procedure

Pretreatment operation in cellulose finishing is mercerization were the fibers are purified and swelled. Mercerized cellulose can be chemically considered as suitable for the preparation of cellulose derivatives.

Before impregnation, cellulose was initially hydrolyzed with 10% NaOH and then soaked in distilled water for 24 h. The fibrous samples were treated in aqueous solutions of

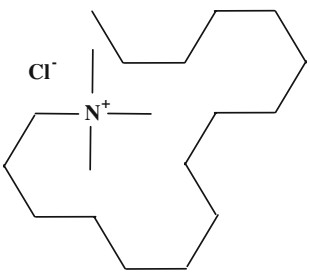

Fig. 1 Semi-detailed formula of Aliquat 1529

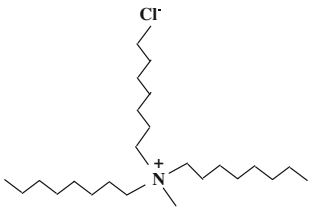

Fig. 2 Semi-detailed formula of Aliquat 336

quaternary ammonium salts at various concentrations. The treatment was carried out during 1 h in a thermostated bath at 30 °C under continuous stirring. After treatment the samples were pressed and rinsed for several times in distilled water in order to remove salts not adsorbed, then filtered, dried under reduced pressure, and weighed. The amount of quaternary ammonium salt adsorbed in cellulose is determined gravimetrically as follows:

$$Q = (w_a - w_b)/w_b(g/g) \tag{1}$$

Were w_a and w_b are the weights of cellulose before and after impregnation respectively.

Grafting Procedure

The grafting was carried out in three stages: initially synthesis of acrylamidomethylated cyclodextrin (CDNMA), then inclusion of benzoic acid in cyclodextrin cavities with formation of the complex CDNMA-IC (inclusion compound), finally grafting on cellulose fiber.

- For the first stage, an amount of β-cyclodextrin was mixed with aqueous solution of *N*-methylol acrylamide in a flask, catalyst formic acid was added and reaction was led at 80 °C during 30 min under stirring. The reaction was stopped by acetone addition and the mixture stored at 5 °C during 24 h for a complete precipitation of CDNMA. For swelling and dye adsorption tests CDNMA was directly grafted on cellulose.
- For the inclusion step, CDNMA and benzoic acid (cyclodextrin chemical host) were mixed in distilled water under stirring during 30 min. Complex IC was precipitated by acetone addition, and then filtered, washed, and vacuum dried. The product is called CDNMA-IC and used, after grafting on cellulose, for antibacterial study.
- Finally, the grafting was carried out following the general procedure of Lepoutre and Hui [14], using ceric ions initiation technique. The reaction was carried out by introducing a known quantity of fibrous cellulose in water (30% consistency) into the flask, the sample was diluted sixfold with water acidified with nitric acid to pH 2 and followed by a suitable quantity of CDNMA-IC. After 5 min of contact time and under a nitrogen atmosphere, ceric ammonium nitrate (approximately 5 wt.% of cellulose) dissolved in 1% HNO_3 was added into the reaction mixture. After standing at room temperature for 3 h with occasional stirring, the grafted cellulose was filtered, washed, dried in reduced pressure, and weighed. The product is called cellulose-g-CDNMA-IC. The grafting level was measured gravimetrically by the percent increase in weight as follows:

$$\%\,\text{Graft} = \left[\left(w_g - w_0\right)/w_0\right] \times 100 \tag{2}$$

Were w_0 and w_g are the weights of the initial and grafted sample respectively.

Measurement Procedure

– Characterization

Measurements were recorded in a KBr phase by using a Shimadzu M850 Model FTIR Spectrophotometer with 20 scans and 2 cm^{-1} resolution for untreated, treated, and grafted samples of cellulose fibers. The fibers microstructure was studied using a Philips XL 30 ESEM scanning electron microscope (SEM).

– Swelling measurements

Swelling evaluation was carried out by measuring the amount of liquid soaked up by the material as a function of time, until saturation. The measurement technique was described in previous work [15]. The fibrous sample was dried, weighed, and then charged in a small tea bag of polypropylene tissue (whose weight is well known). The tea bag was fixed to a support joined to the arm of an analytic scales, the sample was next soaked in the test liquid and at last weighed at regular time intervals. The swelling ratio was performed as follows:

$$\% S_r = [(w_s - w_d)/w_d] \times 100 \quad (3)$$

Were w_d and w_s are the weights of dry and swollen sample respectively.

In all events the experimental determinations have been done three times for each sample, in normal atmosphere at 23 °C.

– Dye adsorption experiments

Reactive dyeing is now the most important method for the coloration of cellulosic fibers, for this purpose we choose to study adsorption of a reactive dye on the grafted fibers.

The dye aqueous solutions were prepared by dissolving the solutes into deionized water to the required concentrations without pH adjustment. All the kinetic experiments were performed at the natural pH of solutions. Samples of 0.2 g of fibrous cellulose were soaked in 50 mL of sample solutions of dyestuff having a known initial concentration and stirred for 24 h.

The concentrations of the dye sample solutions were determined using UV spectroscopic measurements. Absorbance values were measured after various time intervals with a Shimadzu Model UV-1202 spectrophotometer. Each experiment was duplicated under identical conditions at ambient temperature (23 °C).

The amount of adsorption at equilibrium q_e (g/kg) was obtained as follows:

$$q_e = (C_0 - C_e) \times V/W \quad (4)$$

Where C_0 and C_e are the initial and equilibrium liquid-phase concentrations, respectively g/m^3, V is the volume of the solution (m^3), and W is the weight of fibrous sample used (kg).

– Antibacterial activity analysis

The antimicrobial activity of a substrate-bound antimicrobial is dependent upon direct contact of microbes with the active chemical agent. The antimicrobial activity of the fibrous samples is quantitatively evaluated according to AATCC 100-1999 standard were surface antimicrobial activity is determined by comparing results from the test sample to simultaneously run controls. This test determines the antimicrobial activity of treated specimen by shaking samples of surface bound materials in a concentrated bacterial suspension for a 1-h contact time; the suspension is serially diluted both before and after contact and cultured. The number of viable organisms in the suspension is determined and

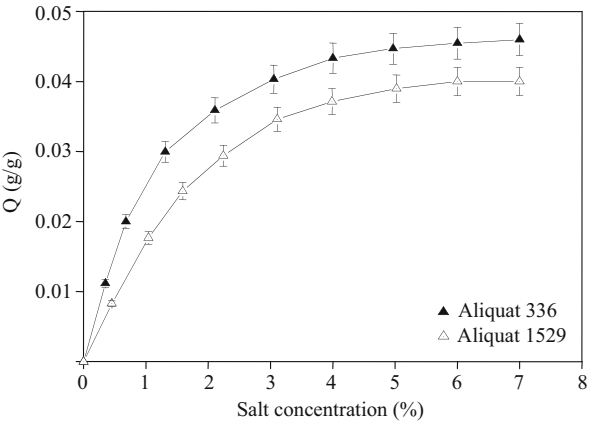

Fig. 3 Competitive adsorption of ammonium salts on cellulose pulp

the percent reduction is calculated based on initial counts or on retrievals from appropriate untreated controls.

In laundering test AATCC 61-2001 method was used to investigate the stability of treated samples after home laundering. In this method, a cycle of Launder-Ometer washing was considered equivalent to five manual washings [16]. A Launder-Ometer was fitted with stainless steel cylinder, a volume of 150 mL of water, 0.15% detergent, and stainless steel balls were added to the cylinder which was rotated for 45 min at 42±1 rpm and 48 °C. These conditions are estimated to be equivalent to five washing cycles in a home laundry. The fibers within the cylinder were rinsed with three portions (300 mL) of distilled water and then air-dried at ambient temperature.

The bacterial reduction was evaluated as follows:

$$\text{Percentage of Reduction } (\%) = [(A - B)/\ A] \times 100 \tag{5}$$

Were A and B are the amount of bacterial colonies on run control and on the test sample respectively.

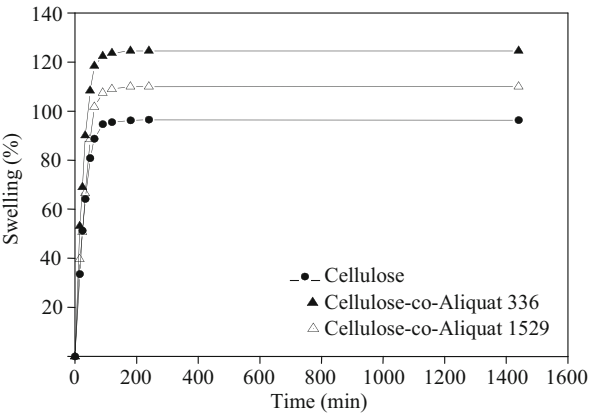

Fig. 4 Swelling kinetics of cellulose–ammonium salts system in deionized water

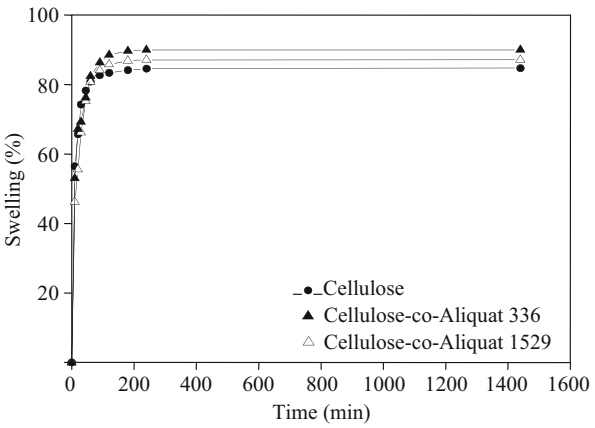

Fig. 5 Swelling kinetics of cellulose–ammonium salts system in saline solution (0.9% NaCl)

Results and Discussion

Cellulose–Ammonium Salts System

If the cellulose has a great affinity for water (absorbency), its internal network retention is rather weak; in addition its fibrous structure doesn't prevent bacteria transmission. To improve the retention and biocompatibility of cellulose, we tried to functionalize it by chemical treatment with a specific finish using impregnation method by quaternary ammonium salts. The latter are molecules with a structure of cationic nitrogen and whose general formula is $R_4N^+X^-$. They are significant to their antimicrobial activity, their non-toxicity, and their affinity for adsorption and might be used for wide applications.

The antimicrobial activity of quaternary ammonium salts results from their amphiphilic structure and surfactant properties. The biocidal action is based on their membrane degradation activity, which can, at suitable concentration, be able to destroy the bacterial cell.

Figure 3 illustrate the adsorption isotherms of the two salts on cellulose. Compared to Aliquat 1529, the higher adsorption level of Aliquat 336 can be explained by its longer alkyl molecular chain (increase in hydrophobicity and physical interactions); this phenomenon was also observed by Ma and Sun [16]. Due to its amorphous character, the fluff pulp seems to have enhanced performance in adsorption; it is able to fix a great quantity of quaternary ammoniums.

We measured the swelling rate of the fibrous cellulose–ammonium salts systems, then of the untreated cellulose. The absorption kinetics of fibrous structures is shown in Fig. 4 for the swelling in deionized water and Fig. 5 for the swelling in physiological saline solution.

Table 1 Bacterial reduction ratio for cellulose-co-Aliquat 1529 (initial concentration=3%).

Bacterial stocks	Contact time (hours) and bacterial reduction (%)					
	0 washing			5 washings		
	1	3	24	1	3	24
Escherichia coli	93.0	95.6	100	75.4	93.9	97.8
Pseudomonas aeruginosa	93.2	96.9	99.7	72.5	80.3	93.9
Bacillus subtilis	93.4	97.0	99.4	90.0	94.8	92.2

Errors: ±2–3% (1 h contact); ±1–2.4% (3 h contact); ±0.5–1.2% (24 h contact)

Table 2 Bacterial reduction ratio for cellulose-co-Aliquat 336 (initial concentration=3%).

Bacterial stocks	Contact time (hours) and bacterial reduction (%)					
	0 washing			5 washings		
	1	3	24	1	3	24
Escherichia coli	98.9	100	100	80.4	89.1	92.2
Pseudomonas aeruginosa	94.4	95.4	99.0	70.4	74.2	78.0
Bacillus subtilis	94.6	97.0	98.0	84.8	84.8	89.2

Errors: ±2–2.6% (1 h contact); ±1.6–2.8% (3 h contact); ±1–1.5% (24 h contact)

For the fibrous cores, practically an equivalent distribution of liquids is observed; the same tendency is noted in the two cases: a fast absorption then a spreading with an equal saturation in the same period of time. In general, the absorption level of the untreated samples was improved due to the presence of the quaternary ammonium salts linked on cellulose. The results obtained in the adsorption of quaternary ammoniums seem to be confirmed by the more important level of the swelling of cellulose treated by Aliquat 336.

In order to confirm the antimicrobial effect and washing durability of cellulose fibers modified by quaternary ammoniums salts finish or chemical grafting, antibacterial tests were run. The biocidal treatment must give to cellulose washing durability, compatibility with the chemical processes (absorption, dyeing), easy to apply, and the fiber structure remains unharmed. Tables 1 and 2 show results of the antibacterial tests carried out on cellulose–ammonium salt systems.

The samples treated by Aliquat 1529 showed a maximum effectiveness after 24 h, we did not detect any bacteria growth, particularly for the *E. coli*. This activity remains effective even after washing, which clearly improves the standards of this material by giving a permanent character to the chemical modification.

The results of samples treated by Aliquat 336 show a better effectiveness; the bacterial reduction is noted only after 3 h of contact. In fact, a longer alkyl chain induces an increase in the antibacterial effectiveness [17]. In both cases we noted a more effective effect on *E. coli*, this one being more vulnerable to the mechanical rupture of its cytoplasmic membrane [18]. The mechanism of intervention of quaternary ammonium salts is related to the destruction of this membrane [4], our results are reasonable; the *Subtilis* spores of *bacillus* have a better resistance to disinfecting agents [19]. The effectiveness of quaternary ammonium salts against bacteria is directly related to their contact surface with the medium of these microorganisms. Their presence even at weak concentration remains sufficient to start a protection. In Tables 3 and 4 we show the bacterial reduction results obtained for an initial concentration of quaternary ammonium salts of 0.1%.

Table 3 Bacterial reduction ratio for cellulose-co-Aliquat 1529 (initial concentration=0.1%).

Bacterial stocks	Contact time (hours) and bacterial reduction (%)		
	0 washing		
	1	3	24
Escherichia coli	80.0	86.9	100
Pseudomonas aeruginosa	90.0	92.4	95.4
Bacillus subtilis	60.8	62.9	99.3

Errors: ±1–2.2% (1 h contact); ±1–2% (3 h contact); ±1–2% (24 h contact)

Table 4 Bacterial reduction ratio for cellulose-co-Aliquat 336 (initial concentration=0.1%).

Bacterial stocks	Contact time (hours) and bacterial reduction (%)		
	0 washing		
	1	3	24
Escherichia coli	95.6	97.6	99.6
Pseudomonas aeruginosa	93.6	96.9	98.0
Bacillus subtilis	96.6	97.6	98.5

Errors: ±1.2–1.8% (1 h contact); ±1–2% (3 h contact); ±0.5–1% (24 h contact)

In all cases the resistance to washings was particularly good.

The quaternary structures are effective on the two types of bacteria Gram positive and Gram negative, they are largely used thanks to their non-toxic and no irritating properties, also for their polycationic porous and absorbing properties.

Grafted Cellulose System

The principle of development of functional cyclodextrin–celluloses is based on the permanent fixing of supramolecular compounds on their surface. These compounds are ligands with a three-dimensional specific structure allowing inclusion of particular chemical molecules. Among supramolecular compounds, cyclodextrins are cyclic oligosaccharides resulting from the enzymatic degradation of starch, they have capacity to form compounds of crystalline inclusion (ICs) with small and active molecules such benzoic acid; this latter can form complexes with the α- and β-cyclodextrins.

In this part the fibrous cellulose was chemically modified by grafting of acrylamido-methylated β-cyclodextrin and inclusion of benzoic acid in the free cavities of cyclodextrin, as an antimicrobial agent. It is well-known that during grafting on cellulose with a redox initiator, a part of radicals resulting from the initiator decomposition create active centers on cellulose to start grafting, therefore the grafting yield depends significantly on the active centers created on cellulose. As redox systems, we used cerium (IV) ammonium nitrate. When ceric salts were used as an initiator on grafting onto cellulose, it is proposed that a ceric ion–cellulose complex is initially formed as a result of one electron transfer. Then ceric ion is reduced to cerous ion and a free radical is created on the cellulose backbone.

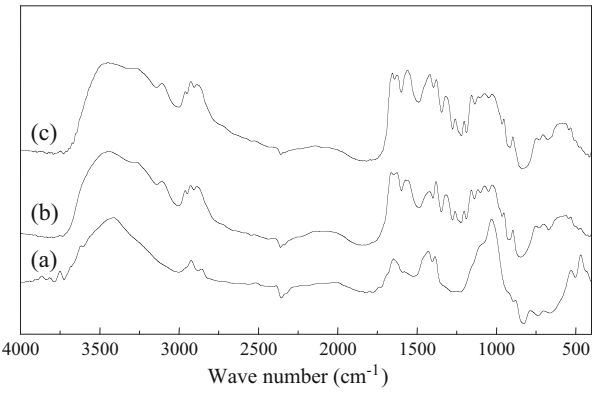

Fig. 6 Infrared spectra of CDNMA (*a*), cellulose (*b*), and CDNMA/IC grafted cellulose (*c*)

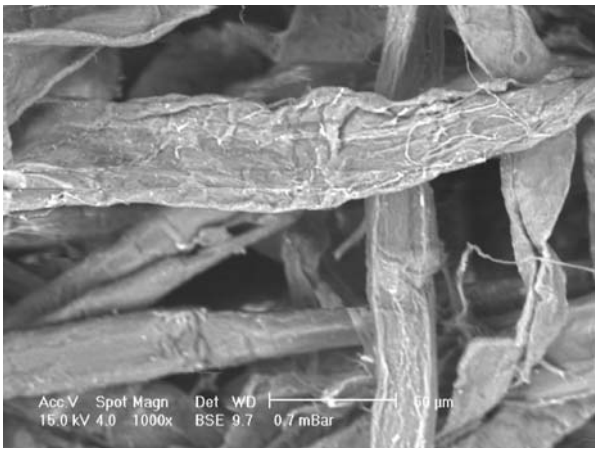

Fig. 7 SEM micrographs of untreated cellulose

The radical site on cellulose then initiates grafting of acrylamidomethylated cyclodextrin-benzoic acid (CDNMA-IC) which is present in the reaction mixture.

The result of grafting amount was 39.2±2% for cellulose-g-CDNMA 37±1.7% for cellulose-g-CDNMA-IC systems; the permanent grafting was confirmed by infrared analysis spectroscopy through new characteristic bands on cellulose-g-CDNMA-IC spectra (Fig. 6). Figure 6 shows the following characteristic bands:

- The bands at 1,028–1,033 cm^{-1} and 1,157 cm^{-1} represented on Fig. 6a are characteristic of cyclodextrin (C–O–C), these same bands are observed on the cellulose-g-CDNMA-IC spectrum (c), which confirms the grafting. The same result was found by George et al. [20] and Zhang et al. [21].
- The band at 1,647 cm^{-1} illustrated on Fig. 6a characteristic of carbonyl groups (C=O), confirms fixing of *N*-methylol acrylamide on cyclodextrin. The band at 945 cm^{-1}; characteristic of monosubstituted alcene groups (Trans) indicates formation of CDNMA, and its absence in Fig. 6c confirms the grafting of CDNMA on the cellulose support.
- The band at 1,280 cm^{-1}; present on the cellulose-g-CDNMA-IC spectrum is characteristic of carboxylate group of the cyclic benzoic acid, it confirms the inclusion of benzoic acid in the cyclodextrin cavity.

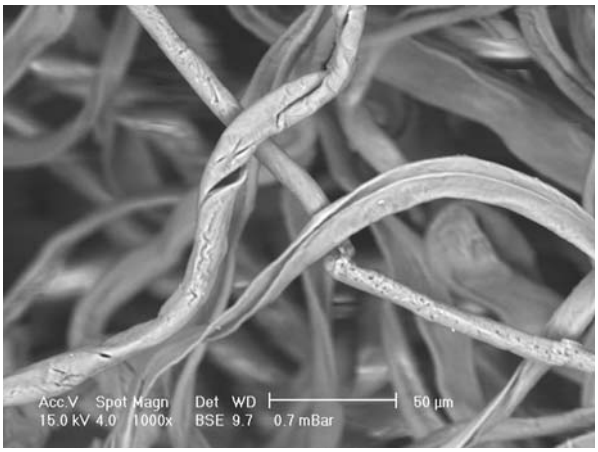

Fig. 8 SEM micrographs of cellulose–g–CDNMA

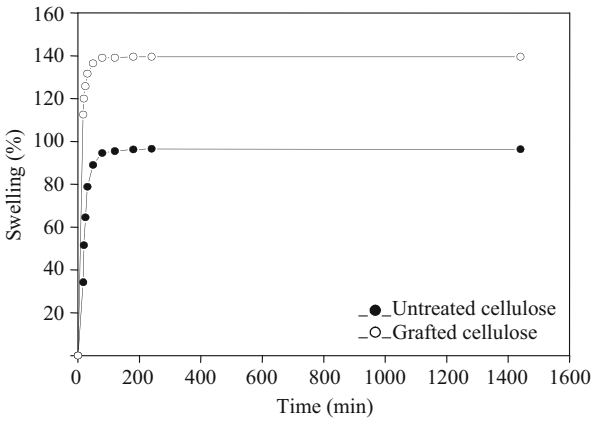

Fig. 9 Swelling kinetics of cellulose–g–CDNMA system in deionized water

We observed the changes induced by the grafting process in the fibers morphology, the untreated fibers in Fig. 7 show a surface composed of fibrils, which is characteristic of wood pulp fibers. The fibers are typically flattened with an irregular fibrillary structure; in Fig. 8 one can observe a polymer layer coating grafted fibers, these fibers become thicker and more plump.

The swelling properties of cellulose materials arise from the interactions between hydroxyl groups of cellulose and water molecules. The absorption tests were carried out on untreated and grafted samples, Figs. 9 and 10 show the results obtained for the swelling in deionized water and in saline solution respectively.

For the cellulose-g-CDNMA samples, absorption was increased of more than 50% in the two test liquids, the principal reason of this swelling improvement arise from the osmotic pressure effects. For all samples, the absorption levels of saline solution remain restricted to 50–60% of those of deionized water. This phenomenon observed by C.C. Chen et al. results from the counter ion effect of Na^+ around the polymer, which induces a collapse of its internal network [22].

It was known that liquid-phase adsorption process is very efficient for the removal of dyes and organic pollutants from process or waste effluents. The kinetics and adsorption equilibrium of a commercial reactive red dye on our fibrous supports were studied. Figure 11 shows adsorption isotherms of reactive dye by the untreated and grafted samples from aqueous solution. Cellulosic fibers treated in order to increase their fixing capacity should be able to work as an

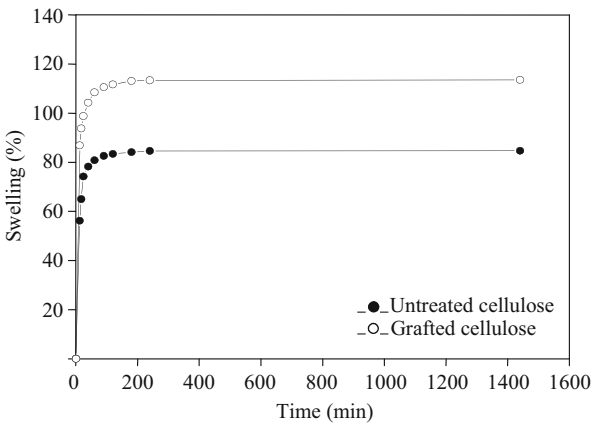

Fig. 10 Swelling kinetics of cellulose–g–CDNMA system in saline solution (0.9% NaCl)

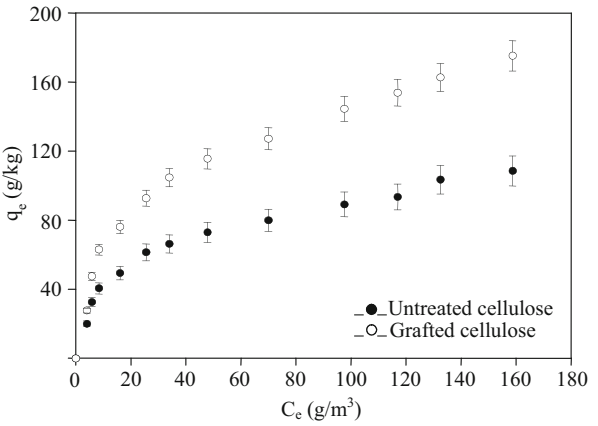

Fig. 11 Equilibrium adsorption of reactive dye on cellulose fibers

exchanger of dyeing molecules, which may be regenerated to allow a great number of cycles. Adsorption results of reactive dye on treated samples show their ability to fix this kind of molecule. These results show the clear improvement of the dye fixing on the grafted supports.

Benzoic acid inclusion in CDNMA was prepared as described and grafted onto cellulose before the antimicrobial activity was tested. The carried out tests on cellulose-g-CDNMA-IC fibers gave the following results on Table 5.

Although the action mechanism of benzoic acid as an antimicrobial agent is not quite understood, some authors used it successfully against the bacterial activity of various stocks [23]. Our results show that in *E. coli* and *B. subtilis*, the bacterial growth is totally inhibited after 24 h of contact; the effect is appreciably reduced for *Pseudomonas*. In addition, washing does not much influence the activity because the biocidal agent is fixed in a permanent way.

Conclusion

Biomaterial study was carried out through chemical modification of cellulose to allow new biological functions on fibers, with improvement of liquid absorption and increase in antimicrobial activity.

In our experimental procedure we first tried to modify cellulose by a simple physical treatment, adsorption of quaternary ammonium salts on the fibers surface. Remarkably, the antimicrobial activity of the treated samples do not decrease so much after washing, in addition the fibers swelling in liquid medium was enhanced.

Table 5 Bacterial reduction ratio for cellulose-g-CDNMA-IC.

Bacterial stocks	Contact time (hours) and bacterial reduction (%)			
	0 washing		5 washings	
	3	24	3	24
Escherichia coli	97.8	100	96.9	99.0
Pseudomonas aeruginosa	86.4	93.6	88.5	94.6
Bacillus subtilis	99.2	99.1	98.5	99.5

Errors: ±1–2% (3 h contact); ±1% (24 h contact)

Subsequently, in order to preserve these new functions we thought to bind, in a final way, an active molecule on the fibers surface. We exploited the inclusion capacity of cyclodextrin to graft a complex of cyclodextrin-active molecule on cellulose. The method used is very complex, but effective, the samples treated show a large biological activity; higher than the finished samples.

Cellulose fluff pulp was grafted with CDNMA so that free-hosting CD cavities would be available for the direct formation of inclusion compounds with suitable hydrophobic species on the fiber surface. FTIR, SEM, and liquid absorbency tests were performed to assess that the structure and surface properties of the fibers were not changed after the grafting process. Benzoic acid included in CDNMA–cellulose fluff pulp possessed antimicrobial activity, particularly against *B. subtilis* and *E. coli.*

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