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Full Length Research Paper

Synthesis and characterization of β-cyclodextrin-benzoic acid inclusion complex and grafting with cellulosic polymer

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The cyclodextrins (CDs) are well known for their ability to form inclusion complexes with various types of guest molecules, which fit partially or completely into the host CDs cavity as shown by crystallographic results. Such beneficial property of CDs has been applied in many industries, for example, foods, pharmaceuticals and agriculture. Benzoic acid (BA) has been proven to form inclusion complexes with α-CD and β-CD. Globally, the fashion industry is more interested in new and versatile fabrics, characterized by specific mechanical and physicochemical properties, for the production of polymers with highly specific properties such as, antibacterial properties. In this work, we reported a study on the formation of the inclusion complex between acrylamidomethylated β–cyclodextrin and benzoic acid molecules, then on the grafting of cellulosic polymer (rayon and cotton fibers). The grafting was initiated by ceric ions Ce (IV) and confirmed by infrared analysis (FTIR). Microscopic analysis was carried out to evaluate properties of structure and surface of grafted fibers. Our results indicated the formation of a permanent chemical bond between β-cyclodextrin and polymers material. The cellulosic polymers can be effectively modified without significant change in the structural properties; more so, the antibacterial molecules probes remain integrated into the fiber surface. In addition, absorption tests showed that the grafted functions clearly improve retention of liquids by cellulose; however, the bacterial reduction obtained by these new functions is very significant on the Gram^{+} and Gram^{-} bacteria.

Key words: β-Cyclodextrin, benzoic acid, cellulosic polymer, grafting, antibacterial activity.

INTRODUCTION

The applications of polymers as raw materials in nontraditional sectors are today known as a strong dynamics of growth. Among these new opportunities, the practical application in the fields biomedical, pharmaceutical or from the membranes profited from the original fibrous material contribution was indicated under the generic term of "bio polymeric" (Specklin, 1994). The fibrous polymers implemented a new chemistry, generally associated to a technology of avant-garde which places them at the first rank of the textile innovation. The associated processes are either of the traditional treatments by application of resins, or of emergent technologies such as, the grafting, plasma or the laser. These functional polymers are presented in the form of carrying markets and many developments are thus possible in the short, average and long terms. However, the innovations are sometimes very fast and the regulation of the market is not entirely assumed; new tests, standards and labels are necessary to preserve the consumer and to control the market of these innovating products.

By offering an impressively large specific surface associated with a possibility of practically working on the cellulose, a place of exchange was constituted without equals. There are several possible ways to bring an additional function to cellulose: new fibers, modification of

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the fibrous structure, and physical or chemical treatment by a specific finish. These new functionalities can either bring a protection to counter the risks ("anti" function), or a contribution of positive effects (function "pro") (Hsieh and Young, 1996). Thus, by the contribution of functions, the formerly passive cellulose becomes active.

Among the various techniques, it is certain that grafting makes it possible for cellulose to function best. The method of grafting by copolymerization gained a great importance in the modification of the physical and chemical properties of the cellulose (Gürdag et al., 1997; Lokhande and Gotmare, 1999). The grafting is made possible to follow the growth of a polymer chain on the active sites of the chain of cellulose.

The capacity of cyclodextrins includes hydrophobic molecules such as, antimicrobial agents and other chemicals can be exploited to produce new grafted materials with particular properties. The toroidal shape and the presence of internal hydrophobic hollow cavities in cyclodextrins produced the capability of these hosting species includes a very wide variety of different molecules and to form stable Inclusion Compounds ICs (Martin Del Valle, 2004).

In this work, we reported a study on the grafting of acrylamidomethylated β-cyclodextrin (CDNMA) on cellulose (cotton and rayon fibers), then on the inclusion of benzoic acid molecules in the free cavities of cyclodextrin. The grafting is initiated by ceric ions Ce (IV) and confirmed by infrared analysis (FTIR). Microscopic analysis was carried out to evaluate properties of structure and surface of grafted fibers.

EXPERIMENTAL PROCEDURE

Test materials

(1) Fibrous support in waste cotton is constituted of short fibers collected from cotton mill, then washed and bleached in the laboratory. The nature is a Syrian Gossypium variety. Physical form: spirally white fibers, Length of fibers: 8 to 14 mm, Conventional Moisture content: 8.5%, cellulose content: 88 to 90%, hemicelluloses content: < 1%, product density: 1.54 g/cm^3.
(2) Regenerated used cellulose fibers (rayon) were provided by Svenska Rayon (Sweden). The fibers have a 5 to 15 mm length and a product density of 1.59 g/cm^3. Before use, the fibers were cleaned in boiling water for 12 h and then soxhlet was extracted with dichloromethane for an additional 12 h.
(3) β-Cyclodextrin hydrated, $C_{42}H_{72}O_{36}.H_2O$ (Aldrich), benzoic acid (Reachim), Formic acid (Merck), Sodium carbonate (Merck), Acetone (Panreac) and Ceric ammonium Nitrate (Aldrich) were of reagent grade and were used as received.
(4) N-methylolacrylamide (Aldrich) was distilled at 60°C under reduced pressure to extract inhibitor (hydroquinone).

Synthesis

The grafting is carried out in three stages: the initial stage is the synthesis of acrylamidomethylated cyclodextrin (CD-NMA), then the synthesis of complex CD-NMA/IC (inclusion of active molecule), and finally, the grafting of the complex obtained on cellulose.

Synthesis of CD-NMA

A quantity of β-cyclodextrin is mixed with an aqueous solution of N-Methylolacrylamide in a two-necked, round bottom flask equipped with a thermometer and a condenser. Catalyst formic acid is added and reaction is led at 80°C for 30 min under magnetic stirring. The reaction is stopped by acetone addition and the mixture was stored at 5°C for 24 h for a complete precipitation of CD-NMA. After filtration and washing with cold acetone, the product vacuum was dried and kept in desiccators (Figure 1).

Formation of complex CD-NMA-IC

CD-NMA and benzoic acid (cyclodextrin chemical host) are mixed in distilled water under magnetic stirring for 30 mn. Complex IC (inclusion compound) is precipitated by the addition of acetone, and then filtered, washed and vacuum dried (Figure 2).

Grafting of the CD-NMA-IC on cellulosic polymer

The grafting of CD-NMA-IC onto cellulosic support was carried out in a two-necked, round bottom flask equipped with a condenser and a nitrogen atmosphere.

Cellulosic sample was added to ceric ammonium nitrate solution in aqueous HNO_3, and it was left for 20 min with magnetic stirring and nitrogen purge. CD-NMA was added, and the mixture was stirred under nitrogen atmosphere for 1 h at 40°C. Finally, the fabric was washed carefully with running water for the removal of any unreacted chemicals, neutralized with Na_2CO_3 solution, washed again with running water and finally boiled for 30 min. The grafted cellulose was filtered and dried.

The grafting yield was evaluated through this relation:

$$\% \text{ Grafting} = (W_g - W_0) \times 100/W_0 \quad (1)$$

Where: W_0 and W_g are the weights of the unreacted and grafted sample respectively.

Swelling measurements

Absorption is measured by the amount of liquid which is linked to the materials after soaking and drainage time. Retention is the amount of liquid held by the same sample after a time of centrifugation (retention under pressure). The procedure inspired from the German Pharmacopoeia (STN2: 117:87 standard) was described in detail (Aliouche et al., 2000).

Swelling evaluation was carried out by measuring the amount of liquid soaked up by the material according to the time of saturation. The measurement technique was also described in the same previous work.

In all events, the experimental determinations were done three times for each sample, in normal atmosphere and 20°C of temperature. For deioized water and in physiological Salt solution, NaCl at 0.9% was used for absorption characterization of hygienic products (Herrmann, 1996).

$$G = (W_a - W_s)/W_s \text{ (g/g)} \quad (2)$$

Where: W_s and W_a are the weights of the dry and wet sample respectively.

Antimicrobial activity analysis

The antibacterial activity of the fibrous samples is quantitatively

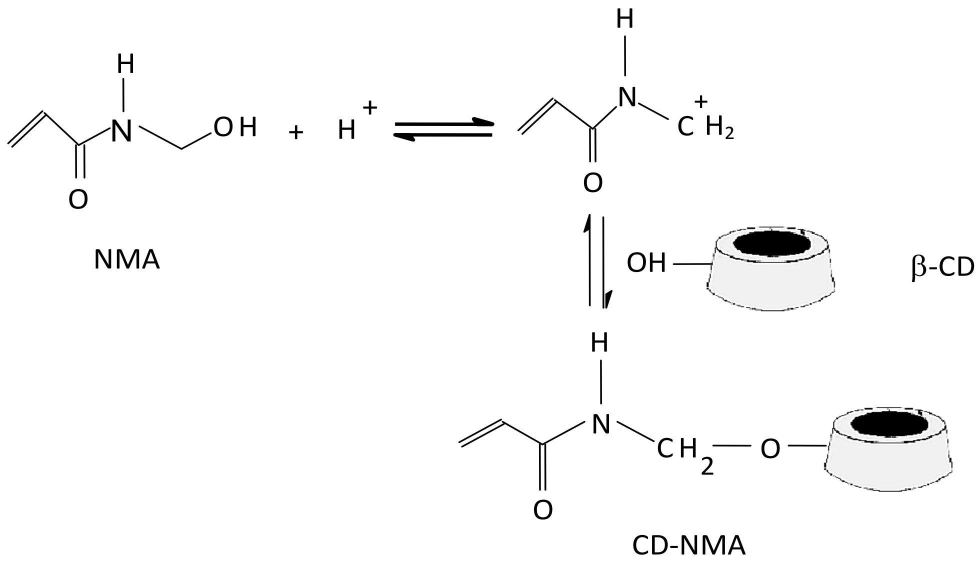

Figure 1. Synthesis of CD-NMA.

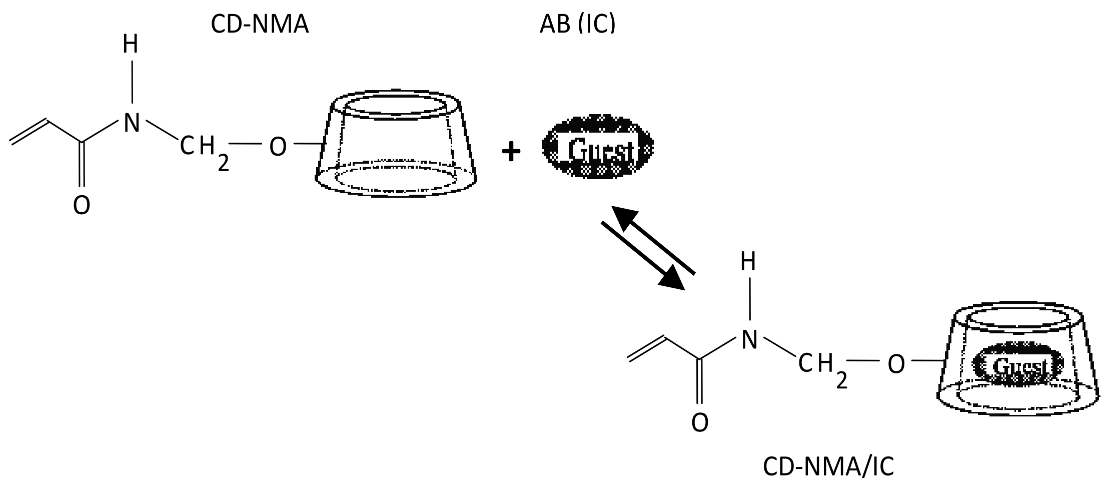

Figure 2. Formation of the complex CD-NMA/IC.

evaluated according to a modified Test Method 100-1999-AATCC. The bacterial colonies are counted and the bacterial reduction was evaluated following this relation:

Percentage reduction (%) = (A - B).100/A (%) (3)

Where A is the number of bacterial colonies counted from untreated sample and B is the number of bacterial colonies counted from modified sample.

RESULTS AND DISCUSSION

Grafting mechanism

The grafting yield for fibrous support is up to 55% in the rayon and 25% for the cotton fibers. The grafting amount was higher; however, rayon fibers were used as substrates for grafting. This is probably an effect of the less crystalline structure of rayon fibers; Crystallinity of rayon is approximately 30%, while cotton is 65 to 85% crystalline (Rebenfeld, 1985). This may result in a better transportation of monomers and a higher degree of accessibility for graft copolymerization in rayon fibers.

The results were confirmed by the infrared spectroscopic analysis. The measurements were recorded in a KBr phase by using spectrophotometer Shimadzu type Model M850 with untreated and grafted samples of cellulose fibers.

The grafting was confirmed by new characteristic bands of the monomers:

(1) Bands at 1028 to 1033 cm^{-1} and 1157 cm^{-1} characteristics of cyclodextrin Figures 3.

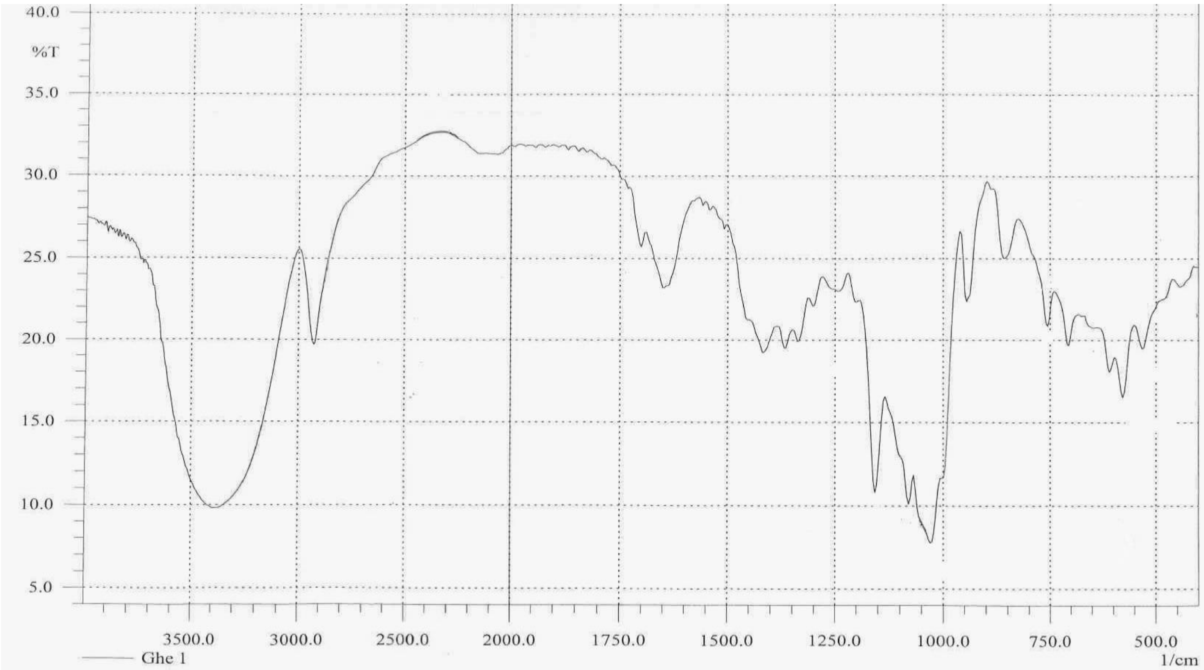

Figure 3. FTIR spectra of CD-NMA.

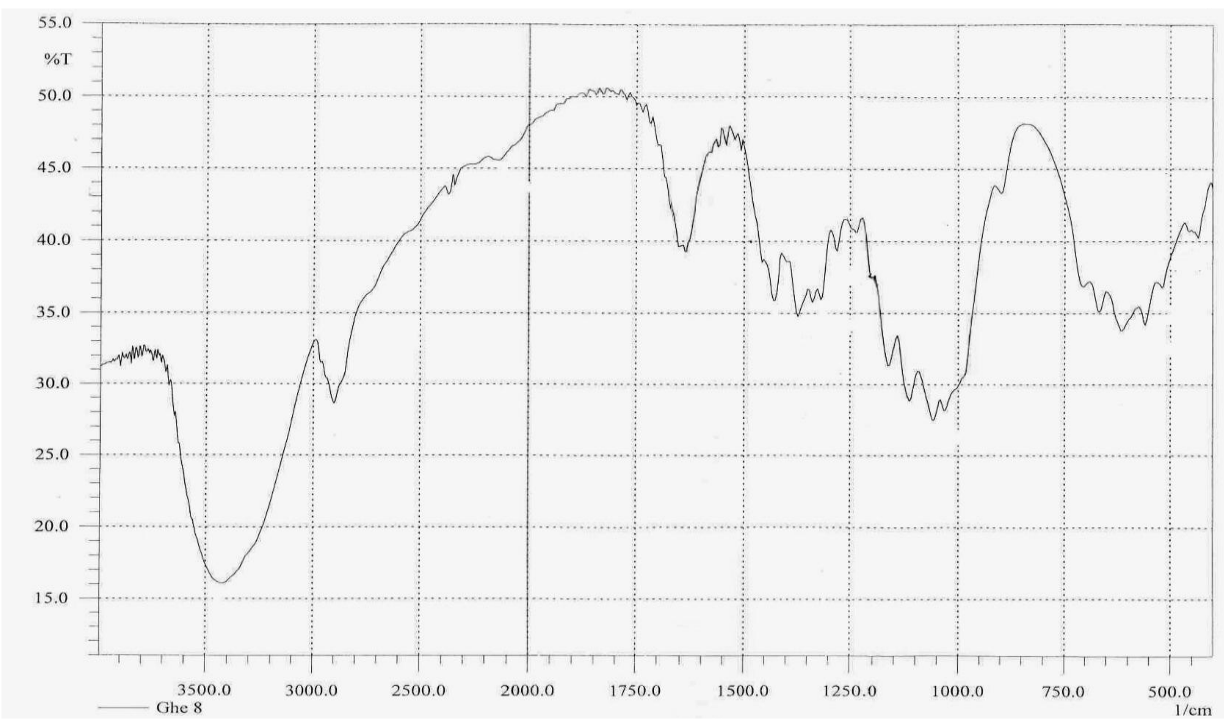

Figure 4. FTIR spectra of cotton grafted CD-NMA.

(2) Band at 1747 cm^{-1}; characteristic of the carbonyl group (C=O), which confirmed the fixation of N-méthylol acrylamide to β-Cyclodextrin Figures 3. In addition, the appearance of the band at 945.1 cm^{-1} characteristic of alkene group monosubstituted (trans.) on the spectrum.
(3) Figures 3 indicates the formation of CD-NMA, and its disappearance in spectrum.
(4) Figures 4 confirmed the grafting of CD-NMA to

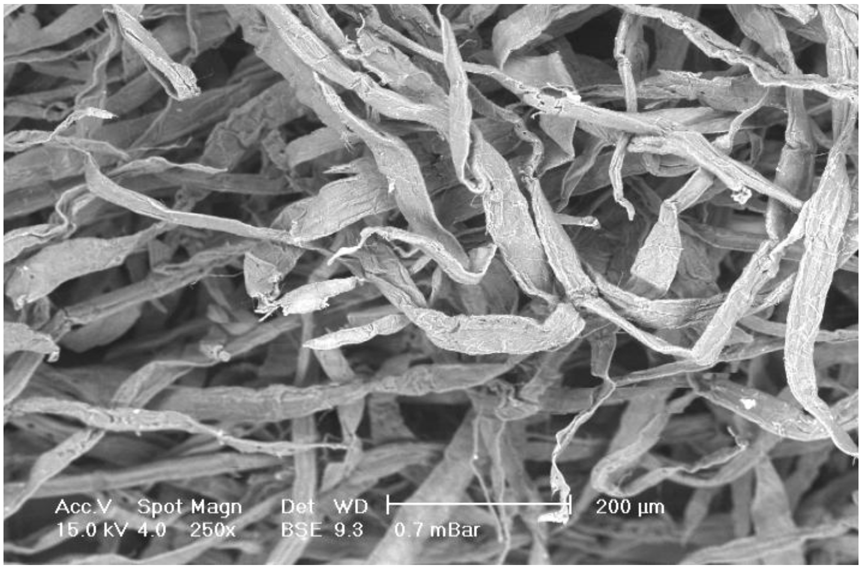

Figure 5. SEM of untreated cellulose.

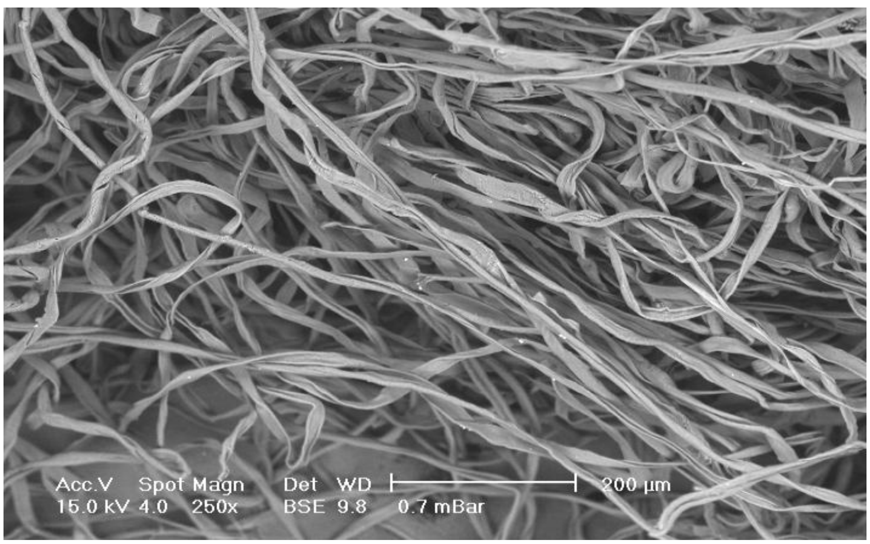

Figure 6. SEM of cellulosic fibers grafted/CD-NMA-IC.

cellulose. Figures 4 Band 1280.6 cm^{-1} was observed on the spectrum of cotton -CD-NMA.
(4) Characteristic cyclic carboxyl Ted group of the benzoic acid situated at 1200 to 1300 cm^{-1}, which confirmed the inclusion.
(5) Bands characteristics of polysaccharide: 3300-3400 cm^{-1} (vibration OH), and 1640 to 1650 cm^{-1} (carbonyl vibration) C=O Figures 4.

We observed the changes induced by the grafting process in the fibers morphology. The surface morphology of grafted and ungrafted fibers is shown in Figures 5 and 6.

The untreated fibers in Figure 5 show a surface composed of fibrils, which is a characteristic of wood pulp fibers. The fibers are typically flattened, of a ribbon shape, with an irregular fibrillary structure. The external fibrils are probably leftover elements of the primary wall. In Figure 6, one can observe the polymer layer coating grafted fibers becoming thicker and plumper.

Swelling behavior of grafted cellulose

Water retention properties of cellulosic materials arose from the interaction between hydroxyls groups of cellulose and water molecules.

Measuring the absorption properties of fiber networks

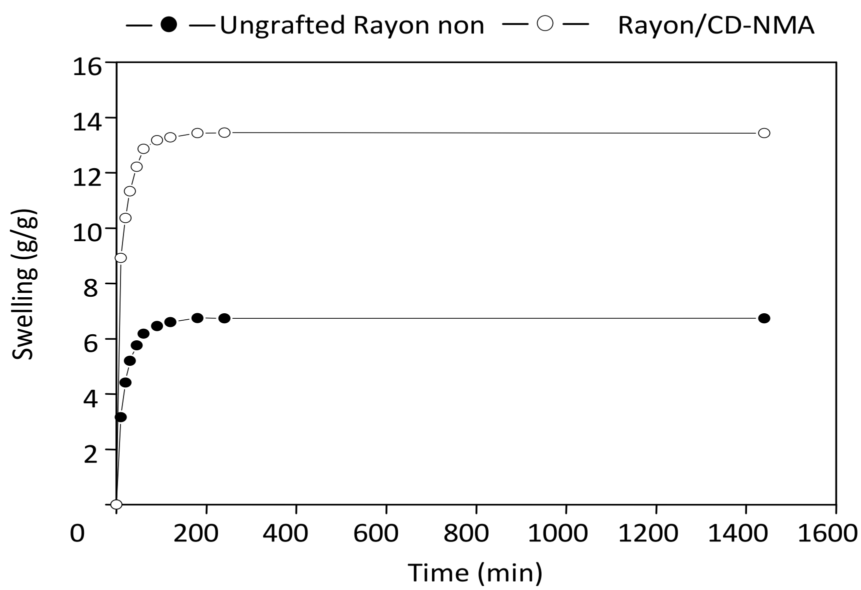

Figure 7. Swelling of rayon grafted with CD-NMA in water.

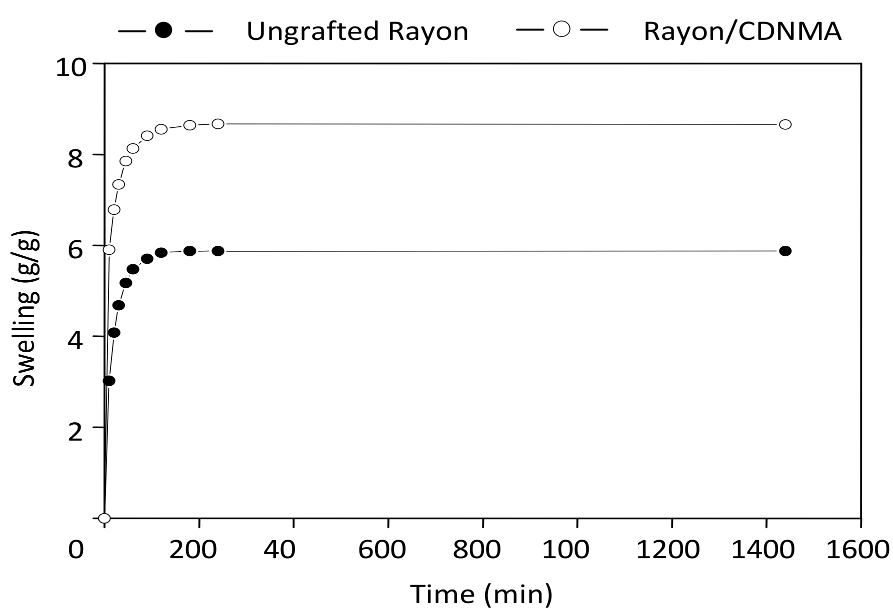

Figure 8. Swelling of rayon grafted with CD-NMA in salt solution.

gave a complex result, composed of fiber swelling and absorption of liquid in capillaries between fibers. Absorption and retention tests were carried out on the grafted and ungrafted samples. We measured the absorption and water retention capacity under load; the results are shown in Figure 7, for the swelling in water and also in Figure 8, for the swelling in the salt solution (NaCl a 0.9%).

Due to less crystalline structure, rayon has a better accessibility for the liquids and consequently, an absorption capacity is higher than for the fibrous cotton structures. Such behavior was also observed by Karlsson et al. (1998) for pH- responsive grafted cellulose fibers. For the sample cellulose-co-CD-NMA, the retention increased at 100% in water and 50% in the salt solution, this phenomenon result from the osmotic pressure of counter-ion.

For a certain graft level and for all samples, salt absorption and retention values remain restricted from 50 to 60% of those of water. This phenomenon was

Table 1. Bacterial reduction ratio for cotton-co-CD-NMA/IC.

Bacterial stocks	Contact time (hours) and bacterial reduction (%)			
	0 (washing)		5 (washing)	
	3	24	3	24
E. coli	71.74	100	67.39	96.88
P. aeruginosa.	37.88	69.69	51.51	67.14
B. subtilis.	95.37	98.49	91.48	97.04

Table 2. Bacterial reduction ratio for viscose-co-CD-NMA/IC.

Bacterial stocks	Contact time (hours) and bacterial reduction (%)			
	0 (washing)		5 (washing)	
	3	24	3	24
E. coli	97.83	100	96.90	98.99
P. aeruginosa.	86.43	93.55	88.50	94.60
B. subtilis.	99.16	99.14	98.50	99.50

observed by Chen et al. (1985) which results from the counter ion effect of Na^+ around polymer, which induced a collapse of its internal network.

Antimicrobial activity study

Here, we are interested in the bacteriological tests in order to confirm the antibacterial effect and washing durability of cellulosic polymers modified by chemical grafting; for this, we earlier chose the bacterial stocks, which must be met in biomedical field which are: Gram$^+$: *Bacillus subtilis* Gram$^-$: *Escherichia coli*, *Pseudomonas aeroginosa* (Pseudo).

The antibacterial tests carried out on cotton and viscose fibers grafted by CD-NMA/IC (after inclusion of benzoic acid in the cyclodextrin) gave the results, which are represented in Tables 1 and 2. These results show that the bacterial growth is completely inhibited after 24 h of contact for *E. coli* and *B. subtilis* on the two grafted supports; this effect is appreciably reduced for *P. aeruginosa.*

Thus, washing does not much influence the activity because the antibacterial fixing is permanent. We can thus note that the activity for the same contact time is weak in cotton CD-NMA compared to rayon –CD-NMA, this is because of the less important grafting amount. However, the action mechanism of benzoic acid as an antimicrobial agent is not quite understood.

Conclusion

Like the majority of polymers with long chain, we showed that it is possible to fix along the cellulose macromolecule of the synthetic links by grafting.

The cellulose is a very reactive matter which is chemically abundant in nature, available and easy to implement. It is preferably used as a material in absorbing biomedical and hygienic applications. In standard atmosphere, the cellulose in various physical forms can absorb up to 10% of moisture. In liquid medium, it has strong capillarity as a result of great absorption. However, if the cellulose has a great affinity for water (absorbent), it retains little liquid in its internal network. To thus improve the retention of cellulose, we tried to fix functions to be able to optimize this characteristic in this work. This functionalization was carried out through one β-acrylamidométhylée cyclodextrin. Cyclodextrins (CDs) are well-known like molecules hosts that are able to associate a broad degree of selectivity of many active molecules by no covalent interactions in their hydrophobic cavity. They are of great interest due to their single capacity to form compounds of crystalline inclusion (ICs) with the small molecules such as the benzoic acid which will play the role of molecule to activate antibacterial.

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