FTIR Analysis for Studying the Possibility of Grafting onto Cotton of Some Compounds Resulted from the Interaction of Carbonyl Compounds with Monochlorotriazinyl-β-Cyclodextrin

VASILICA POPESCU[1], IRINA CRINA ANCA SANDU[2, 3], GABRIEL POPESCU[4]*

[1] Gheorghe Asachi Technical University of Iasi, Faculty of Textiles, Leather Engineering and Industrial Management, 29 Dimitrie Mangeron Blvd., 700050 Iasi, Romania

[2] Munch Museum / Munch Museet, Department of Conservation, Toyengata, 53 0578 Oslo, Norway

[3] Romanian Inventors Forum, 3 Sf. P. Movila St., L11, III/3, 700089, Iasi, Romania

[4] Gheorghe Asachi Technical University of Iasi, Faculty of Mechanical Engineering, 43 Dimitrie Mangeron Blvd., 700050 Iasi, Romania

FTIR analysis is able to prove a grafting process, even when the grafting agencies are complicated. In this paper, the agents were obtained from a series of transformations of two carbonyl compounds (acetone and octanal) based on 2 stages: (1) activation of carbonyl compounds; (2) the combination of MCT-β-CD. Activation of acetone was performed with ethylene diamine and the activation of octanal was performed with HCl. Normally, without an activation step, acetone and octanal not react with MCT- β-CD because the group C=O ketone from acetone and respective group CH=O from octanal not react with the atom of Cl present on the triazine ring, that is the most reactive group from MCT-β-CD. Finally, the grafting agents obtained in the two situations were applied on cotton fabric by a pad-dry-cure technology. Grafting confirmation of each MCT-β-CD derivative produced by two methods qualitative: analysis FTIR and phenolphthalein test. In addition, the grafting has led to the improvement of non-wrinkle effects, effects valued by wrinkle recovery angles (WRA). Statistical analysis of WRA values indicated three conclusions: (1) the populations studied statistical are homogeneous; (2) the mean values of the WRA are representative of these populations; (3) the standard errors of the mean are very low.

Keywords: FTIR, glyoxal, acetone, octanal, MCT-β-CD

In organic chemistry, the carbonyl functional group type is composed of a carbon atom double bonded to an oxygen atom C=O. Group C=O is a divalent function and is found in many classes of organic compounds, either as a freestanding group or a part of some functional groups higher. The main carbonyl compounds are the aldehydes and ketones and certain bifunctional compounds (aldols) [1-3].

Monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) is a cyclic oligosaccharide constituted of 7 glucopyranose units linked by α-(1-4) bonds [4-6]. The reactivity of this compound is given by the presence of multiple reactive groups, as follow: the triazine ring on which are a chlorine atom and an -ONa group on each ring; -OH groups (primary and secondary) located on the interior and exterior cone shape. The -OH groups give a hydrophilic character on the outside of the cone and less hydrophilic inside cone of β-cyclodextrin. However, the most reactive groups from MCT-β-CD are the chlorine atoms, they being responsible for the ether connections with the cellulose, during the grafting process [5, 7-10].

Grafting is a technique that allows a polymer surface modification by attaching on the polymer surface different grafts consisting of simple compounds (aldehyde, ketones, carboxylic acids, alcohols, etc.) or compounds derivatives [5, 11, 12]. The aim of grafting is to improve the reactivity of the support polymer or confer special properties to it: antimicrobial, anti-fungal or other effects (hydrophobic/hydrophilic, fire retardant, UV protection, crease resistant) [5, 13-16].

In this paper the capabilities of carbonyl compounds were used to give two types of reactions: (1) the condensation reactions with amines, when results imines (i.e. acetone +ethylene diamine); (2) the nucleophilic addition reactions to the carbonyl group (for example, addition of HCl at octanal which has two stages, the protonation followed by the addition of nucleophilic reactant).

Compounds obtained at the end of these reactions (a ketimine and respectively a chlorohydrin in case 2) can react with β- cyclodextrins that have reactive groups. When β-cyclodextrin has attached a triazinic ring that have two substitutes (such as -Cl and -ONa) we say that the compound is actually MCT-β-CD. The reactions of a ketimine with MCT-β-CD and chlorohydrin with MCT-β-CD lead to β-CD derivatives that can be applied on cotton in the presence of an alkaline catalyst (NaOH or Na_2CO_3) in specific conditions of temperature, *p*H and time, conditions required by the pad-dry-cure technology.

Experimental part

Materials and methods

In this work were used samples of 100% cotton fabric with specific weight of 100 g/L, previously subjected to desizing and scouring.

The chemicals were obtained from the companies Merck (NaOH, HCl 98%, acetone, ethylene diamine and octanal) and Wacker-Chemie (CAVASOL W7 MCT, i.e. monochlortriazinyl beta-cyclodextrin Na-Salt). The chemical structures of these chemicals are showed in the figure 1.

The two carbonyl compounds (acetone and octanal) were used to create two working systems, namely: system 1 is acetone + ethylene diamine; system 2 is octanal/in

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* *email: gpopescu65@yahoo.com*

acid catalysis (both for 15 and 5 min, respectively. Finally, was added 20% MCT-β-CD and the pH of each system was adjusted at 12 by means of NaOH (table 1).

The newly obtained derivate was then applied on the cotton sample using a pad-dry-cure technology, for which we used a mini-padder and a minitherm ERNST BENZ AG apparatus (Textilmachinen Rumlang – Zurich). The solution necessary for impregnation was made as follows: (1) carbonyl compound and an activating agent were brought in contact (as indicated in table 1); then were heated (at high temperatures) and stirred continuously for 15 min; (2) a solution with 20 % MCT-β-CD (with 350 g/L laboratory concentration) was added to the first solution from the beaker, stirring continuously for 15 min; NaOH was added to get *p*H = 12.

This final solution was added to the mini-padder and material padding was carried out, GS = 80%. This was followed by drying (100°C, 3 min) and condensation (160°C, 3 min). Finally, the samples were washed and dried at room temperature.

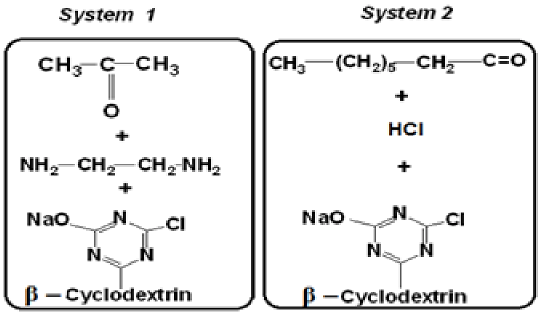

Fig. 1. The two systems used for grafting on cellulose

For comparison purposes, table 1 presents two witness samples for each final sample, namely: a witness sample treated only with a carbonyl compound, and the second witness treated with the solution of carbonyl compound and an activating agent (HCl (as catalyst), ethylene diamine). It was done in this manner to notice the modifications produced by the interactions between reactants after each stage.

FTIR analysis

FT-IR analyses of all samples were performed on Multiple Internal Reflectance Accessory (SPECAC, USA) with ATR KRS-5 crystal of thallium bromide- iodine, having 25 reflections, and investigation angle of 45°. This accessory device was attached to the Spectrophotometer FTIR IR Affinity-1 Schimadzu (Japan); the spectra registration was realized with 250 scans in the 4000-600 cm^{-1} rang. After the registration, the absorption spectra have been electronically superposed using the Spekwin 32 academic software.

Test with phenolphthalein

On the final samples, the presence of MCT-β-CD can be rendered evident by means of a simple test that uses phenolphthalein. An alcoholic 1 % phenolphthalein solution was prepared by means of ethanol. The magenta color appears when *p*H > 9, obtained by NaOH addition. It is very important that the solution *p*H exceeds 9, because at *p*H < 8.5 the solution becomes colorless, according to literature [17-19].

Two drops of this solution were put on each treated sample and was observed the preservation or disappearance of magenta color. On the cotton, untreated sample, two magenta stains appeared, but on the samples grafted with MCT-β-CD there is no stain, because the phenolphthalein dianion penetrates the cyclodextrin cavity, forming a host-guest compound.

The explanation of this behaviour is ascribed to the hydrogen bonds between the two partners when a de-localization of the conjugated π electrons occurs [17-19].

Taking-up degree

Taking-up degree was determined by gravimetric measurements. This index was computed using the equation 1:

$$Y_P = 100\,(W_f - W_i)/W_i \qquad (1)$$

where:

Yp = take-up degree (%);

W_i = initial mass of sample (i.e. before wrinkle-proofing) expressed in grams;

W_f = final mass of sample (i.e. after wrinkle-proofing) expressed in grams.

Wrinkle-proofing angles (WRA) were determined according to the German standard DIN 53890, on Metrimpex FF-01 apparatus [20-26]. Each WRA value was determined as the average of 10 measurements along two directions: warp and weft.

Table 1

EXPERIMENTAL PROTOCOL

TWO witnesses				*Final samples*	
FIRST WITNESS		*SECOND WITNESS*			
Code first witness	*Solution for padding*	*Code**	*Solution for padding*	*Code final sample*	*Solution for padding*
W0	Untreated cotton	-	-	-	-
W1	-	-	-	W1	20% MCT-β-CD NaOH (pH = 12) (15 minutes)
W2	10% acetone (15 minutes)	W2E	10% acetone 1% ethylene diamine (15 minutes)	S4	20% MCT-β-CD NaOH (pH = 12) (15 minutes)
W3	10% octanal (15 minutes)	W3H	10% octanal 0.02 mL HCl conc. (as catalyst) (15 minutes)	S5	20% MCT-β-CD NaOH (pH = 12, (15 minutes)
W4	10% octanal (5 minutes)	W4H	10% octanal 0.02 mL HCl conc. (as catalyst) (5 minutes)	S6	20% MCT-β-CD NaOH (pH = 12) (15 minutes)

* the initials H and E from the code for the second witness come from the first letter of the name of activating agent (hydrochloric acid and ethylene diamine)

Statistical analysis of WRA values

In this work were calculated the standard deviation (SD), the standard error of the mean (SEM) and the coefficient of variation (CV). These values were calculated using a MATLAB software [27, 28] where the standard deviation SD of the set of distinctive statistic data $\{WRA_1, WRA_2,\ldots WRA_{10}\}$ was calculated with the equation 2:

$$SD = \left[\frac{\sum_{i=1}^{n} \left(WRA_i - \overline{WRA}\right)^2}{n} \right]^{1/2} \tag{2}$$

where:

SD - standard deviation (shows the degree of WRA values dispersion);

n - number of experiments (n = 10).

The standard error of the mean and the coefficient of variation were calculated using the equations 3 and 4:

$$SEM = \frac{SD}{n^{1/2}} \tag{3}$$

where:

SEM - standard error of the mean;

n - number of experiments (n = 10).

$$CV = \frac{SD}{\overline{WRA}} \times 100 \tag{4}$$

where:

CV - variation coefficient;

SD - standard deviation;

$\overline{WRA}$ - the average of WRA.

Results and discussions

MCT- β - CD grafting onto cotton

The presence of MCT-β-CD in the two systems is extremely important because the chlorine atoms attached to the triazinic cycle of β-CD are responsible for the grafting onto cotton of some derivatives obtained from interacting with each of the two carbonyl compounds. For understanding the mode of action of each derivative of MCT-β-CD used in this paper, it is necessary to present both the analysis of FTIR of MCT-β-CD powder (fig. 2 and table 2) and comparative analysis of two spectra 1) MCT-β-CD grafted on cotton; 2) untreated cotton (fig. 3).

The grafting MCT-β-CD on cotton is possible only in the presence of a catalyst (NaOH) when the condensation temperature of the pad-dry-cure technology is higher than 160°C.

The presence of MCT-β-CD on cotton is indicated, clearly, in figure 3.

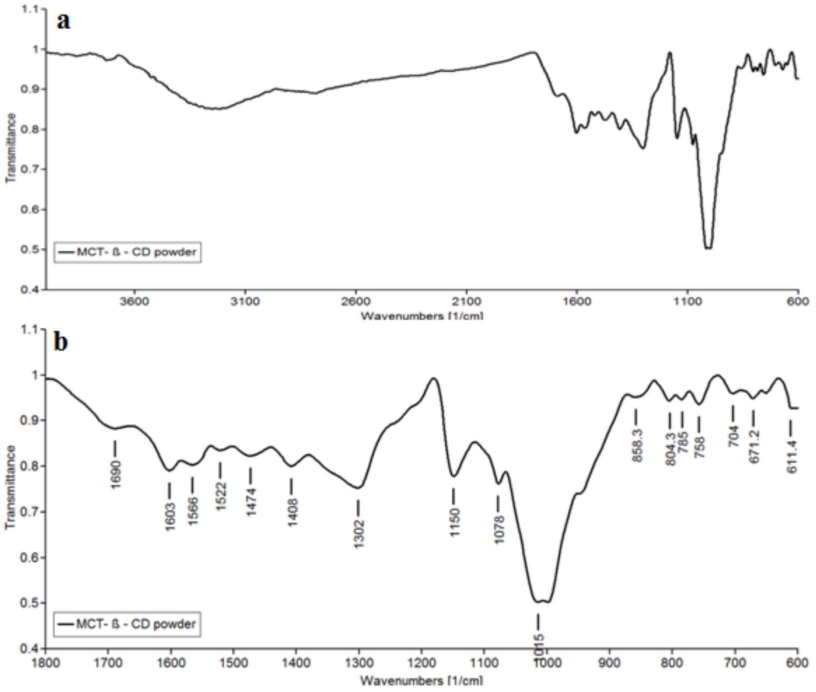

Fig. 2. FT-IR spectrum for MCT- β –CD powder between 4000-600 cm^{-1} (a) and detail in 1800-600 cm^{-1} (b) on wavenumbers

Table 2

THE MAIN ABSORPTION BANDS FOR MCT-β-CD POWDER

IR (cm^{-1})	Assignments
3276	OH stretching
2923-2784	CH stretchings
1603	water absorption
1527	C=N stretching
806-783	C-Cl stretching

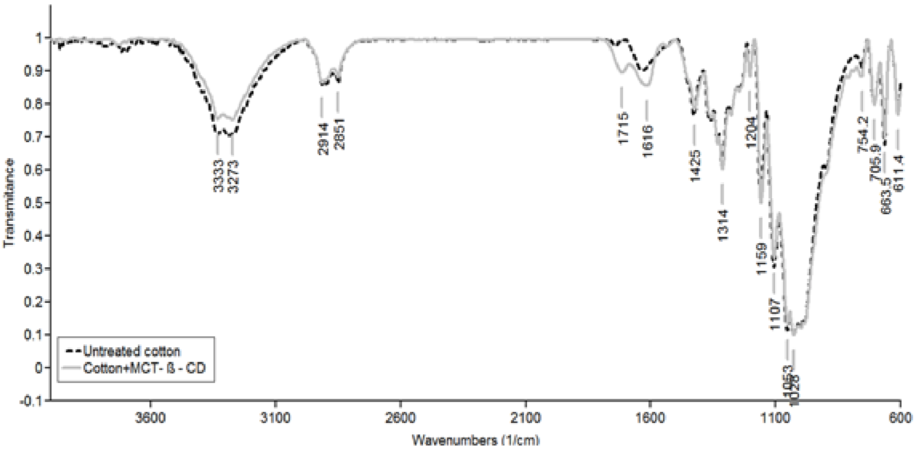

Fig. 3. Comparative FTIR spectra: untreated cotton and cotton grafted with MCT-β-CD

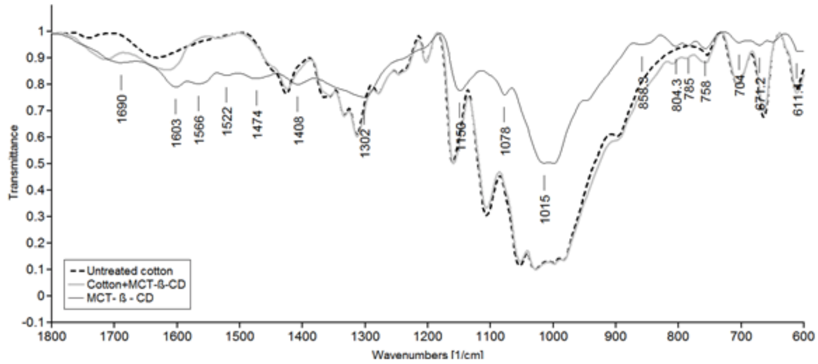

Fig. 4. Comparative FTIR spectra between 1800 - 600 cm^{-1} wavenumbers

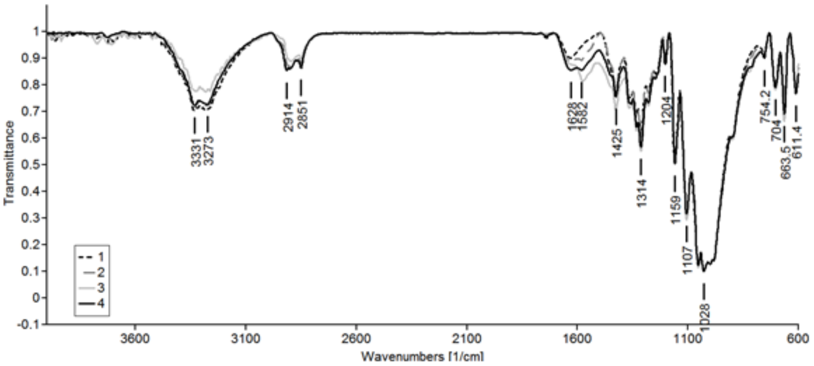

Fig. 5. FTIR spectra for untreated cotton (1), cotton + acetone (2), cotton + acetone + ethylene diamine (3) and cotton + (acetone + ethylene diamine) + MCT-β-CD (4)

The presence of MCT-β-CD onto cotton is confirmed by the appearance of the peak at 1532 cm^{-1} (C=N stretching from triazine), the increase of the height of peaks from 1603 cm^{-1} (water absorption by β-CD) and the appearance of peaks at 804.3 and 785 cm^{-1} (corresponding to chlorine atoms bound to MCT cycle and not involved in the chemical reaction with cellulose; it is known that Catavex product has 3 MCT cycles). The ether bonds [29-31] formed between the cotton sample and MCT-β-CD are highlighted by the presence of peaks from 1028 and 1204 cm^{-1} afferent to C-O-C symmetric and asymmetric vibrations (figs. 3 and 4).

System (acetone + ethylene diamine (ED)) + MCT-β-CD

Acetone interaction with ED (first stage) forms an imine (Schiff base). This fact is confirmed by the appearance of two peaks on cotton + (acetone + ED) spectrum (fig. 5): 1) at 1532 cm^{-1}, assigned to the primary NH_2 group of ED (final group not involved in the chemical reaction for the formation of Schiff base; it is known that ED is a symmetric diamine NH_2-CH_2-CH_2-NH_2); 2) at 1582 cm^{-1} for C=N stretching from Schiff base [29-31].

Getting the Schiff base in contact with MCT-β-CD generates a compound based on the formation of an amine bridge between the two partners, from the interaction of a Cl atom of MCT-β –CD and the NH_2 group from the Schiff base. This new compound has a big length (therefore, a big number of C-C bonds), which will determine the increase of the peaks from the range 2914-2851 cm^{-1} and 1425-1358 cm^{-1}. In the final sample (i.e. cotton + (acetone + ED) + MCT-β-CD), the peak afferent to the C=N group (from the Schiff base, as well as from each triazine cycle attached to β-CD) appears shifted at 1582 cm^{-1}, while the chlorine attached to triazine but uninvolved in chemical reactions appears shifted at 806 cm^{-1}.

The compound obtained from the reaction (acetone + ED) + MCT-β-CD is bound to cotton through ether bridges realized from the interaction of the primary OH group of cellulose and a chlorine atom situated on the second triazine cycle attached to β-CD. This ether bridge is confirmed by the increase of the peaks from 1028 cm^{-1} and 1204 cm^{-1} afferent to C-O-C symmetric and asymmetric vibrations.

The values of the taking-up degrees and wrinkle-recovering angles (WRA) for the witness samples (W0, W2), semi-final sample (W2E) and final sample S4 are indicated in table 3.

The hierarchy of the increasing of taking-up degrees and wrinkle-recovering angles is the following: W0, W2, W2E, and S4.

The presence of MCT-β-CD is confirmed only in the case of the sample S4, by the disappearance of magenta stains (at test with phenolphthalein) and the highest values of the taking-up degrees and WRA.

Table 3

GRAFTING RESULTS FOR SYSTEM (ACETONE + ETHYLENE DIAMINE) + MCT-β-CD

Sample	Code sample	Taking-up degree (%)	Statistical analysis of WRA				FF^d Test
			$\overline{WRA}$ (degrees)	SD^a	SEM^b	CV^c	Stain/no stain
Untreated cotton	W0	-	168	1.15	0.36	0.68	stain
Cotton+ acetone	W2	0.8	173	1.09	0.35	0.63	stain
Cotton+(acetone+ ED)	W2E	3.63	180	1.41	0.45	0.78	stain
Cotton+[(acetone+ED) + MCT-β-CD (with NaOH catalyst]	S4	9.31	186	1.18	0.37	0.64	no stain

[a] *SD is the standard deviation;*

[b] *SEM is the standard error of the mean;*

[c] *CV is the coefficient; of variation;*

[d] *FF is the abbreviation for phenolphthalein.*

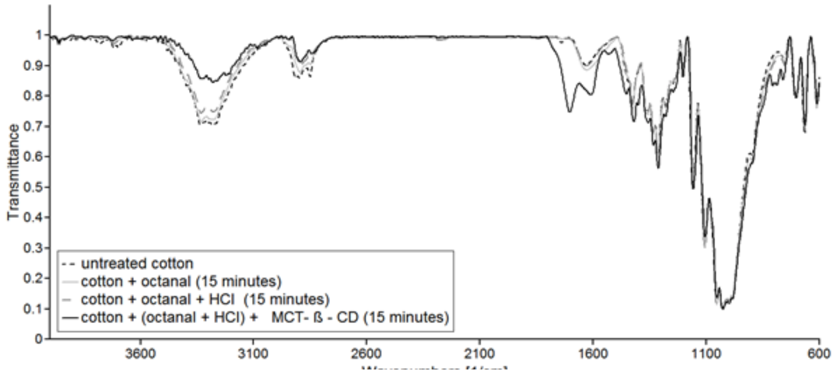

Fig. 6. FTIR spectra for (octanal + HCl) + MCT-β-CD system (contact time 15 min)

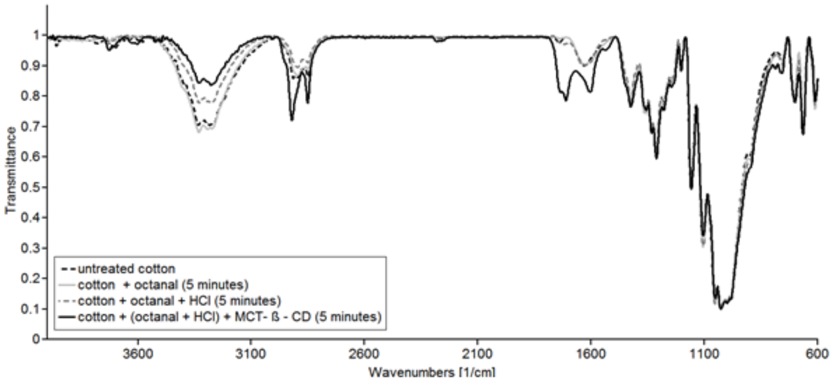

Fig. 7. FTIR spectra for (octanal + HCl) + MCT-β-CD system (contact time 5 min)

System (octanal + HCl) + MCT-β-CD

To study this system was used two times contact: (a) 15 min; (b) 5 min.

a)System (octanal + HCl) + MCT-β-CD (15 min): octanal and HCl are maintained in contact during the first 15 minutes under intense stirring; during this time interval, octanal reacts with HCl, forming the corresponding chlorohydrin. Then, MCT-β-CD is added, stirring the mixing intensely for 15 min. The material is padded with this solution, dried at 100°C for 3 min, and cured at 160°C for 3 min.

As the FTIR spectrum of the final sample indicates, one obtains one COO group, whose presence is confirmed by the significant increase of the height of the peak at 1703 cm^{-1} (C=O stretching from ester). Perhaps, the chlorine from chlorohydrin reacted with Na from the ONa group attached to the triazine group from β-CD during the condensation, NaCl being eliminated. The presence of an ester is also confirmed by the characteristic aspect of the absorption band from the range 3331-3221 cm^{-1} (fig. 6) which is yet the result of overlapping the OH stretching of alcohol type.

The presence of octanal on the cotton samples is evidenced by increasing peak at 1628 cm^{-1} (for the C=O stretching) [29-31]. The addition of HCl used as an octanal activation (for conversion into the corresponding chlorohydrin) has a negative effect: it causes the degradation of the cellulosic support, as evidenced by the lower peaks in the 2920 - 2851 cm^{-1} (afferent to C-H stretchings).

As in the previous figures (figs. 3 and 4), the MCT-β-CD presence on the final sample is more than obvious. An ether bond is realized between the final compounds (product resulted from chlorohydrin reaction with MCT-β-CD) and the cellulose from the cotton sample, due to the interaction of cellulose primary OH group and Cl attached to triazine cycle from β-CD. The increase of the peaks at 1028 and 1204 cm^{-1} afferent to C-O-C symmetric and asymmetric vibrations confirms this ether bridge [29-31].

b) System (octanal + HCl) + MCT-β-CD (5 min) is applied similar to the previous one (at the point a), the difference consisting in the reactants contact time: 5 min instead of 15 min. The reaction between reactants occurs as in the same manner, with the formation of an ester group between the chlorohydrin (obtained from interaction of octanal with HCl) and MCT-β-CD. The only difference is that the smaller contact time generated both a smaller yield of the chemical transformations (the reason that the characteristic allure of carboxyl acids in the range 3331-3221 cm^{-1} is less evident), as well as a poorer degradation of the cotton due to HCl presence (fig. 7). The poorer degradation is noticeable at the final sample due to higher peaks afferent to C-H stretching (2920-2851 cm^{-1}), probably due to a bigger number of C-C bonds from the chlorohydrin and MCT-β-CD attached to cellulose, which will determine bigger WRA values (table 4).

The contact time between (octanal + HCl) and cotton is extremely important because it influences the degree of degradation of the textile support. Taking into account the fact that the two systems with octanal were identical as concentrations of reagents used, the influence of the contact time is evidenced by figure 8 where the comparison of final samples indicate that a short time (5 min) is more appropriate because it does not cause degradation. Degradation of cellulosic support is evidenced by the size of the peaks in the areas 2920-2851 cm^{-1} and is afferent to C-H stretchings.

The values of taking-up degrees and wrinkle-proofing angles for the samples treated with octanal (for times contact 15 and 5 min), and for cotton sample grafted with MCT-β-CD (samples S5 and S6) are presented in table 4. The phenolphthalein tests indicate the presence of MCT-β-CD only for the final samples S5 and S6. The disappearance of the magenta stain from the samples S5 and S6 indicates the MCT-β-CD presence as the result of grafting the derivate obtained from the reaction (octanal + HCl) + MCT-β-CD.

Conclusions

The interaction between the two carbonylic compounds (acetone and octanal) with MCT-β-CD is confirmed by FTIR spectra; the presence of MCT-β-CD is confirmed by the presence of chlorine atoms not involved in chemical reactions (but attach on the triazinic cycle of β-CD) and the disappearance of the magenta stains at the

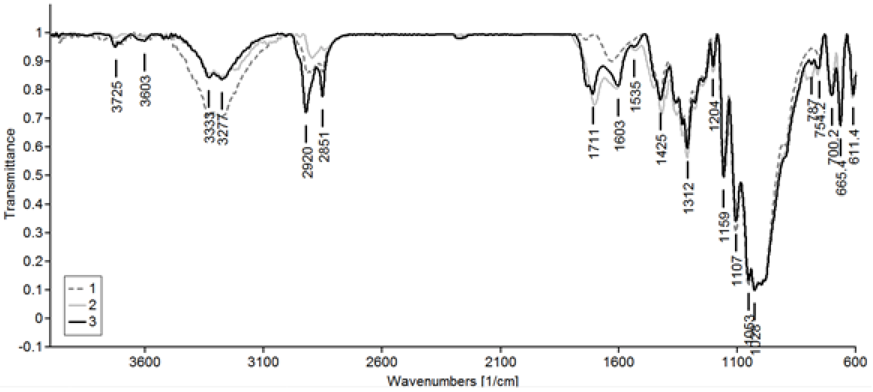

Fig. 8. FTIR spectra for untreated cotton (1), cotton + (octanal + HCl) + MCT-β-CD (15 min) (2) and cotton + (octanal + HCl) + MCT-β-CD (5 min) (3)

Table 4

GRAFTING RESULTS FOR SYSTEM (OCTANAL + HCl) + MCT-β-CD (15 and 5 min)

Sample	Code sample	Taking-up degree (%)	Statistical analysis of WRA				FF[d] Test
			$\overline{WRA}$ (degrees)	SD[a]	SEM[b]	CV[c]	Stain/no stain
Untreated cotton	W0	-	168	1.15	0.36	0.68	stain
Cotton+ octanal (15 min.)	W3	0.62	210	1.18	0.37	0.56	stain
Cotton+octanal+HCl(15min.)	W3H	0.30	184	1.41	0.45	0.77	stain
Cotton+[(octanal+HCl)+ MCT-β-CD/NaOH](15min.)	S5	18.12	195	1.41	0.45	0.73	no stain
Cotton+ octanal (5 min.)	W4	0.50	190	1.41	0.45	0.74	stain
Cotton+octanal+HCl(5min.)	W4H	0.20	185	0.67	0.21	0.36	stain
Cotton+[(octanal+HCl)+ MCT-β-CD (with NaOH catalyst)] (5 min.)	S6	12.3	196	0.77	0.25	0.39	no stain

[a]SD is the standard deviation;
[b]SEM is the standard error of the mean;
[c]CV is the coefficient; of variation;
[d]FF is the abbreviation for phenolphthalein.

phenolphthalein test. The graftings on cotton of the final MCT-β-CD derivatives were highlighted by the increases of the taking-up degrees and WRA values. The statistical analyses applied on the two systems indicate the following: (1) for the WRA values, the populations studied statistical are homogeneous; (2) the mean values of the WRA are representative of these populations; (3) the standard errors of the mean are very low.

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