Highlighting a Cotton Grafting Process Using the Spectral Subtraction Method and Statistical Analysis

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Spectral subtraction method was used to prove the grafting onto cotton fabrics of some derivatives of glyoxal with monochlorotriazinyl- β -cyclodextrin (MCT- β -CD). Glyoxal was initially brought in contact with HCl. The formed compound was brought in contact with MCT- β -CD, in presence of NaOH as catalyst. The resulted product was applied on cotton samples using the pad-dry-cure technology. The presence of MCT- β -CD on the final samples was confirmed by a spectroscopic analysis (spectral subtraction method) and the phenolphthalein test. Spectral subtraction method notifies any change between two (or more) FT-IR spectra. This method is very useful when the analyzed spectra are very similar and the classic FT-IR analysis fails to clearly highlight what is different between those 2 spectra, because the overlays are illegible. The grafting effects were confirmed by the increases of take-up degrees and wrinkle recovery angles (WRA). The WRA results were statistic analyzed with the standard deviation SD, the standard error of the mean (SEM) and the coefficient of variation (CV). The taking-up degrees considerably increased as compared to the reference samples, and the WRA values depend on the length and the flexibility of the product grafted on cotton.

Keywords: FT-IR, spectral subtraction method, glyoxal, MCT-β-CD, grafting

Due to its poly-functional structure, MCT- β -CD can react with numerous carbonyl products; it is known that the carbonyl group is one of the most reactive organic functions, generally participating in addition reactions. MCT- β -CD can react with aldehyde/aliphatic ketones or with dialdehydes (ex. glyoxal, which is more reactive than the aliphatic aldehydes). Glyoxal (C₂H₂O₂) is also known as Ethanedial; Ethandial; Ethanedione; (CHO) ₂; Biformyl; Diformyl: Diformal; Glyoxal aldehyde; 1, 2-Ethanedione or Etane-1, 2 dione [1, 2]. Glyoxal reactivity is very high and depends on its form of presentation. The anhydrous glyoxal does not exist in a stable form and it can only be produced in laboratory. In exchange, glyoxal is commercialized as 40 % solution, consisting of about 11% glyoxal and the rest is in hydrated forms of gem-diol, dimer and trimer type, [2-7] whose structures are presented in figure 1 [6-11].

The anhydrous glyoxal can react with a water molecule resulting monohydrated glyoxal (equation 1) [10]; the addition of another water molecule can lead to the



Fig. 1. The hydrated forms of 40 % glyoxal solution [6-11]

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dihydrated form of gem-diol form (form I: ethane-1,1,2,2-tetrol) (equation (2)) [3, 6-11].



(gem-diol form)

The form I of glyoxal can polymerize and forms a dimer 2-dihydroxymethyl- (1,3) dioxalane-4,5-*trans*-diol (II), or a trimer Bis(Dioxalane) (i.e. 2,2'-bi-1,3-oxalanyl-4,4',5,5'-tetrol) (III)- both *cis* and *trans* configurations. The existence of these oligomers depends on glyoxal concentration and on pH [3, 6-9]. Both glyoxal dimer and trimer are also di-hydrated forms [10, 11]. The dimer is formed through the reaction of nucleophile addition of two monohydrated molecules, and the trimer is obtained through the reaction of monohydrated form, with the dimer (equations (3) and (4)) [10].



Dimer: 2-dihydroxymethyl-(1,3) dioxalane-4,5-*trans*-diol(II)





In this work was realized the grafting of cotton with a glyoxal - MCT- β -CD derivative. The glyoxal was initially brought in contact with HCl. The formed compounds reacted then with MCT- β -CD. The obtained product was grafted on cellulose, using NaOH as catalyst, and pad-dry-cure technology as method of application. The grafting was confirmed by a spectroscopic analysis (the spectral subtraction), the phenolphthalein test, and the increases of take-up degrees and WRA, respectively.

Experimental part

Materials and methods

The samples subjected to experiments came from a 100 % cotton fabric with specific weight of 100 g/m², previously subjected to desizing and scouring. All the chemical substances were used in this work as such, without previous purification. They were obtained from the companies Sigma Aldrich (glyoxal as 40 % solution), Merck (NaOH, HCl) and Wacker-Chemie (CAVASOL W7 MCT, i.e. monochlortriazinyl beta-cyclodextrin Na-Salt).

In this work were used 2 cotton samples types, as follows: untreated sample (S0) and grafted samples (S1, S2 and S3). Each grafted sample was obtained in 2 stages:

realization of the grafting agent and applying it on the cotton sample. The grafted samples S1 and S2 were obtained using 10% glyoxal (S1) and 10% glyoxal and an activating agent (1% HCl and 15 min stirring for S2). The graftings on S1, S2 and S3 samples were identically performed, on 10 samples of cotton, in order to perform a good statistical analysis of the results / effects.

For the final sample (S3), the grafting agent was obtained in 2 stages: firstly, 10% glyoxal and 1% HCl were stirred for 15 min . Secondly, the *p*H was adjusted at 12 (using NaOH) and 20% MCT- β -CD was added and the stirring was maintained for another 15 min. The final compound/derivative is considered the grafting agent; this agent was applied on the cotton sample using a pad-dry-cure technology; as equipment we used a mini-padder and a minitherm ERNST BENZ AG (Textilmachinen Rumlang- Zurich). The main parameters used for each stage were as follows: 80 % squeezing degree, in padding stage; drying at 100°C for 3 min and condensation at 160°C for 3 min. Finally, the washing and drying (at room temperature) were performed.

Samples S1 and S2 were obtained using pad-dry-cure technologies and the same main parameters, as at S3. All samples, inclusive the final samples (S3) were performed for 10 times, identically, as required by the statistical analysis, for the calculation of the deviations / errors.

FT-IR analyses of all samples were performed on Multiple Internal Reflectance Accessory (SPECAC, USA) with ATR KRS- 5 crystal of thalium 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 range. After the registration, the absorption spectra have been electronically superimposed (having transmittance on Y axis because the bands are more visible) using the IRanalyze software from LabCognition company.

Spectral subtraction method notifies any change between two (or more) FT-IR spectra. This method is very useful when the analyzed spectra are very similar and the classic FT-IR analysis fails to clearly highlight the difference between those 2 spectra, because the overlays are illegible [12, 13]. Spectral subtraction method was used only after all spectra were prepared in a certain way, respecting the following steps: atmosphere correction (CO₂, water), smoothing (with Savitzky-Golay algorithm to attenuate the background noise; the order of the polynomial fit function applied for smoothing was chosen according to the size of noises, namely 9 or higher), baseline correction (concave Rubberband algorithm), normalization, final smoothing and saving in % transmittance of each spectrum. In addition to baseline correction and standard normal variate correction, was used the detrending algorithm, which permitted to correct the drifted baseline and to remove the offset and the tilting from spectra [12]. For an easy understanding of spectral subtraction method, all spectra have absorbance on Y axis. The spectral subtraction method uses the mathematical equation 1[12, 13]:

A grafted sample spectrum - $F \times A$ reference spectrum = result (5) where:

A grafted sample spectrum are the absorbances of grafted sample; A reference spectrum are the absorbances of the reference sample;

F= scalar factor; the intensities of the reference sample are scaled by the scaling factor in advance, by the software. The scalar factor F=1.

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To perform the subtraction operation, the entire spectrum (within the range 4000-600 cm⁻¹ wavenumbers, with a number of points equal to 1764, XTYPE =1, YTYPE=128 and data spacing of 1.92881) was taken into account [12]. The result of the spectral subtraction method is a new spectrum (the difference spectrum) with bands above and below the zero line (i.e. positive and negative values). Positive values indicate that the analyzed samples had higher absorbance intensities than the reference sample. Negative values (i.e. bands located below the zero line) on the difference spectrum indicates that the reference sample had higher values of the absorbance intensity than the analyzed sample [12, 13].

Test with phenolphthalein: was performed according to the indications from the literature [14-16]. The test consists in adding a drop of phenolphthalein (in alcoholic solution) on samples (untreated or treated) and perceiving the presence or absence of magenta stain. A magenta- colored stain is present only on the untreated cotton. The presence of MCT- β -CD on the final samples, leads to the disappearance of the magenta stain.

Taking-up degree was gravimetrically determined by using a digital scale with a very high precision (six decimals). Each value was determined performing measurements on 10 identical samples and computing the arithmetic mean.

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

Statistical analysis of WRA values was performed using MATLAB software [17, 18] The WRA results were statistic analyzed with the standard deviation (SD), the standard

error of the mean (SEM) and the coefficient of variation (CV). These values were calculated as in our previous work [19].

Results and discussions

FT-IR analysis of 40 % glyoxal solution

FT-IR spectroscopy (fig. 2) confirms the existence in the 40% solution of a mixture of glyoxal and hydrated forms of the monomer and oligomers (dimer and trimer) [3, 8, 10-14].

Table 1 presents the specific absorption bands. The data from table 1 agrees with those from literature [3, 8-11, 20, 21].

Spectral subtraction method is the best way that can highlight the presence of grafting agent on the cotton sample.

Spectral subtraction method applied for Glyoxal + *MCT*-β-*CD system*

Initial, the spectral subtraction method was applied for many subsystems (figs. 3 and 4).

According to literature, the 40 % glyoxal solution contains mainly ethane bis-gem diol, i.e. the hydrated form (I) [20, 21]. The diols presence in the glyoxal solution is confirmed by O-H stretching vibration at 3300 cm⁻¹ (very strong intensity, broad); O-H plane deformation vibration at 1450-1330 cm⁻¹ (medium intensity) and C-O stretching vibration at 1100-1000 cm⁻¹ (one or more intense bands) (fig. 3).

In this work, by maintaining the glyoxal solution in contact with HCl for 15 min , dehydration reactions are triggered; some OH groups from the gem diol forms (I) or from dimer and trimer are transformed in C=O (aldehyde type), which generates vibrations at 1746 cm⁻¹ (fig, 3). By applying the dehydration product on a cotton sample



Wavenumbers (cm ⁻¹)	Assignment	
3399	OH stretching	
2852	C-H stretching (as a shoulder)	
1639	Overlapping of O-H scissoring bend of liquid H2O and C-H stretching	
1386	Overlapping of CH bend with OH bend	Table 1
1280	Overlapping of CH bend (in monomer and trimer) with OH bend	ABSORPTION BANDS
1174	n ^a C-C linkage (trimer)	CHARACTERISTIC
1072	Overlapping of n C-OH stretching (gem diol) with n C-C stretching (trimer)	FOR 40 % GLYOXAL
1021	overlapping of n C-O stretching with C-OH bend	SOLUTION
1009	n C-OH	-
970	Overlapping of n C-O-C stretching with C-C (linkage)	
950	Dioxalane and nondioxalane linked C-O-C asymmetric stretch	-
865	Overlapping of n C-O stretching (for monomer and dimer) with deformation OH	
812	Overlapping of n C-O (mono, dimer) with OH bend	
770	O-C-O bending (ring in trimer)	
760	O-C-O bending (monomer)	

^an= normal linearity, for an aliphatic chain.



Fig. 3. FT-IR spectra: spectra overlapping (a) and the result of spectral subtraction (b)

Wavenumbers (1/cm)

through pad-dry-cure technology, one can notice the presence of a C=O group (at 1746 cm⁻¹) and OH groups (from the dimer or trimer), observable by slightly higher peaks at 1053 and 1107 cm⁻¹. Yet, within the range 3333-3273 cm⁻¹ appears a decrease of the heights of peaks corresponding to OH stretching as the result of intermolecular bonds between the glyoxal solution and the neighboring chains of cellulose polymer (broad strong intensity). Another explanation of the decrease of peaks from this range could be the involvement of the OH groups in ether bonds with cellulose, which is possible in acid catalysis.

The utilization of HCl as catalyst also generates a slight degradation of the textile support, manifested through the decrease of peaks height within the range 2851 - 2916 cm⁻¹, assigned to C-H vibrations. The small degradation effect manifested by HCl can be confirmed by the comparison of FT-IR spectra (for cotton+ glyoxal (without HCl) and cotton + glyoxal in acid solution (HCl)), within the range 2851-2916 cm⁻¹. This fact can see clearly in figure 3, as negative values on the difference spectrum. At 1630 cm⁻¹ appears the water absorption deformation (vibration) band, which is more pronounced in the case of cotton grafted with glyoxal (appear below zero line), as compared to cotton grafted with glyoxal, in the presence of HCl.

The explanation is based on water elimination (and the C=O groups are remade) in the glyoxal-hydrated forms, in the presence of HCl.

In order to understand the behavior of MCT- β -CD on cotton, firstly were realized and analyzed the spectra of MCT- β -CD powder and cotton grafted with MCT- β -CD in base catalysis (NaOH) (fig. 4).

In figure 4a the presence of MCT- β -CD can be confirmed by the appearance of some peaks specific to C=N bonds from triazine cycle (1535 cm⁻¹), by the chlorine not-involved in the chemical reactions (787 cm⁻¹), as well as by the ether bonds formed between the textile support and MCT- β -CD (noticeable by the presence of peaks from 1028 and 1204 cm⁻¹, afferent to C-O-C symmetric and asymmetric vibrations). Figure 4b can highlight more clearly the presence of MCT- β -CD onto cotton with the help of the positive values appeared in the difference spectrum.

Cotton grafted with the final compound resulted from the reaction glyoxal/H⁺ with MCT- β -CD/NaOH is illustrated in figure 5. The presence of MCT- β -CD on the final sample (S3) is confirmed by the appearance of the peak at 1535 cm⁻¹ (in-plane stretching mode, assigned to C=N group from triazine ring) and the peak at 787 cm⁻¹ (corresponding to chlorine atoms bound to MCT cycle and not-involved in the chemical reaction with cellulose; it is known that



Fig. 4. FT-IR spectra: spectra overlapping (a) and the result of spectral subtraction (b)

CAVASOL W7 MCT product has 3 MCT cycles) (fig. 5a). On the difference spectrum (fig. 5b) all these peaks give positive values.

As the reaction with MCT- β -CD occurs in alkaline medium (NaOH), this leads to a disproportioning reaction (Cannizzaro reaction) of the mono/di-hydrated forms of glyoxal, generating glycolates). The increase of the height of the peak at 1705 cm⁻¹ confirms the presence of the COO⁻ groups from glycolates. Having a strong polar character given by the COO⁻ and OH groups, these glycolates will not penetrate the β -CD cavity, but will react with MCT- β -CD by means of the chlorine atoms, also forming ether bonds.

NaOH used in this work has a multiple role: a) neutralizes HCl; b) favors the reaction of disproportioning and glycolates generation; c) produces certain degradation of the textile support; d) serves as catalyst for MCT- β -CD grafting stage, favoring the formation of ether bonds between the following partners: 1) primary OH group from cellulose and chlorine atom attached on triazine ring from the newly-formed derivative, chlorine-triazine- β -cyclodextrin-**O**-glycolate (with an etheric bond); 2) OH from glycolate and Cl from another MCT cycle attached by β -cyclodextrin.

This behaviour is confirmed by the following changes:

- the increase of the peaks height at 1204 and 1157 cm⁻¹ (symmetric and asymmetric C-O-C) (fig. 5a and positive values in fig. 5b);

- the decrease of the absorption bands of C-H stretching from the range 2847-2897 cm⁻¹;

- the decrease of the peaks in the range 3395 - 3271 cm⁻¹ due to the implication of OH group in ether groups, and respectively due to the formation of some partial networks.

Figure 5b it is the difference spectrum, as a result of the subtraction method and has positive and negative values. The positive values indicate that the absorbance intensities of the analyzed sample were bigger than those of the reference sample. Instead, the bands located below the

zero line (negative values) on the difference spectrum indicate that the reference sample had higher values of the absorbance intensity than the analyzed sample.

Grafting results

In literature there are many works that shown the modification of cellulosic fabric with glyoxal or β -cyclodextrin is possible [14-16, 22-26]. However, the grafting of cotton with glyoxal - MCT- β -CD derivatives has not been studied.

Taking-up degrees results: the derivative obtained from the reaction of glyoxal/H⁺ with MCT- β -CD leads to an increase of the mass of the final sample, S3; this fact could confirm the grafting process. Table 2 presents the takingup degrees and the phenolphthalein test results for the Glyoxal + MCT- β -CD system. The data from table 2 indicate that the final sample (S3) have the biggest takingup degree, namely 13 %.

Phenolphthalein test: the two drops of basic phenolphthalein solution put on the cotton untreated sample generate two magenta stains. Stains appeared on the samples S1 and S2.

Instead, on the final sample (S3) there is no stain, because the phenolphthalein dianion penetrates the cyclodextrin cavity, forming a host-guest compound. The important role in the disappearance of magenta color is ascribed to the hydrogen bonds between the two partners when a de-localization of the conjugated π electrons occurs [14-16].

Anti-creasing effect is highlighted by the arith<u>metic</u> mean of wrinkle recovery angles, abbreviated with WRA. To calculate the arithmetic mean of WRA we used the determinations performed on the 10 identical samples of S0, S1, S2 and S3 types. The results are shown in figure 6.

Figure 6 indicates that the untreated cotton sample had the lowest value for WRA (168 degrees), being followed by the sample treated with glioxal/H⁺ (171 degrees); the using of HCl (on the sample S2) supports the hypothesis of



Sample	Code	Taking-up	FF ^a test			
	sample	degree	(Stain/no			
		(%)	stain)			
Untreated cotton	S0	-	stain			
Cotton+ glyoxal	S1	1.20	stain			
Cotton+ Glyoxal/H ⁺	S2	6.45	stain			
Cotton+[(Glyoxal/H ⁺) +	S3	13.0	no stain			
MCT-β-CD/NaOH]						
EE is the abbraulation for above labthalain						

FF is the abbreviation for phenolphthalein.

Fig. 5. FT-IR spectra for glyoxal + MCT-β-CD system: spectra overlapping (a) and the result of spectral subtraction (b)

Table 2TAKING- UP DEGREES AND THEPHENOLPHTHALEIN TEST RESULTSFOR THE GLYOXAL + MCT-β-CD SYSTEM



Sample	Coue	30	SEM	
Untreated cotton	S0	1.15	0.36	0.68
Cotton+ glyoxal	S1	0.54	0.17	0.29
Cotton+ Glyoxal/H ⁺	S2	1.12	0.35	0.65
Cotton+[(Glyoxal/H+)+	S3	0.72	0.23	0.38
MCT-\beta-CD/NaOH]				

^aSD is the standard deviation,

*SEM is the standard error of the mean;

^eCV is the coefficient of variation;

a certain damage of the textile support. Final sample (S3) grafted with glyoxal- MCT- β -CD derivative had the biggest WRA (188 degrees).

Statistical analysis of WRA: the results indicate that the population studied statistical is homogeneous and the average values corresponding to the WRA are representative of this population. In addition, the standard errors of the mean (SEM) and coefficient of variation (CV) are very low (table 3).

Conclusions

The analysis of the FT-IR spectra completed with spectral subtraction method allowed elucidating the reaction mechanisms. Spectral subtraction method notifies any change between two FT-IR spectra. This method was very useful because the analyzed spectra were very similar and the classic FT-IR analysis failed to clearly highlight what was different between those 2 spectra (when the overlays were illegible). The spectroscopic analysis of the final sample indicated the formation of ether bond between cellulose and the derivative used in this grafting process.

The presence in 40% glyoxal solution of several hydrated forms (gem-diol, dimer and two trimers (*cis* and *trans*)) makes difficult the interpretation of glyoxal behavior in the systems studied in this work.

Grafting of glyoxal - MCT- β -CD derivative onto cotton leads to increasing of taking-up degrees, WRA and to the disappearance of the magenta stain at the phenolphthalein test. The statistical analyses results indicate that the populations studied statistical are homogeneous.

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Fig. 6. WRA values for 10 samples (type S0, S1, S2 and S3), used for realization WRA (the mean of WRA) (same code as in Table 2)

Table 3STATISTICAL ANALYSIS RESULTS

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