

Comparative Study Concerning the FTIR Analysis and the Performances of Chitosan-Based Wrinkle-Proofing Agents

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The utilization of materials without formaldehyde represents an eco-friendly manner to improve the cotton textiles. Chitosan belongs to this category, as it is a natural polymer extracted from shells. As a wrinkle-proofing agent, chitosan can be used as such or chemically modified with polyfunctional products (polyols, polycarboxylic acids). The ascorbic acid, caffeic acid, diclophenac, oxalic acid and butane tetracarboxyl butane acid respectively have been used to functionalize chitosan. The chitosan/ functionalized derivatives were applied on the cotton textile by pad-dry-cure technology. During the padding stage, the corresponding mixture (chitosan and the functionalization agent) was maintained for 15 minutes at the temperature of 100°C in the presence of 2.5% catalyst. Three catalysts were tested, namely MgCl₂, NaH₂PO₄ and ZnCl₂. The curing was performed at 140°C for two minutes. All the studied chitosan-based products have bonded chemically to the cotton textile, a fact proved by the spectroscopic analyses. Moreover, it has been found that crosslinking networks with cellulose are formed in all the cases. The take-up degree, the wrinkle-recovery angle (both in dry and wet condition), the durability of the effect conferred by treatment and the yellowness degree have been determined as performances of the crease-proofing agents.

Key words: Chitosan, functionalization, FTIR, XPS, crosslinking

The improving treatments, like wrinkle-proofing and permanent press, offer the possibility to obtain from 100% cellulose fibers (or blended with synthetic fibers) some crease-proofed articles, which possess self-smoothing capacity after washing, wrinkle recovering capacity both in dry or wet condition, dimensional and shape stability, permanence of stripes and plies with minimum care efforts [1]. For years, formaldehyde (CH₂O) was used for these operations but, given the ecological inconvenience (formaldehyde release in the working medium, high content of residual formaldehyde on the treated material [2]), many countries imposed strict rules concerning its utilization. That is why the crosslinking agents with a low CH₂O content or non-formaldehyde systems are now used more and more. An outstanding finish with non-formaldehyde products can be accomplished with the following substances:

- crosslinking agents without CH₂O (for example cyclic derivatives of methylated urea) [3];
- dimethyl glyoxal urea [4];
- polycarboxyl acids of the type: dicarboxyl acids (maleic acid, malic acid) [5, 6]; tricarboxyl acids (citric acid) [7];
- tetracarboxyl acids (butane tetracarboxyl acid - BTCA) [8,9];
- natural polymers used as such or in modified form: reactive derivatives of β-cyclodextrine: MCT-CD (mono-chlorotriazine β-cyclodextrine) [10-12]; chitosan (CS) and its derivatives [13-14].

Chitosan and its derivatives have been used to improve the cotton wrinkle-proofing or to create multiple effects: wrinkle-proofing and antimicrobial effect [15-20]. The crosslinking of cellulose with chitosan can be done through covalent [21,22] or ionic [23,24] bonds to one of the two

chitosan reactive groups, the -OH groups from C₆ and C₃ or -NH₂ group attached to C₂.

This work accomplished a comparative study of the performances offered by chitosan and chemically modified chitosan as wrinkle-proofing agents which covalently bound to cellulose from cotton, forming crosslinking networks. The chitosan modification by means of polyfunctional compounds [polyols (ascorbic acid), mono- or polycarboxylic acids (caffeic acid, diclofenac, oxalic acid and butane tetracarboxyl acid)] has been analyzed from both the spectroscopic point of view and the standpoint of the created wrinkle-proofing effects.

Experimental part

Materials and methods

The experiments were carried out on a 100% cotton textile previously desized and alkaline scoured [25, 26]. The characteristics of the cotton textile were: plain weave, yarn count 19 Tex on warp and 17 Tex on weft, specific weight = 100g/m².

The utilized chemicals and their characteristics are presented in table 1.

Chitosan functionalized with ascorbic acid (AS-CS) which is a polyol having in its structure 4OH groups, its scientific name is *(R)-3,4-dihydroxy-5-((S)-1,2-dihydroxyethyl) furan-2(5H)-one*. Mixing 5% chitosan with 5% ascorbic acid (conditions: 2.5% NaH₂PO₄, T = 100°C, t = 15 min) results in new products which confer good wrinkle-proofing effects.

Also, the following carboxylic acids were used for chitosan functionalization, for exemple: caffeic acid, diclofenac, oxalic acid and butane tetracarboxyl acid.

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Nr crt.	Agent's Name	Abreviation	Chemical structure	Company
1	chitosan	CS		Sigma-Aldrich
3	ascorbic acid	AS		Sigma-Aldrich
4	caffeic acid	AC		Sigma-Aldrich
5	diclofenac	AD		Sigma-Aldrich
6	oxalic acid	AO	HOOC-COOH	Sigma-Aldrich
7	butane tetracarboxyl acid	BTCA		Merck

Table 1
CHEMICALS USED IN EXPERIMENTS
AND THEIR CHARACTERISTICS

Code	Impregnation recipe	Drying/curing recipes
CS	5%Chitosan+2.5%NaH ₂ PO ₂	T _{drying} = 85 °C
CS1	5%Chitosan+2.5%MgCl ₂	t = 2minutes
CS2	5%Chitosan+2.5%ZnCl ₂	
AS- CS	5%Chitosan+5% ascorbic acid +2.5%NaH ₂ PO ₂	T _{curing} =140°C
AC -CS	5%Chitosan+5%cafeic acid+2.5%NaH ₂ PO ₂	t = 2minutes
AD -CS	5%Chitosan+5%diclofenac+2.5%NaH ₂ PO ₂	
AO -CS	5% Chitosan+5% oxalic acid +2.5%NaH ₂ PO ₂	
BTCA- CS	5%Chitosan+5% butane tetracarboxyl acid+2.5%NaH ₂ PO ₂	

Table 2
CODING OF THE SAMPLES
ACCOMPLISHED IN THE WEFT
DIRECTION

Working Procedure

We made 16 samples of 100% cotton textile: 8 samples along the warp and 8 samples along the weft. The treatment conditions and their coding are presented in table 2. Chitosan and its functionalized derivatives were applied through pad-dry-cure technology [1]. The parameters of this technology are as follows:

- chitosan dissolution or its functionalization with polyols or polycarboxylic acids respecting the following working conditions: T = 100°C, t = 15 min in the presence of a catalyst;

- textile padding with the above synthesized crease-proofing agent;

- squeezing down to TG= 80%;

- drying at T = 85°C, t = 2 min;

- curing at T = 140°C, t = 2 min. The efficiency of three catalysts: MgCl₂, NaH₂PO₂ and ZnCl₂ were tested, according to table 2.

Analysis method

FTIR - ATR

The FTIR-ATR analysis of the cotton samples treated with chitosan or its derivatives were performed on Multiple Internal Reflectance Accessory (SPECAC, USA) with ATR KRS-5 crystal of thallium bromide-iodide, having 25 reflections and investigation angle of 45°. This accessory device was attached to the Affinity-1 Spectrometer from Shimadzu (Japan). The spectra were recorded with 250 scans in the 4000-600cm⁻¹ range. After recording, the absorption spectra have been electronically superposed using the Panorama soft from LabCognition Company.

XPS

The XPS analysis of the cotton samples was performed on Axix Ultra DLD Kratos Analytical device with Aluminium monochromatic source (power 150 W) at University Lille 1, France in frame of Regional Platform of Surface Analysis.

Take-up degree (Y_p)

The passage of chitosan/chitosan derivatives from the treatment solution into the textile material at the end of the pad-dry-cure technology can be appreciated by means of the take-up degree Y_p, that was determined by using the equation (1):

$$Y_p = 100 \cdot (W_a - W_b) / W_b \quad (1)$$

Y_p - take-up degree;

W_b⁰ - cotton mass before wrinkle-proofing;

W_b^a - cotton mass after wrinkle proofing.

Wrinkle-recovering angle (WRA)

The wrinkle-proofing effects produced by any wrinkle-proofing agents are appreciated through the values of the wrinkle-recovering angle. The wrinkle-recovering angles were determined by respecting the German standard DIN 53890. A Metrimpex FF-01 apparatus was used to determine the wrinkle-recovering angle along the warp direction and weft direction respectively, as the average of 10 measurements.

Wrinkle-proofing durability

By using the SR EN ISO 105-CO6L1999, the treated samples were tested from the standpoint of wrinkle-proofing effect durability. The tests were performed on a

Mathis Polycolor 2002 machine and consisted in home laundering test. The samples were subject to 5-10 cycles of repeated washings, followed by rinsing with distilled water at 40 °C and drying at room temperature.

Yellowness Index (YI)

The yellowness index (YI) is the index that needs to be calculated in the case of extended exposure or processing in the presence of substances like organic acids, or catalysts like acid salts.

The yellowness index was determined using the Spectroflash SF300/Datacolor Spectrophotometer and the ASTM Method E313/73. The formula used for YI is indicated by eq. (2) [27].

$$YI = (1 - 0.847 \cdot \frac{Z}{Y}) \cdot 100 \quad (2)$$

where YI is the yellowness index of cotton sample and Y, Z are the tristimulus values obtained using D65/10° or C/2° of illuminant/observer.

Results and discussions

Chitosan was studied as a possible eco-friendly wrinkle-proofing agent, both in its initial form (unmodified), and in its functionalized form. The chitosan functionalization can be accomplished by chemical modification with poly-functional substances (polyols, polycarboxylic acids).

FTIR-ATR Analysis of Chitosan

Chitosan is a heteropolymer obtained from chitin through the N-de-acetylating process in alkaline medium. Chitosan has a chemical structure similar to that of cellulose; the difference appears only at the C₂ level when, instead of the secondary OH group (as in cellulose) in the neighboring pyranosic units, an alternance of the aminic groups with -NH-CO-CH₃ acetyl group occurs, the first one prevailing (when the de-acetylating degree is close to 100%).

Chitosan and untreated cotton have very similar IR spectra. The differences between them are due to the amino group at C₂ or group -NH-CO-CH₃ (peaks numbers: 1, 4, 5, 10, 11, 12 and 15). The slight differences appear for absorptions afferent to all vibrations. IR spectra of chitosan and untreated cotton are shown in figure 1.

The groups afferent to chitosan powder and untreated cotton are presented in table 3.

Chitosan effects as wrinkle-proofing agent have been studied by applying it on 100% cotton samples in the presence of three different catalysts: MgCl₂, NaH₂PO₂ and ZnCl₂. It was noticed that each of these catalysts results not only in chitosan grafting on cotton, but rather in the generation of a network between the cellulose macromolecular chains, which is equivalent with the crosslinking of cellulose. These statements are confirmed by the FT-IR spectra presented in figure 2.

Figure 2 presents the spectra resulted after the curing reaction of cotton samples and 5% chitosan in the presence of the three catalysts. It has been noticed that MgCl₂ and NaH₂PO₂ are the most efficient, their spectra being almost identical.

The characteristics of cellulose from cotton fabric were maintained in each spectrum at which is added the contribution of the chitosan. Chitosan presence on the treated sample is proved by the occurrence of the peak at 1543cm⁻¹ (fig. 2 and table 3) which is assigned for primary -NH₂, as it is well known that cotton does not possess amine groups. In the treated samples, the peak from 1636cm⁻¹ increased as the result of the presence of acetyl group from chitosan, the responsible for this vibration being to -C-O stretching. At the same time, one can notice increases of the peaks from the range 2916-2849cm⁻¹. This is due to the increase of absorption specific to asymmetric and symmetric stretchings, as the result of chitosan bonding to the cellulose macromolecular chain.

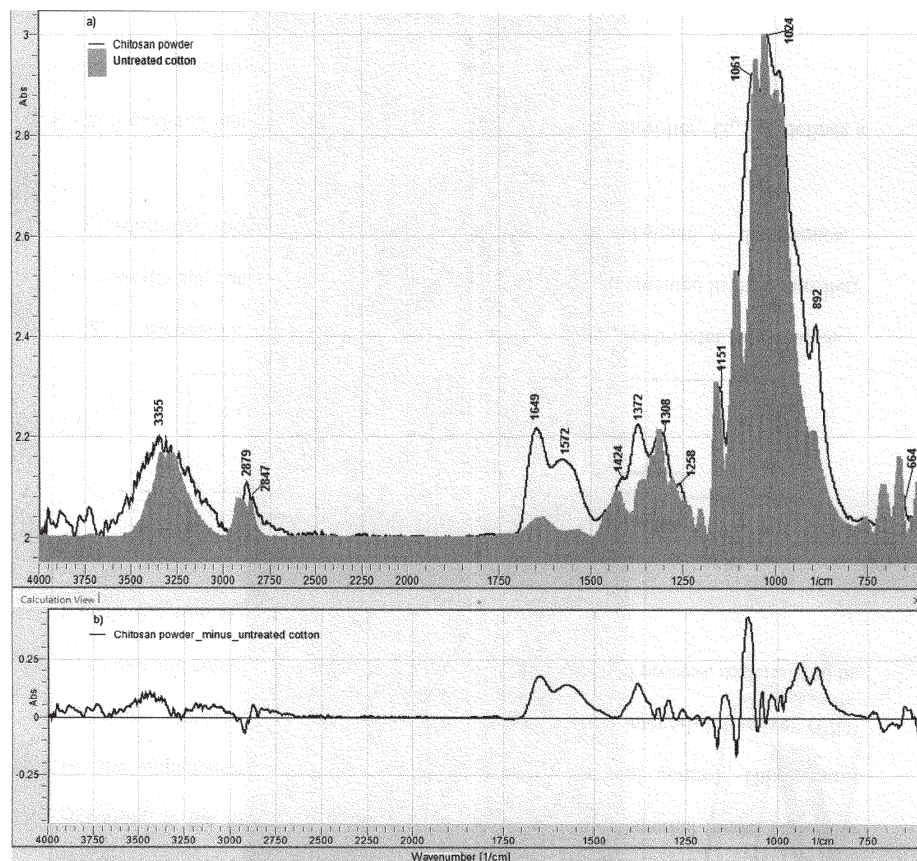


Fig. 1. FTIR-ATR spectra for chitosan and untreated cotton

Chitosan powder				Untreated cotton		
Peak no.	IR(cm ⁻¹)	Assignments	Intensity	IR(cm ⁻¹)	Assignments	Intensity
1	3355	O-H, NH ₂ asymmetric and symmetric stretchings	m, w	3336	OH stretching	s
2	2879	CH ₂ from C ₆ and CH ₃ (from acetyl groups) antisymmetric stretching	m	2916	CH ₂ antisymmetric stretching	w
3	2847	C-H stretching	w	2855	CH stretching and CH ₂ symm. stretching	w
4	1649	NH deformation, amide II	m-s	1630	(Highlights the water presence)	m
5	1572	N-H bending of NH ₂	m	-	-	-
6	1424	CH ₂ bending (From C ₆)	m-w	1430	CH ₂ deformation	m-w
7	1372	CH bending and sym. CH ₃ deformation	m-w	1366	CH deformation	m-w
8	-	-	-	1338	OH deformation	w
9	1308	Overlapping: 1) OH from C ₃ (deformation in plane); 2) CH ₂ (from C ₆) deformation	w m-w	1317	CH ₂ (from C ₆) deformation	m-w
10	1258	Combination; 1) N-C-O stretching, amide IV 2) OH bending	m	1239	OH bending	m
11	1151	Overlapping: 1) Asymmetric bridge oxygen (C-O-C) stretching; 2) CN stretching	m m-w	1160	asymmetric bridge oxygen (C-O-C) stretching;	m
12	1061	Overlapping: 1) C-O stretching of C ₃ -OH; 2) CN stretching	S w	1053	C-O stretching of C ₃ -OH;	m-s
13	1024	C-O stretching of C ₆ -OH	s	1028	C-O stretching of C ₆ -OH	s
14	892	Glucose ring stretching	m	892	Glucose ring stretching	m
15	706	NH, Wagging (broad peak)	s	-	-	-
16	664	OH deformation out-of-plane	w	663	OH deformation out-of-plane	w

Table 3
ASSIGNMENT OF IR BANDS FOR
CHITOSAN AND UNTREATED
COTTON

In order to reveal the treatment-induced modifications, in the detail from figure 2b the spectrum of the standard sample was subtracted from the spectra corresponding to chitosan treated samples. One can notice that cellulose crosslinking occurs as the result of the curing reaction between chitosan and cellulose in the presence of any of the three catalysts, at 140°C. This is proved (fig. 2b) by the negative values from 1153, 1105, 1053cm⁻¹ (corresponding to the secondary and primary OH groups) as the result of the existence of smaller peaks for the treated samples, as compared to the standard sample. If the crosslinking does not occur, these peaks should have been higher than at the untreated cellulose, because chitosan attached to cotton leads to the increase of the number of primary and secondary OH groups. In addition, an increase of the peaks at 1153 and 1020cm⁻¹ (which correspond to C-O-C asymmetrical and symmetrical stretchings) appear, proving the formation of ether bridges between cotton and chitosan during curing.

XPS analyses

In figure 3, the spectra obtained after spectroscopic analysis XPS confirm the realization of chemical bonds between cotton and chitosan.

By comparing the spectra of the untreated sample and those of chitosan powder, one can notice that, besides C1s and O1s atoms, the N1s atoms also appear in the case of chitosan, in amount of 6.41% at.

The chitosan presence in the treated samples is confirmed by two aspects:

- the presence in the treated sample XPS spectrum of the N1s atoms at the position 397, at a percentage of 1.22% (at.);
- the increase of the percentage of C1s atoms (at the position 283) in amount of 77.47%, as compared to 74.90% in the untreated sample.

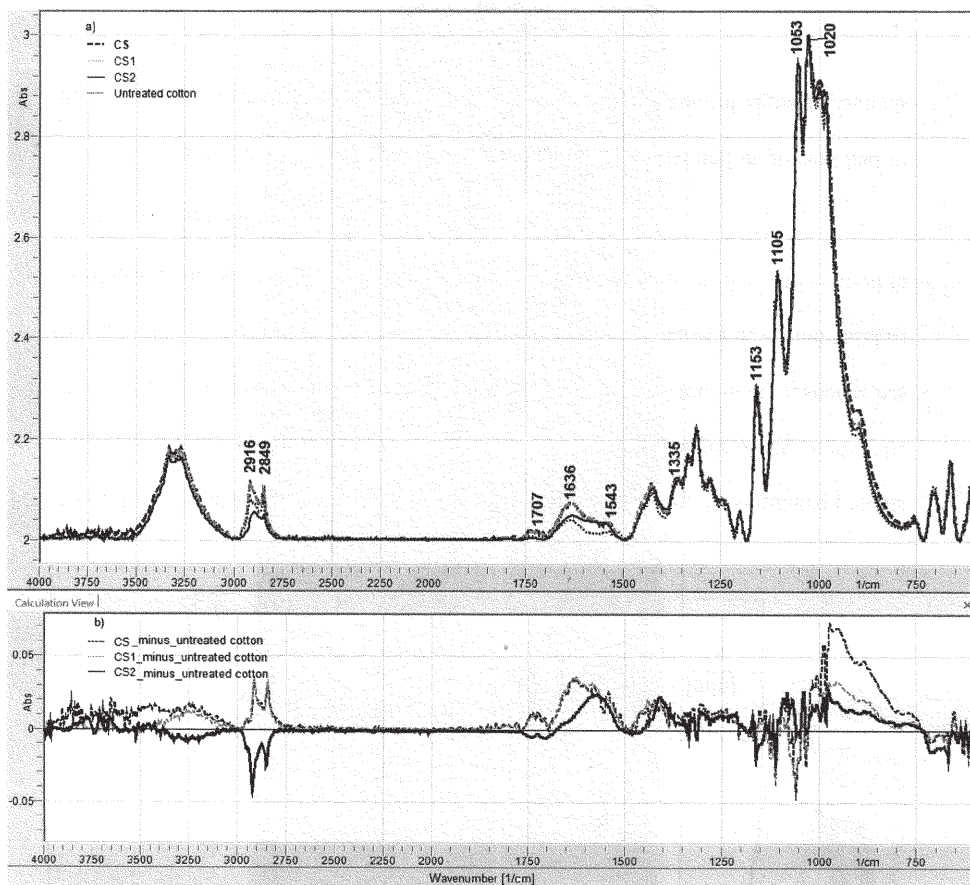


Fig. 2. FTIR spectra:
 a) overlapping spectra for untreated cotton respectively treated with chitosan in presence of catalysts NaH₂PO₂ (abbreviation CS), MgCl₂ (abbreviation CS1) and ZnCl₂ (abbreviation CS₂);
 b) subtraction spectra

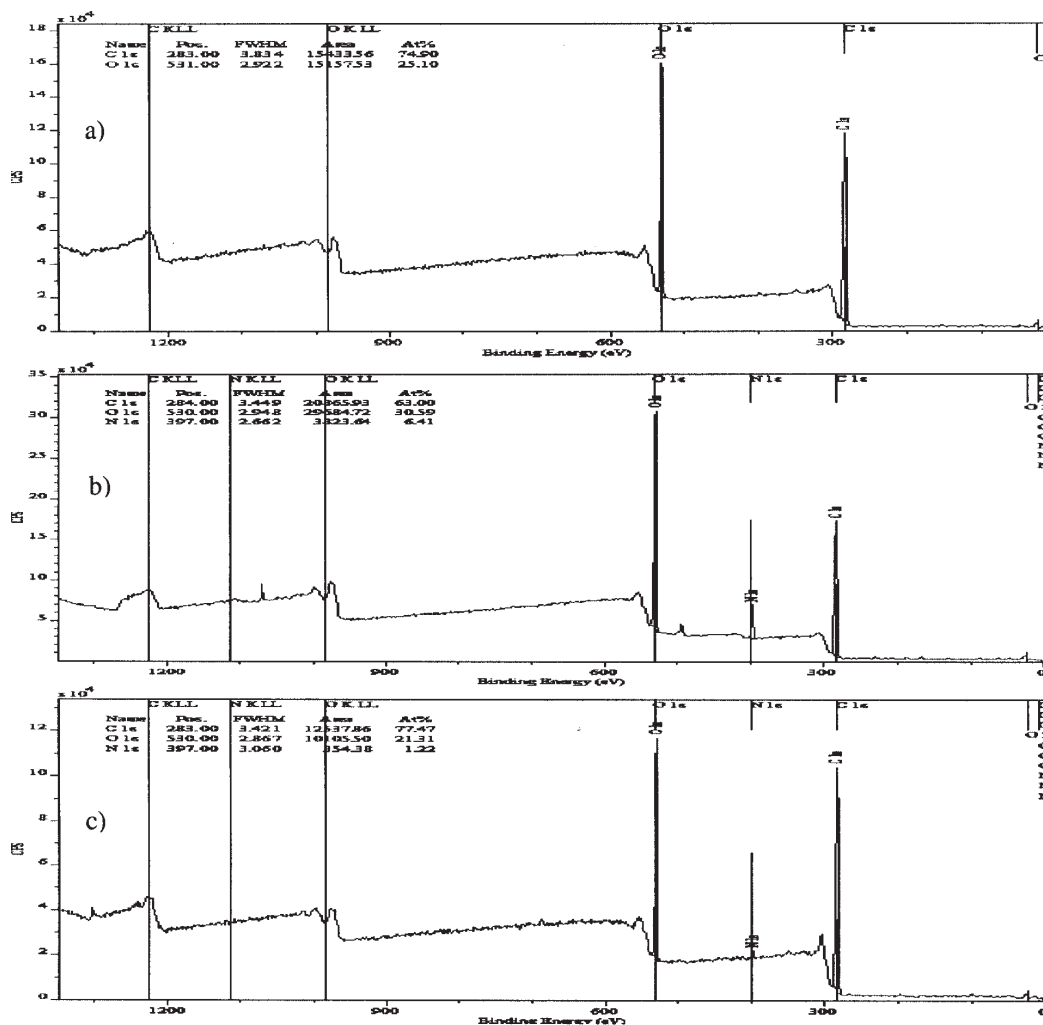


Fig. 3. XPS spectra:
 a) untreated sample;
 b) chitosan powder;
 c) chitosan-treated sample;

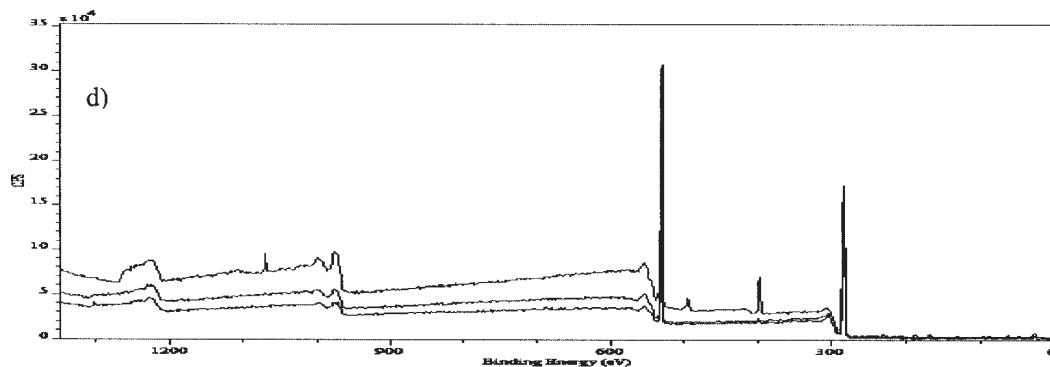


Fig. 3. XPS spectra:
d) overlapping all spectra

Sample code	Sample component	dry WRA	wet WRA	Yi	Y _P [%]	Effect durability [%]	
						Y _P after 5 washings	Y _P after 10 washings
	Control sample	150	139	15.04	-	-	-
CS	cotton+chitosan+ 2.5% NaH ₂ PO ₂	173	158	15.37	2.8	0.57	0.5
CS1	cotton+chitosan+ 2.5% MgCl ₂	177	151	15.31	1.24	0.4	0.38
CS2	cotton+chitosan+ 2.5% ZnCl ₂	170	145	15.5	1.1	0.3	0.25

Table 4
CHITOSAN PERFORMANCES AS
CREASE-PROOFING AGENT

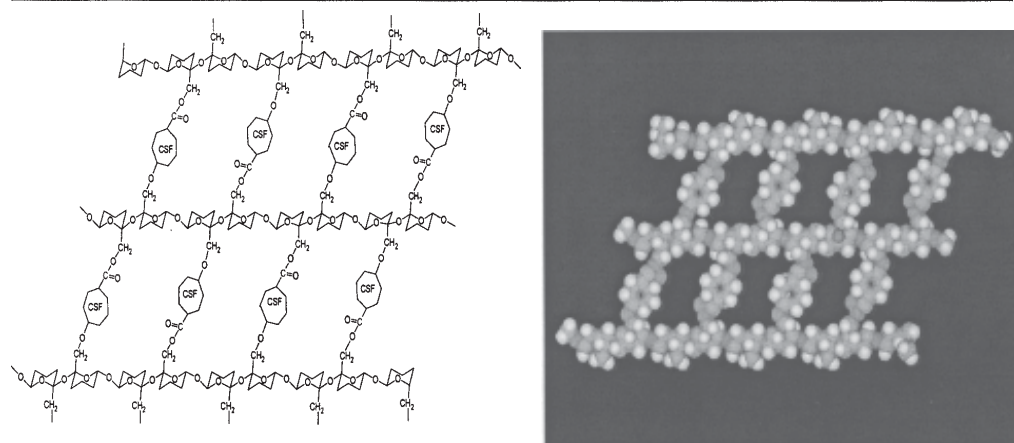


Fig. 4. Chemical structure of crosslinked cellulose through ether and ester bridges between cellulose and chitosan modified through functionalization (abbreviated with HOOC-CSF-OH)

Chitosan performances

Chitosan performances as wrinkle-proofing agent for cellulose have been studied from the point of view of wrinkle-recovering angle (dry WRA and wet WRA), each one being calculated as the sum of the angles along warp and weft), yellowness index Yi after treatment, wet pick-up (determined just after curing reaction), durability of the effect (estimated after 5 and 10 cycles of repeated washings). The values obtained for the performances of chitosan applied on cotton are presented in table 4.

By analyzing the data from table 4, one can infer that NaH₂PO₂ and MgCl₂ have similar effects created by interaction between cotton and chitosan. For both dry and wet samples, wrinkle recovering angles have very close values. The yellowness index Yi is around 15.3, therefore quite close to that of the standard sample. This leads to the assumption that chitosan treatment does not result in cotton degradation. Among the three catalysts, large differences occur only at the levels of wet pick-up and durability of wrinkle-proofing effects. From this point of view, the presence of the catalyst NaH₂PO₂ is more indicated, to the detriment of the other two catalysts (MgCl₂ or ZnCl₂).

FTIR analyses of chitosan functionalized with polyfunctional compounds

Chitosan is an eco-friendly non-formaldehyde product with good wrinkle - proofing effects. In this work we have

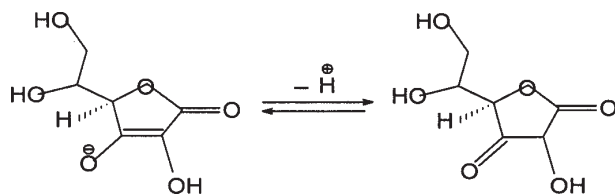
studied the effect of the chitosan derivatives resulted from chitosan reaction with polyols (ascorbic acid, AS) or with carboxylic acids, such as: caffeic acid (AC), diclofenac (AD), oxalic acid (AO) and butane tetracarboxylic acid (BTCA). The reaction conditions were: time of contact 15 min, at the temperature of 100°C, in the presence of 2.5% catalyst. At the end of the curing phase of the pad-dry-cure technology, the cross-linked cellulose is obtained under the condition of utilization of a curing temperature of 140°C in the presence of NaH₂PO₂ as catalyst. We started from the assumption that at least one of the functional groups of every mentioned polyfunctional compound is able to form a covalent bond with chitosan, increasing its functionality due to the increase of the number of HOOC or OH groups, as compared to the unmodified chitosan. The crosslinking of cellulose with these new products (abbreviated as HOOC-CSF-OH) is only based on covalent ether or ester bonds.

All spectra of samples treated with chitosan functionalized with alcohols or carboxylic acids keep the characteristics of cellulose, adding the characteristics of chitosan modified by functionalization.

FTIR analysis for chitosan functionalized with a polyol, ascorbic acid (AS-CS)

The presence of several functional groups (OH and C=O groups) in the ascorbic acid makes possible both the

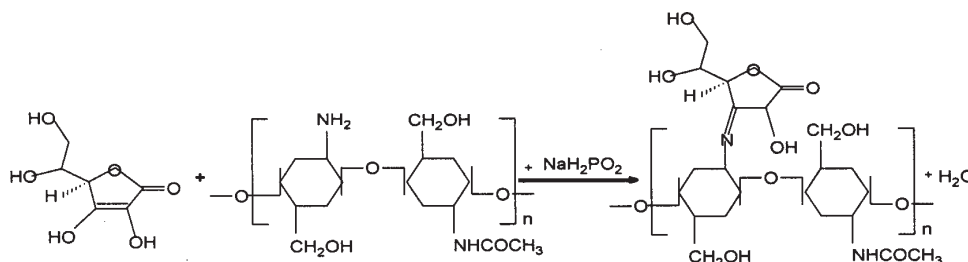
reaction with chitosan (by generating a covalent bond), and the crosslinking reaction of cellulose (by generating ether bridges (C-O-C) during the curing operation). In the presence of chitosan, which has several $-NH_2$ reducing groups, ascorbic acid behaves as an oxidizing agent, due to the presence of the two $-C=O$ groups from its diketone structure, (scheme 1):



Scheme 1

This is possible because ascorbic acid converts very quickly in two unstable diketone tautomers through protons transfer, even if it is more stable in the enol form. The enol proton is lost and regained by the double-bond electrons, producing a diketone. There are two possible forms: 1,2-diketone and 1,3-diketone. This fact is confirmed by chemical reactions 1-2 and figure 5.

Chitosan reacts with ascorbic acid according to chemical reaction (scheme 2).



Scheme 2

The difference between the spectra afferent to samples treated with chitosan and respectively with chitosan functionalized with ascorbic acid, was made by means of the Panorama 3.2 software. We proceeded to the subtraction of the absorptions of vibrations afferent to the peaks of the samples treated with modified chitosan minus that of sample treated with unmodified chitosan. In this way, the ascorbic acid influence is clearly shown. As compared to the sample treated only with chitosan, the

sample treated with chitosan functionalized with ascorbic acid (in the presence of NaH_2PO_2) has two smaller peaks within the range $3331-3271\text{cm}^{-1}$ (also revealed by the negative values from fig.5b), as the result of the increased number of $-OH$ groups from the ascorbic acid. At 1570cm^{-1} the characteristic absorption $-C=C$ stretch vibration from the 4 ring cyclical alkenes was recorded. The $-C=O$ stretching vibration appears at 1639cm^{-1} . In addition, increases the peak from 706cm^{-1} (assigned for $-NH$ deformation vibration, out-of-plane).

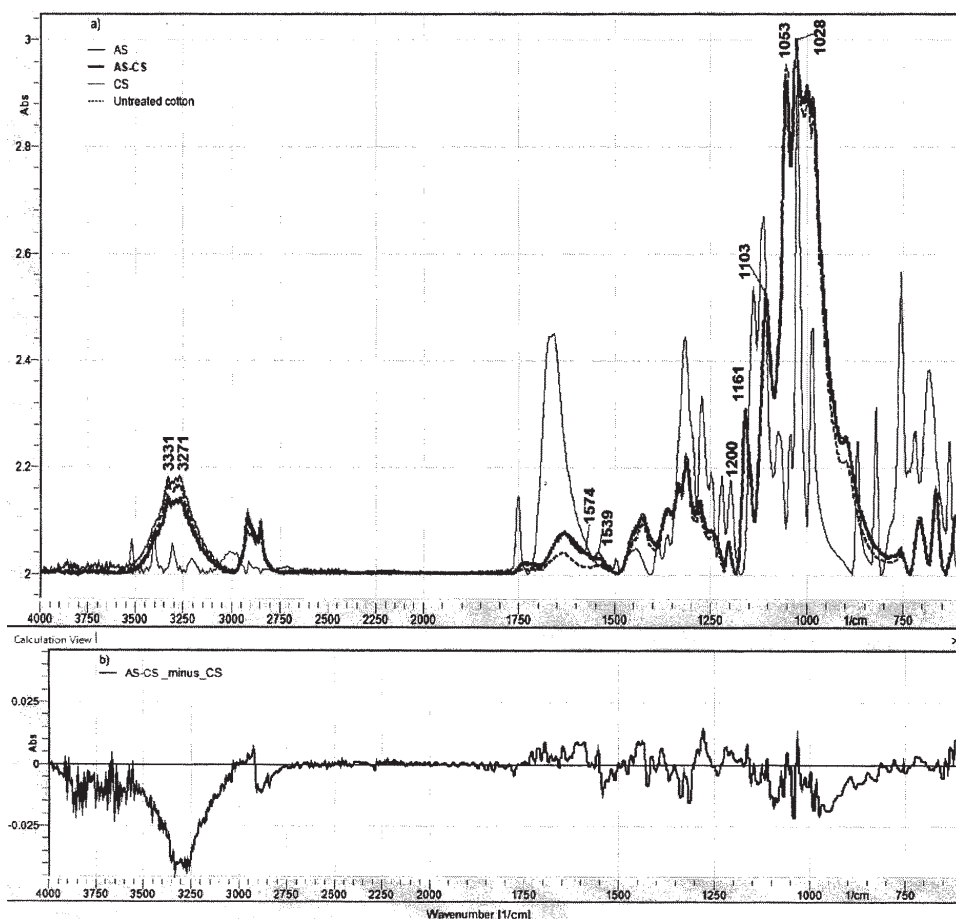
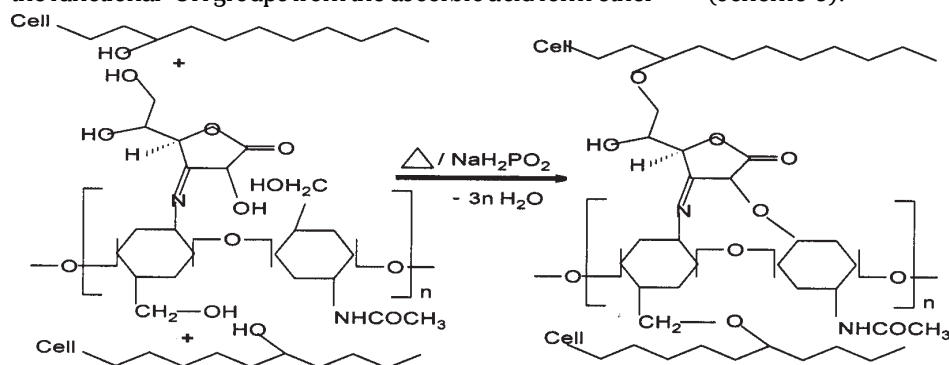


Fig. 5. FTIR spectra: a) overlapping spectra for pure ascorbic acid (AS), untreated cotton and cotton treated with non-functionalized chitosan (CS) respectively by chitosan functionalized with ascorbic acid (AS-CS); b) subtraction operation

At the same time, the diminution of the peak at 1539 cm^{-1} (assigned for N-H bending) leads to the hypothesis that the reaction between chitosan and the ascorbic acid occurs at the level of amine group from chitosan (negative values appear in fig. 5b), even if in a small proportion. It is well known that around this value only the -NH_2 group from the primary amines is assigned, as the secondary amines have no bands in this zone. In this case, a C=N bond could be form, whose absorption can be noticed at 1574 cm^{-1} . In the spectrum characteristic to cotton treated with chitosan functionalized with ascorbic acid, the presence of OH free groups can not be noticed, since no increase in the peak from 1053 cm^{-1} occurred; this leads to the hypothesis that the functional -OH groups from the ascorbic acid form ether

bridges with cellulose (at the level of the -OH primary groups of cellulose, as in fig. 4), leading to its stiffening, which can be noticed in smaller wrinkle recovering angles (WRA) than in the case of utilization of unmodified chitosan as wrinkle-proofing agent. This hypothesis is also supported by the diminution of the peaks afferent to the secondary OH group (assigned at 1103 cm^{-1}) and primary OH groups (assigned at 1053 cm^{-1} , revealed by the negative values in figure 5b) and by a small increase of the peaks around the values 1200 and 1028 cm^{-1} , characteristic to C-O-C asymmetrical and symmetrical stretching vibrations.

Ascorbic acid can also form ether bridges [28] with chitosan (not only with cellulose) as in chemical reaction (scheme 3).



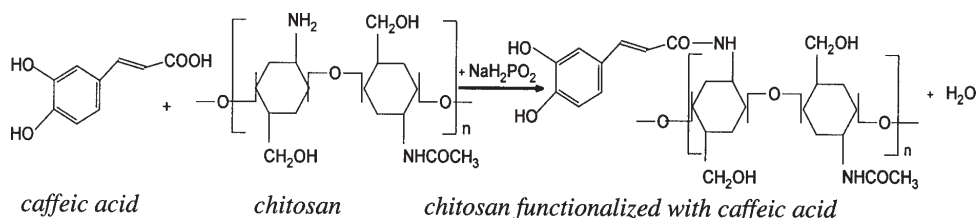
Scheme 3

FTIR analyses for samples treated with chitosan functionalized with carboxylic acids

The following carboxylic acids were used for chitosan functionalization: caffeic acid, diclofenac, oxalic acid and butane tetracarboxyl acid.

Caffeic acid is a hydroxycinnamic acid. It has as functional groups: two OH groups. Normally, the caffeic

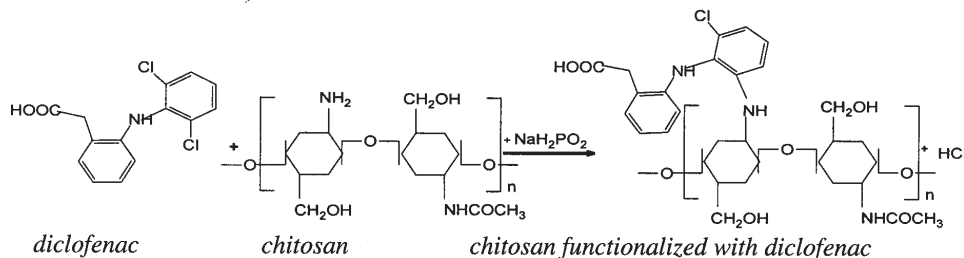
acid reacts with other substances by means of the OH groups. Yet, in the presence of chitosan, the COOH group of caffeic acid is the one which preferably will react with NH_2 group from chitosan [29]. Showing off the types of functional groups specific to each of them, the reaction between caffeic acid and chitosan can be written according to chemical reaction (scheme 4):



Scheme 4

This new product, named chitosan functionalized with caffeic acid, has available OH groups that can form ether bridges with cellulose during the curing reaction at 160°C .

Diclofenac is 2-(2,6-dichloroanilino) phenylacetic acid, which in combination with chitosan, can confer wrinkle-proofing effects. Diclofenac reacts with chitosan according to the chemical reaction (scheme 5):



Scheme 5

Chitosan functionalized with diclofenac can form both ether and ester bridges with cellulose (as in fig. 6) during the curing reaction [30,31].

In figure 6a, one can notice that both samples treated with chitosan functionalized with caffeic acid and chitosan functionalized with diclofenac have IR spectra similar to samples treated with unmodified chitosan. The presence of the caffeic acid and of diclofenac respectively is confirmed by:

- positive values around 670 cm^{-1} assigned for C-H deformation vibration of ring of 6 adjacent hydrogens respective at 1037 cm^{-1} (for C-H in-plane deformation vibration of ring hydrogens);
- appearance of the peak at 1734 cm^{-1} , which is characteristic to the C=O stretch vibration from COO groups (from diclofenac);
- differences between the size of peaks from the range $2918\text{-}2851\text{ cm}^{-1}$, as compared to those of the unmodified chitosan; namely, diclofenac leads to higher peaks as the

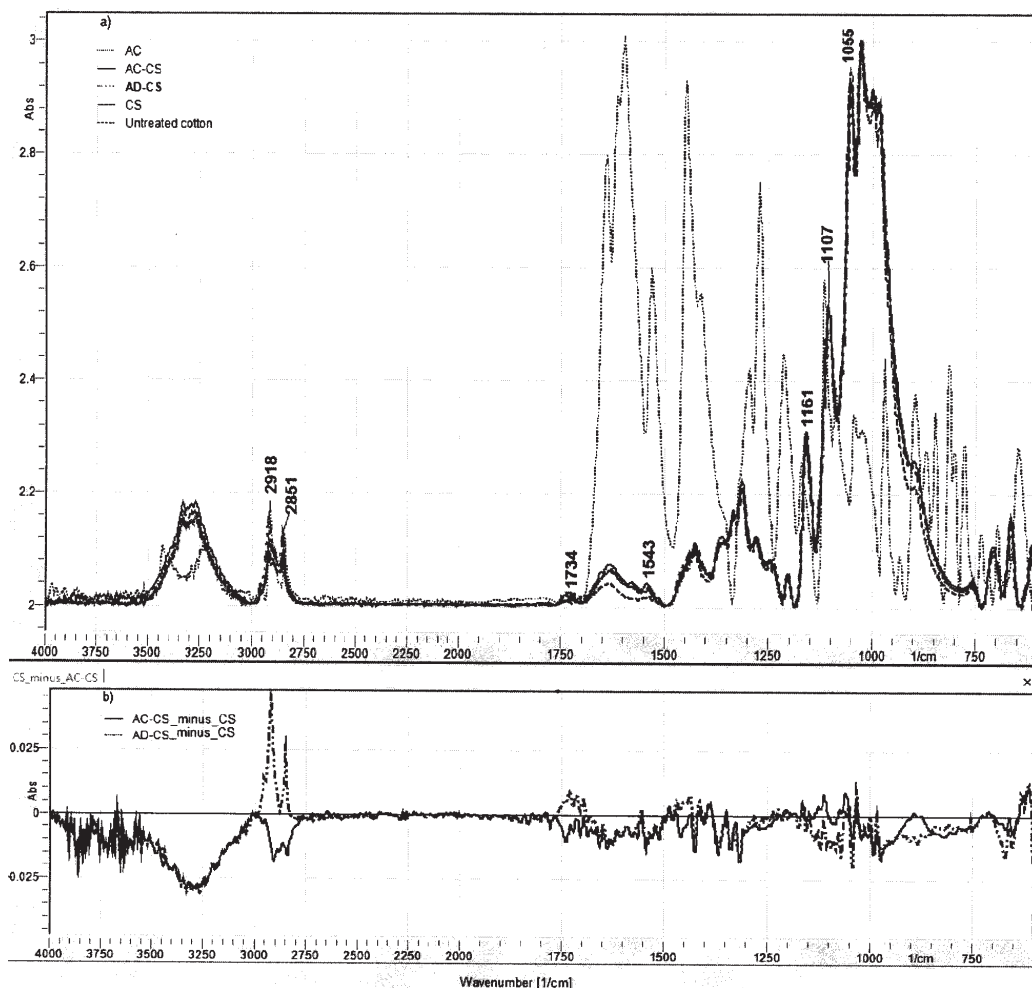
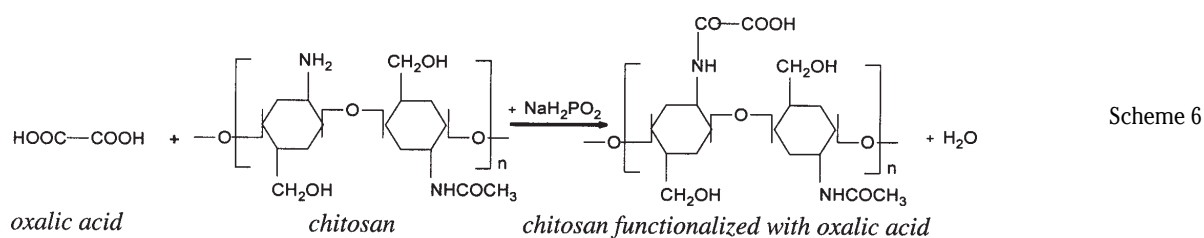


Fig. 6. FTIR spectra: overlapping spectra for pure caffeic acid (AC), untreated cotton and samples treated with chitosan functionalized with caffeic acid (AC-CS) respective with diclofenac (AD-CS); b) subtraction operation

result of its structure, richer in CH groups deriving from diclofenac reaction with two chitosan molecules and formation of the covalent bond by means of the two chlorine atoms. The chemical reactions (4) and (5) are confirmed by the diminution of the peak from 1543cm^{-1} , characteristic to N-H stretching vibration, as the result of

the conversion of the primary NH_2 group from unmodified chitosan into secondary group, which does not absorb within this range.

Oxalic acid is a bifunctional compound used for chitosan functionalized and any carboxylic group can react with of the amine group of chitosan, or at the main -OH group according to chemical reaction (scheme 6):



The FTIR spectra confirm the transformations produced by the oxalic acid on chitosan.

Figure 7 confirms that the COOH group from the oxalic acid reacts with chitosan at the level of NH_2 group, being transformed in an amidic group, the other COOH group of the oxalic acid remaining unchanged.

This results, on the one side, in the extinction of the peak from 1543cm^{-1} (assigned for NH_2 stretch) and, on the other side, in the increase of the peak from 1632cm^{-1} afferent to C=O from amide. A new peak (704cm^{-1}) appears on the spectrum of the sample treated with chitosan functionalized with oxalic acid, corresponding to

NH wagging (broad peak). As compared to the spectrum of the sample treated with chitosan, there is a decrease of the peaks from 3329cm^{-1} and 3269cm^{-1} corresponding to the primary N-H asymmetric and symmetric stretch respectively (easily visible in fig. 7b through the negative values), as well as an increase of the peaks at 2920 and 2851cm^{-1} afferent to C-H stretch (positive values in fig. 7b).

Also, positive values appear near 1425 and 1327cm^{-1} due to C-O stretching vibration respective by O-H in plane deformation vibrations.

Butane tetracarboxyl acid is a polycarboxylic acid that could be used for functionalization of chitosan.

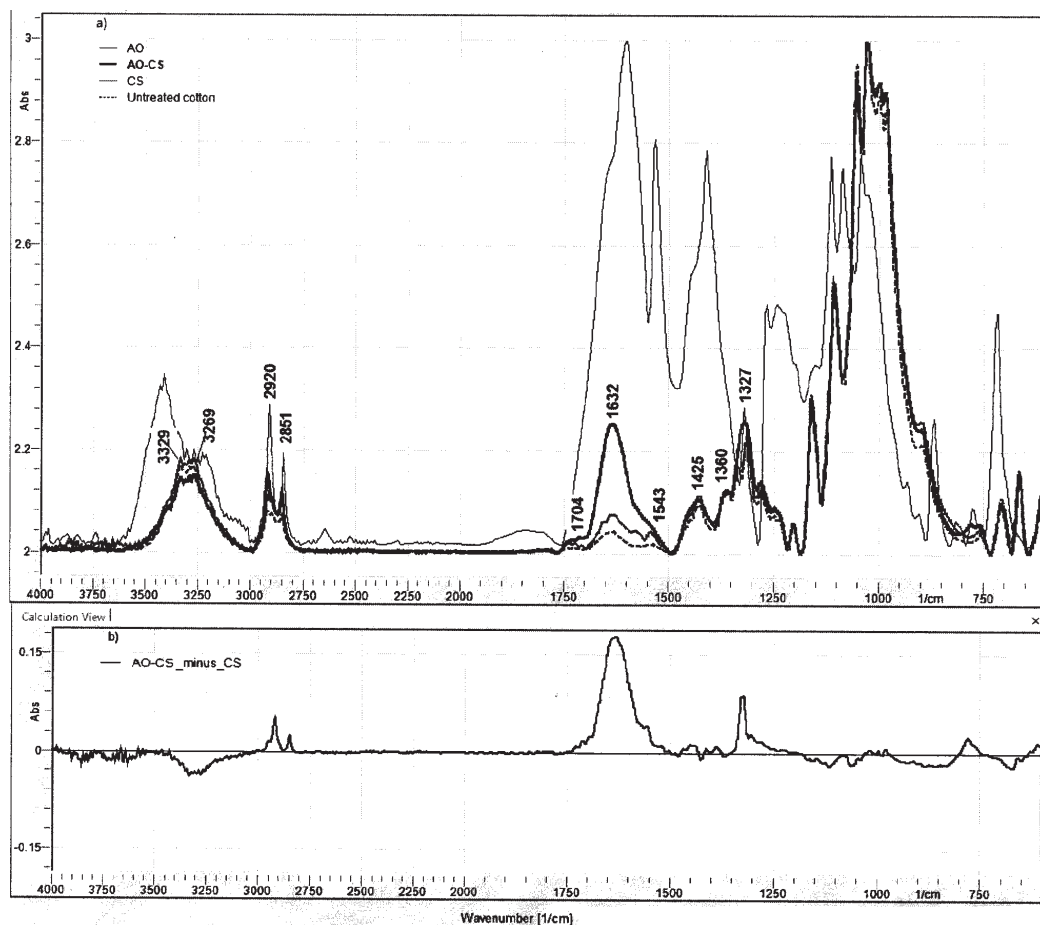
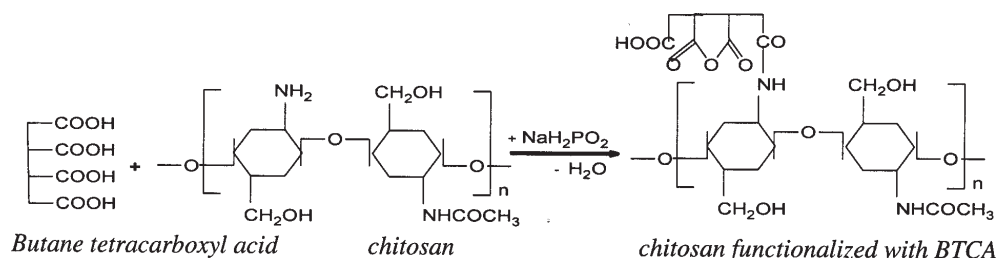


Fig. 7. FTIR spectra: a) overlapping spectra for pure oxalic acid (AO) and the untreated cotton samples, respective by treated with nonfunctionalized chitosan (CS) or functionalized with oxalic acid (AO-CS); b) subtraction operation

Chitosan functionalization with *butane tetracarboxyl acid* at 100°C for 15 min in the presence of 2.5% NaH_2PO_2 occurs according to the chemical reaction (scheme 7):



Scheme 7

The reaction occurs at the NH_2 group of C_2 from chitosan. So, the bridge between chitosan and butane tetracarboxylic acid is amidic type. This is confirmed by the increase in peaks at 3270cm^{-1} (assigned for N-H stretching vibration), 1648cm^{-1} (assigned for C=O stretching vibration), 1710cm^{-1} (combination of N-H deformation and C-N stretching vibrations) and around 1310 and 1200cm^{-1} (mixed C-N stretching and N-H bending vibrations) (fig. 8a).

The occurrence of a peak at 1713cm^{-1} confirms the existence of at least one COOH group uninvolved in the chemical reaction.

The other COOH groups can condense to form a specific group of anhydrides (i.e. $\text{O}=\text{C}-\text{O}-\text{C}=\text{O}$) that register two bands (1740 and 1713cm^{-1}) due to C=O stretching vibrations. The C-O-C bond of the anhydride is confirmed by positive values (fig 8b) afferent to the peaks of 1202 and 1047cm^{-1} .

The increase of the peaks from 2918 - 2851cm^{-1} confirms the amplification of the C-H vibration in the new crosslinking agent butane tetracarboxylic acid-chitosan.

The existence of the OH free groups (from COOH) determined the increase of the peaks from the range 3331 - 3270cm^{-1} . Positive values appear around 950cm^{-1} (OH out-of plane deformation, H bonded in dimerized acids) near 1425 and 1360cm^{-1} and for coupled C-O stretching vibration and O-H deformation vibrations.

Chitosan functionalized with butane tetra carboxyl acid form both etheric bonds (between group OH primary from chitosan and group OH primary from cellulose) as well as links ester bonds (between groups COOH of butane tetracarboxyl acid linked to chitosan and other groups OH from cellulose). The proves are the positive values for C=O stretching vibration (from esters, at 1740cm^{-1}) and for C-O-C bond (from etheric bond, at 1200 and 1047cm^{-1}), even if are the overlapping with the bands afferent to anhydrides.

Performances of functionalized chitosan products

The wrinkle-proofing effects conferred by chitosan functionalized with mono-tetracarboxylic acids are presented in table 5.

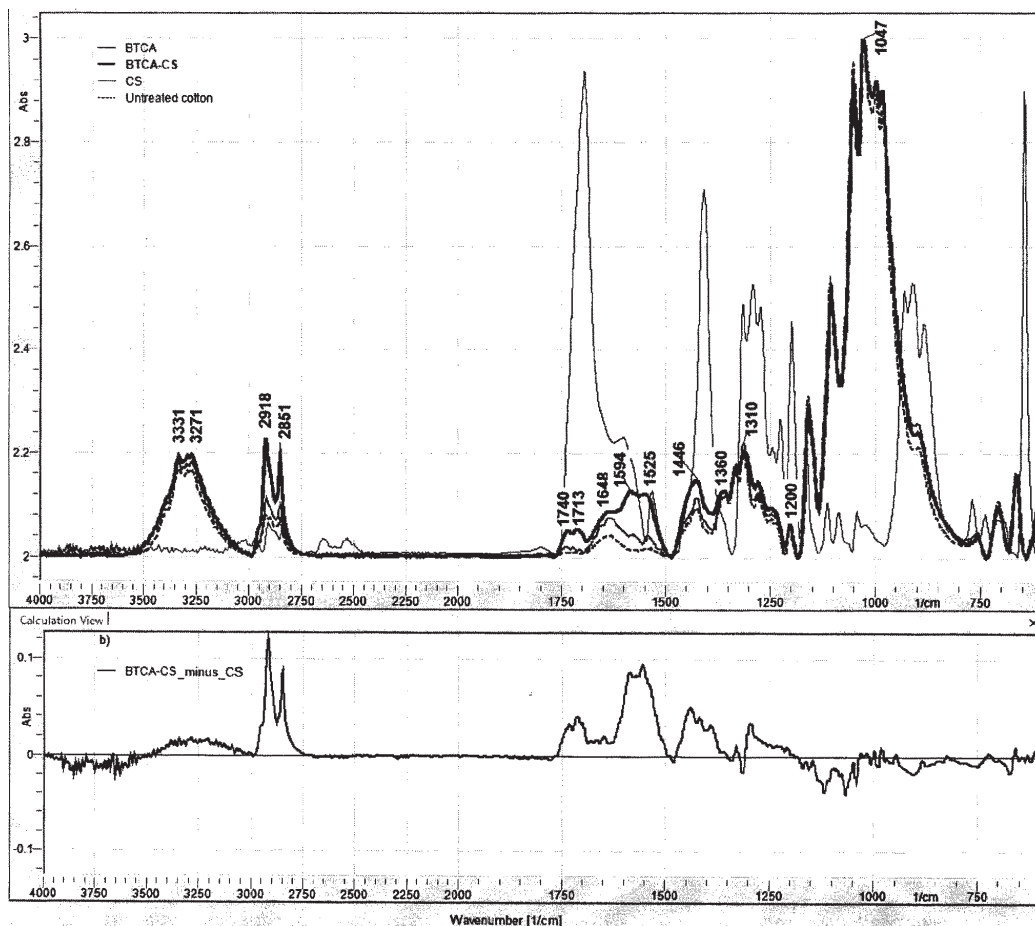


Fig. 8. FTIR analysis: a) overlapping spectra for pure butane tetracarboxyl acid (BTCA), untreated cotton respectively treated with nonfunctionalized chitosan (CS) or functionalized with butane tetracarboxylic acid (BTCA-CS); b) subtraction operation

Table 5
PERFORMANCES OF CHITOSAN FUNCTIONALIZED WITH CARBOXYL ACIDS AS WRINKLE-PROOFING AGENT

Sample's codes	Sample component	dry WRA	wet WRA	Y _i	Y _p [%]	Effect durability [%]	
						Y _p after 5 washings	Y _p after 10 washings
	Control sample	150	139	15.04	-	-	-
CS	cotton+chitosan+NaH ₂ PO ₂	173	158	15.37	2.8	0.57	0.3
AC-CS	cotton+chitosan+AC+NaH ₂ PO ₂	182	169	21.92	7.38	6.54	0.83
AD-CS	cotton+chitosan+AD+NaH ₂ PO ₂	169	152	17.85	8.97	4.39	1.11
AO-CS	cotton+chitosan+OA+NaH ₂ PO ₂	154	147	17.37	1.41	1.24	1.12
BTCA-CS	cotton+chitosan+BTCA+N aH ₂ PO ₂	195	181	18.93	1.23	1.05	0.93

The table 5 confirms better wrinkle-proofing effects for chitosan functionalized with caffeic acid, yet the durability of the effect significantly diminishes after 10 washings, and the high yellowness index confirms a stronger degradation than in the case of unmodified chitosan [32-39].

Even if the wrinkle-proofing effects of chitosan functionalized with oxalic acid are weaker than those of the non-functionalized chitosan, the durability at repeated washings is better than that of nonfunctionalized products.

The performances of the wrinkle-proofing agents derived from chitosan, obtained as the result of chemical reactions between chitosan and butane tetracarboxyl acid are better than those of chitosan. Their better resistance after 10 repeated washings and smaller Y_i values recommend them as possible wrinkle-proofing agents.

Conclusions

In this work we have used chitosan and its derivatives as wrinkle-proofing agents, given the large size of their macromolecular chains, the products were not able to completely penetrate inside part of them remaining outside and interacting with the neighboring chains, thus generating with cotton fibre, a large the so-called crosslinking networks. The good wrinkle-proofing effects of these agents are accounted for by flexibility, i.e. the motion of the macromolecular chains. A rule is always followed in all the cases studied in this paper, namely: the higher the chain flexibility, the higher the length of the macromolecular chain, the higher the treatment temperature (for lending kinetic energy to the chains), and the smaller the energy barrier opposed to rotation.

In the presence of the NaH_2PO_4 or MgCl_2 catalysts, the crosslinking of cellulose with chitosan leads to covalent networks. The crosslinking depends on the structure of wrinkle-proofing agent, more precisely on the position and number of functional groups able to form ether or ester bridges with the primary OH group of cellulose. A strong crosslinking results in a stiffening of macromolecular chains participating in the network and implicitly in smaller wrinkle-proofing effects.

The FTIR-ATR analyses have shown the groups involved in cellulose crosslinking. At the same time, in all chitosan transformation in functional derivatives (with polyols or polycarboxylic acids), the FTIR spectra have revealed the functional groups actively involved in chemical reactions.

The agents obtained from chitosan with ascorbic acid, caffeic acid, diclofenac, oxalic acid and butane tetracarboxyl acid presented better wrinkle-proofing effects than the unmodified chitosan. The performances of a wrinkle-proofing agent consist in better wrinkle-recovering angle (for both dry and wet samples), better wet pick-up both after the curing stage and after 10 repeated washings, and a lower yellowing after treatment.

Acknowledgement: This work was accomplished with the financial support of the project POSDRU CUANTUMDOC "DOCTORAL STUDIES FOR EUROPEAN PERFORMANCES IN RESEARCH AND INNOVATION" ID79407, project financed by the European Social Fund and the Romania Government.

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Manuscript received: 12.05.2013