

# Comparative Study of the FTIR Analysis and the Performances of N,N,N-trimethyl Chitosan as Wrinkle-proofing Agent

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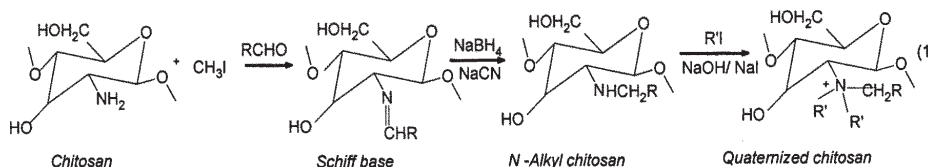
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By functionalizing the N,N,N-trimethyl chitosan with poly-functional compounds of the types polyols (ascorbic acid) and polycarboxylic acids (caffeic acid, diclofenac, oxalic acid and butane tetracarboxylic acid), ionic compounds have been produced having the OH or COOH groups as terminal groups. These groups interact with the OH groups from the cellulose macromolecular chains, producing the cure reaction. In this way, covalent bridges of the ether or ester type are formed between cellulose and the functionalized products, bridges resulting in cellulose cross-linking. Yet, network generated in these cases is of ionic-cross linking type, the name “ionic” deriving from the ionic character of the studied wrinkle-proofing agents. The application of the ionic wrinkle-proofing agents was made according to the pad-dry-cure technology. The spectroscopic (FTIR and XPS) analyses were performed in order to prove the realization of the cellulose cross-linking, its ionic nature and the type of the chemical bond between cellulose and wrinkle-proofing agent. The FTIR and XPS spectra proved the ionic character and the time stability of the functionalized alkylated agents. The performances of the wrinkle-proofing agents based on N,N,N-trimethyl chitosan (wrinkle-recovering angle, yellowness after treatment, and degree of processing and effects durability after repeated washings) have been comparatively presented, to determine the optimum wrinkle-proofing agent. It has been found that the ionic compound formed between butane tetracarboxylic acid (BTCA) and N,N,N-trimethyl chitosan results in the best wrinkle-proofing effects.

Keywords: N,N,N-trimethyl chitosan, FTIR, XPS, BTCA, ionic cross-linking, functionalizing

N,N,N-trimethyl chitosan was first synthesized by Muzarelli [1], and the product was used in the medical field having an antibacterial character due to the presence of the positive charge of the N atom. In time, other researchers synthesized the alkyl chitosan through various methods. The mostly used methods for chitosan alkylation were: reductive alkylation; direct alkylation; Michael addition [2].

The reductive alkylation is based on three stages: formation of a Schiff basis from chitosan reaction with an aldehyde (the reaction occurring at the level of the NH<sub>2</sub>);



Generalized diagram of the trialkyl chitosan production after reductive reaction is given by the chemical reaction (1).

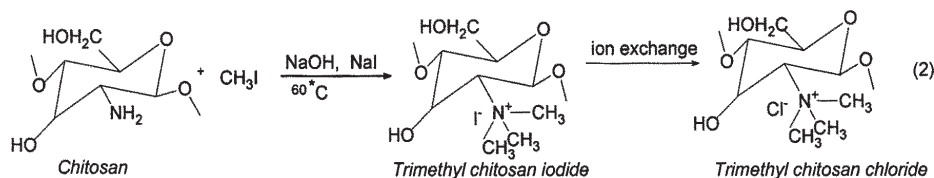
Method of direct alkylation is based on chitosan treatment with an iodide type alkylation agent, because it is easier to avoid alkylation at the O atom of the primary hydroxyl group of chitosan. The reaction occurs under

reduction of the Schiff basis with a reducing agent (NaBH<sub>4</sub>, as a rule); formation of the quaternary salt at the level of the N atom from chitosan, i.e. formation of trialkyl chitosan from the reaction of monoalkyl chitosan with an alkylation agent type R-I iodide, in the presence of NaOH and NaI. If the alkylation agent R-I was methyl iodide, then the process also includes an “ion exchange”- type stage, in which the iodine ion is replaced by chlorine. Though extremely efficient, the methyl iodide is easily volatile and dangerous for human health, since it is carcinogenic [1].

certain conditions of temperature and catalyst, at pH = 8.0 ÷ 8.5 realized with NaOH in the presence of NaI and R-I (usually CH<sub>3</sub>I) as alkylation agent [3]. As in the case of reductive method, the last stage is of ion exchange type, when the iodine ion is replaced by chlorine by means of a NaCl solution.

The scheme of alkylation according to the direct alkylation method is given by the chemical reaction (2).

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*Michael addition* is based on the utilization of  $\alpha$ ,  $\beta$ -unsaturated compounds, such as acrylic acid, which reacts with the  $\text{NH}_2$  groups from chitosan.

Irrespective of the utilized alkylation method, the chitosan production requires the observance of certain conditions: certain molar ratios between reactants, certain temperatures and catalysts.

In this work N,N,N-trialkyl chitosan was obtained through the direct alkylation method proposed by Dormard et al. [3], with slight modifications:  $\text{CH}_3\text{I}$  was used as alkylation agent at  $20^\circ\text{C}$  in the presence of NaOH and NaCl. In order to test the wrinkle-proofing effects, we have used both alkylated products as such, and products resulted from N,N,N-trimethyl chitosan reaction with five functionalizing agents (ascorbic acid, caffeic acid, diclofenac, oxalic acid or butane tetracarboxylic acid).

The unmodified N,N,N-trimethyl chitosan and its functionalized correspondents were then applied on the 100% cotton fabric through the *pad-dry-cure method*. The influence of 3 catalysts in the cure stage ( $140^\circ\text{C}$ ) was tested, a stage meant to remove the water between the primary cellulose OH groups and primary OH groups afferent to alkyl chitosan. This stage is also responsible for cellulose crosslinking.

Therefore, the N,N,N-trimethyl chitosan reaction with each of the functionalizing agents results in an ionic compound; this has enough functional groups able to form bridges to bond cellulose, thus contributing to its crosslinking. Two spectroscopic methods (FTIR and XPS) were used in order to prove the presence of these compounds on the cotton fabric, as well as crosslinking of cellulose.

The investigated wrinkle-proofing effects were: wrinkle recovering angle (WRA), take-up degree ( $Y_p$ ), effects

durability after repeated washings, and textile yellowness index (YI) after treatment.

## Experimental part

### Materials and methods

The experiments were performed on the 100% cotton fabric which was previously desized and alkaline scoured [4, 5]. The characteristics of the cotton fabric were: plain weave with yarn count of 19 Tex on warp and 17 Tex on weft, specific weight  $100 \text{ g/m}^2$ .

The structures of the substances used for N,N,N-trimethyl chitosan functionalizing [6, 7] are presented in figure 1.

We made 16 samples of 100% cotton fabric: eight samples in the warp (U) direction and eight samples in the weft (B) direction. Their treatment conditions and coding are presented in table 1.

N,N,N-trimethyl chitosan was prepared according to the indications from specialized literature, with specification that methyl chloride was used instead of methyl iodide, the ion exchange phase disappearing.

Even if Muzzarelli synthesized [1] the alkyl chitosan for the first time, using it in medicine, this was not applied yet in the textile industry (as wrinkle-proofing agent). The preparation of N,N,N -trimethyl chitosan can be schematized as follows:

- preparation of N,N,N-trimethyl chitosan is conditioned by the utilization of the following molar ratios: Chitosan:  $\text{CH}_3\text{Cl}:\text{NaOH} = 1:6:2$  [8];

- application of N,N,N-trimethyl chitosan or its derivative was performed by pad-dry-cure technology [9]. Its technological parameters are:

- impregnation ( $T = 100^\circ\text{C}$ ,  $t = 15 \text{ min}$ ) of cotton samples with N,N,N-trimethyl chitosan or the functionalized derivatives just synthesized;

- Squeezing down to  $\text{GS} = 80\%$ ;

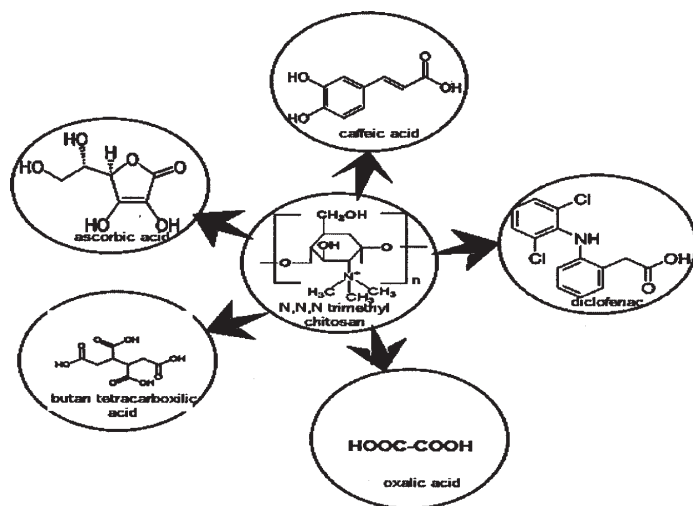


Fig. 1. Substances used for N,N,N-trimethyl chitosan functionalizing

Crt. no.	Sample code	Padding recipe	Drying/curing recipes
1	ACS	5% N,N,N trimethyl chitosan +2.5% $\text{NaH}_2\text{PO}_2$	$T_{\text{drying}} = 85^\circ\text{C}$
2	ACS1	5% N,N,N trimethyl chitosan +2.5% $\text{MgCl}_2$	$t = 2\text{min.}$
3	ACS2	5%N,N,N trimethyl chitosan +2.5% $\text{ZnCl}_2$	$T_{\text{curing}} = 140^\circ\text{C}$
4	AS- ACS	5%N,N,N trimethyl chitosan+5% ascorbic acid +2.5% $\text{NaH}_2\text{PO}_2$	$t = 2\text{min.}$
5	AC-ACS	5%N,N,N trimethyl chitosan +5% caffeic acid +2.5% $\text{NaH}_2\text{PO}_2$	
6	AD- ACS	5%N,N,N trimethyl chitosan+5%Diclofenac+2.5% $\text{NaH}_2\text{PO}_2$	
7	AO-ACS	5%N,N,N trimethyl chitosan +5% oxalic acid+2.5% $\text{NaH}_2\text{PO}_2$	
8	BTCA-ACS	5%N,N,N trimethyl chitosan+5%butan tetracarboxylic acid +2.5% $\text{NaH}_2\text{PO}_2$	

**Table 1**  
CODING OF THE SAMPLES MADE  
IN THE WARP DIRECTION

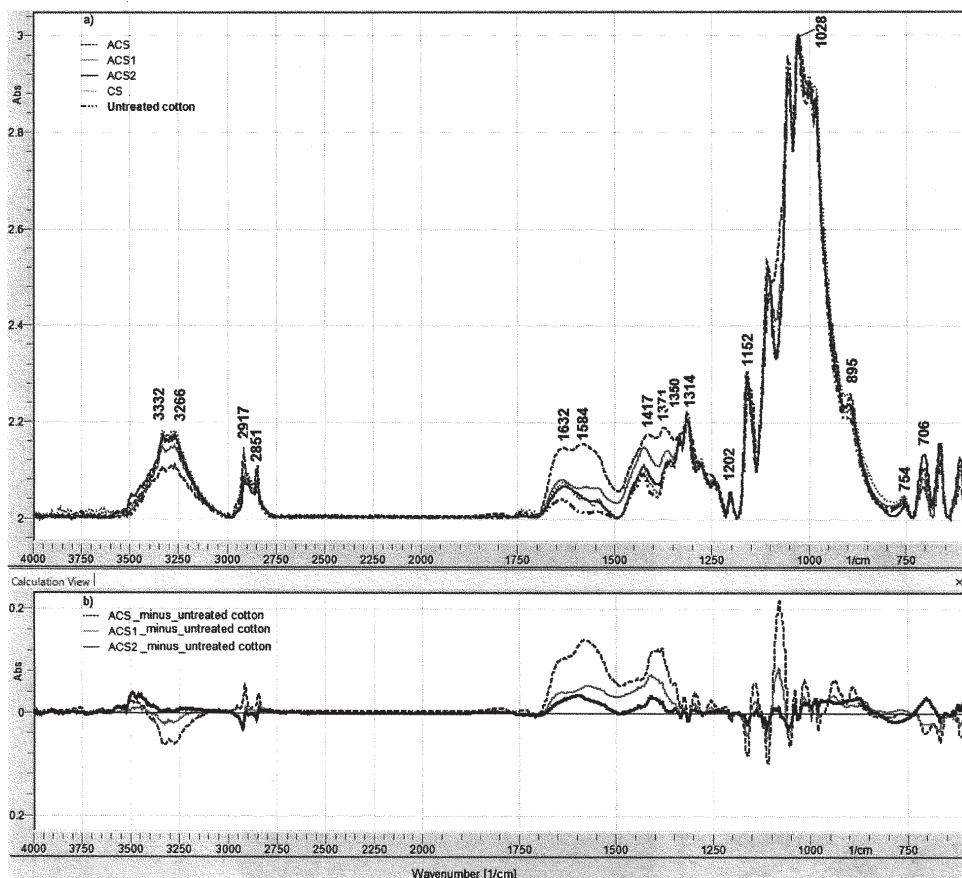


Fig. 2. FTIR spectra: overlapping for samples treated with unmodified chitosan (CS), and with N,N,N-trimethyl chitosan in the presence of the catalysts  $\text{NaH}_2\text{PO}_4$  (for the ACS sample),  $\text{MgCl}_2$  (for the ACS1 sample) and  $\text{ZnCl}_2$  (for the sample ACS2); (b) subtraction operation

- Drying at  $T = 85^\circ\text{C}$ ,  $t = 2$  min;
- Curing at  $T = 140^\circ\text{C}$ ,  $t = 2$  min. In this stage, the efficiency of three catalysts was tested:  $\text{NaH}_2\text{PO}_4$ ,  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ , according to the indications from table 2.
- Sample washing to remove the catalyst deposited on the fabric or the products not involved in cross-linking.

#### FTIR analyses

The FTIR analyses of the cotton samples treated with chitosan or its derivatives was performed on Multiple Internal Reflectance Accessory (SPECAC, USA) with ATR KRS/5 crystal of thallium bromide-iodine, having 25 reflections and the investigation angle of  $45^\circ$ . This accessory device was attached to the spectrophotometer FTIR IR Affinity Shimadzu (Japan). The spectra were recorded with 250 scans in the  $4000\text{-}600\text{cm}^{-1}$  range. After recording, the absorption spectra were electronically superposed using the Panorama software.

#### XPS analyses

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

#### Take-up degree ( $Y_p$ )

The transfer of chitosan and its derivatives from the treatment solution to the textile material at the end of pad-dry-cure technology can be appreciated by means of the take-up degree. The take-up degree  $Y_p$  was determined using the relation (3):

$$Y_p = 100 \cdot (W_a - W_b) / W_b \quad (3)$$

where:  $Y_p$  = take-up degree;  $W_a$  = cotton mass before wrinkle-proofing;  $W_b$  = cotton mass after wrinkle-proofing.

#### Wrinkle recovering angle (WRA)

The wrinkle-proofing effect produced by any wrinkle-proofing agent is appreciated by means of the values of wrinkle-recovering angle WRA.

The wrinkle-recovering angle was determined according to the German standard DIN 53890. The Metrimpex FF-01 apparatus was used to determine the wrinkle recovering angle as the average of 10 measurements along both the warp and the weft directions.

#### Wrinkle-proofing durability

By using the standard SR EN ISO 105-C06:1999, the treated samples were tested from the standpoint of the wrinkle-proofing effect durability. The testing was performed on Mathis Polycolor machine and consisted in home laundering test. The samples were subject to 5-10 repeated washing cycles, followed by rinsing with distilled water at  $40^\circ\text{C}$  and drying at room temperature.

#### Yellowness index (YI)

YI is the index that needs to be calculated in the case of extended exposure or processing in the presence of some organic acids and some catalysts of acid salt type.

YI was determined by using the Spectroflash SF300/Datacolor Spectrophotometer and the ASTM Method E313-73. The formula used for YI is indicated by eq. (4) [10]

$$YI = (1 - 0.847 \cdot \frac{Z}{Y}) \cdot 100 \quad (4)$$

Where: YI is the Yellowness Index of cotton sample, and Y, Z are the CIE tristimulus values obtained using D65/10° or C/2° as illuminant/observer.

#### Results and discussions

As possible wrinkle-proofing agent, N,N,N-trimethyl chitosan has been made studies as it is or modified

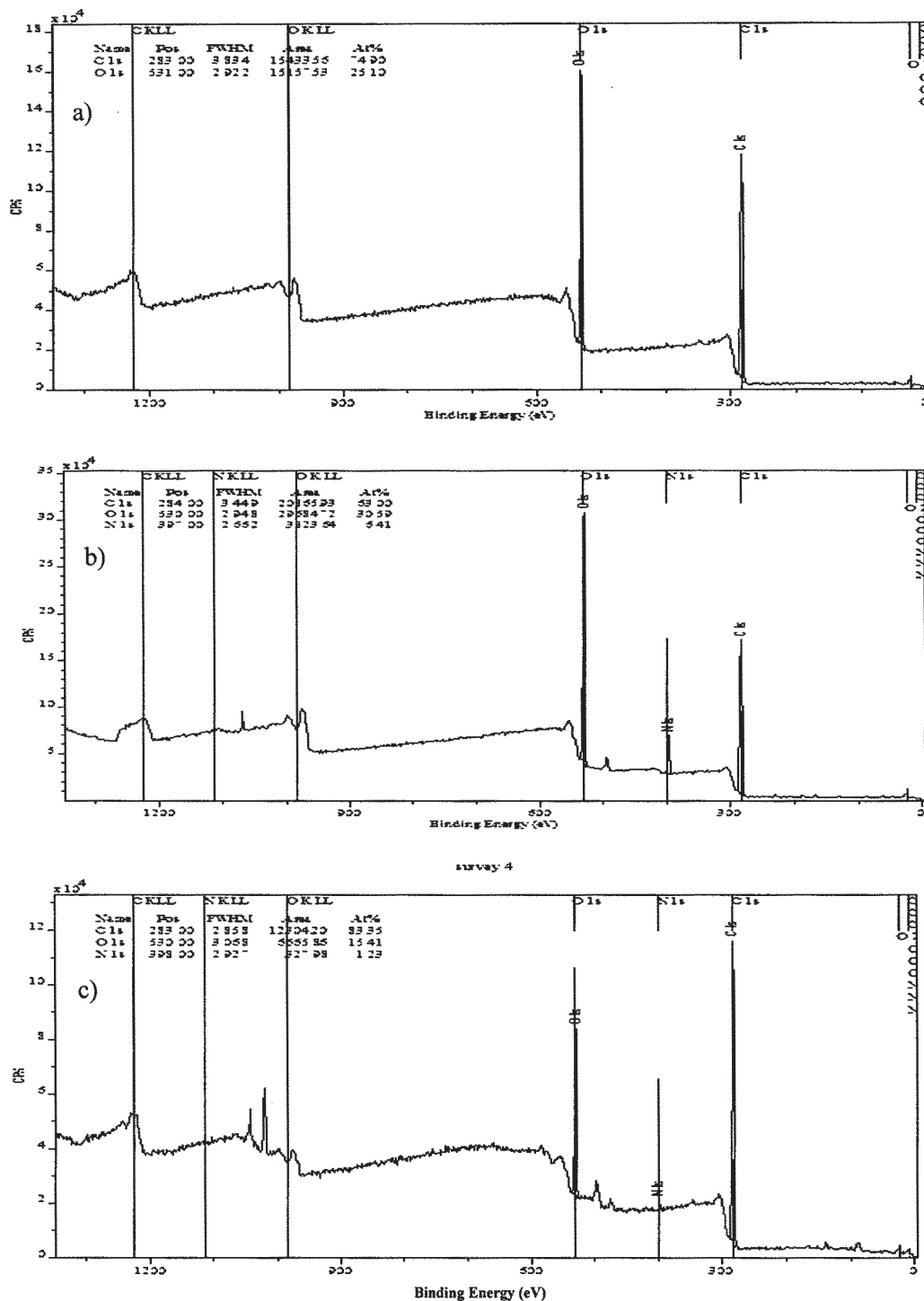


Fig. 3. XPS spectra for:  
 a) untreated sample;  
 b) chitosan powder;  
 c) sample treated with  
 N,N,N-trimethyl chitosan

following the reactions with various poly-functional compounds (fig. 1).

*FTIR analysis of samples treated with N,N,N-trimethyl chitosan*

N,N,N-trimethyl chitosan is a chitosan derivative which was obtained from the direct alkylation reaction of chitosan with  $\text{CH}_3\text{Cl}$  as alkylation agent, according to the method presented in literature [3].

The N,N,N-trimethyl chitosan synthesis was performed in this paper with a molar ratio chitosan:alkylation agent  $\text{CH}_3\text{Cl}:\text{NaOH} = 1:6:2$ . The literature data specify that N,N,N-trimethyl chitosan is obtained in a higher proportion, but the hypothesis of formation of monoalkyl chitosan or dialkyl chitosan is not excluded [1]. Besides the N-alkylation reaction, the O-alkylation reaction can also occur at the level of the primary OH group from both  $\text{C}_6$  and at the level of secondary OH group attached to  $\text{C}_2$  from the chitosan pyranosic unit. The realization of N-alkylation or O-alkylation is obvious from the IR spectra given in figure 2.

Figure 2 presents a comparison between the spectra of cotton treated with unmodified chitosan (CS, in short), in the presence of hypophosphite as catalyst (because it gave the maximum efficiency at previous testing), and the spectra of cotton treated with N,N,N-trimethyl chitosan in the presence of  $\text{NaH}_2\text{PO}_2$ ,  $\text{MgCl}_2$  and  $\text{ZnCl}_2$ .

Irrespective of the utilized catalyst, the chitosan alkylation (either at the level of the N atom or at the level O atom) was proved by the peaks from  $1371$  and  $1314\text{cm}^{-1}$  which correspond to the  $\text{CH}_3$  umbrella deformation (m-w intensity). In the specialized literature [8] it is specified that the existence of a peak in the range  $1470 - 1350\text{cm}^{-1}$  indicates the realization of the N-alkylation in this range, because here is assigned the  $-\text{CH}_3$  deformation (m-w).

In figure 2, the N-alkylation is proved not only by the peak at  $1417\text{cm}^{-1}$ , but also by the increase of the peaks from  $1632\text{cm}^{-1}$  and  $1584\text{cm}^{-1}$  corresponding to the primary/quaternary salts ( $\text{NH}_3^+/\text{N}^+$  asymmetric and symmetric deformation vibrations). In fact, at  $1632\text{cm}^{-1}$  the

Crt. No.	Sample	dry WRA	wet WRA	Y <sub>P</sub> [%]	Durability of effect		Yellowness index
					Y <sub>P</sub> after 5wash cycles	Y <sub>P</sub> after 10 wash cycles	
0	Standard sample	150	139	-	-	-	15,04
1	chitosan+2,5% NaH <sub>2</sub> PO <sub>2</sub>	173	158	2,8	0,57	0,5	15,37
2	N,N,N trimethyl chitosan+2.5%MgCl <sub>2</sub>	181	171	4,21	2,36	1,93	13,82
3	N,N,N trimethyl chitosan+2.5%NaH <sub>2</sub> PO <sub>2</sub>	173	154	6,01	3,61	2,44	13,86

**Table 2**  
PERFORMANCES OF ACS AS WRINKLE-PROOFING AGENT

overlapping of characteristic absorption C=O stretch and of (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup> occurs. The O-alkylation is proved by the existence of the peak from 1584cm<sup>-1</sup>, known to be assigned to N-H stretch. Should the alkylation reaction occur only at the level of chitosan amine group, this peak had disappeared. Its existence indicates that, besides the N-alkylation, an O-alkylation occurred. The process of chitosan alkylation resulted in the increase of the peaks from the range 2978 ÷ 2851cm<sup>-1</sup>, which are assigned to C-H asymmetric and symmetric stretches. The more pronounced O-alkylation shown in hypophosphite presence is revealed by the higher peaks from 1584cm<sup>-1</sup> and by peaks diminution within the range 3332 ÷ 3266 cm<sup>-1</sup> where primary N-H absorb. The inset from figure 2.b indicates the peak from 1152cm<sup>-1</sup> (in the case of MgCl<sub>2</sub> utilization) and its total disappearance when the hypophosphite is used as catalyst. This can result from both the O-alkylation and a more severe cross-linking, in which case more secondary OH groups from the alkylated product interact with the cellulose OH groups and, after water removal (cure reaction at 140°C) C-O-C ether bridges are formed between the two neighboring macromolecular chains. The fact that increases appear at 1152 and 1028 cm<sup>-1</sup> (revealed by the positive values in fig. 2b) means the increase of the C-O-C bonds (asymmetric and symmetric), therefore a more pronounced cross-linking in the presence of NaH<sub>2</sub>PO<sub>2</sub>.

#### XPS analysis

The XPS spectra indicate the presence of N atoms in the samples treated with N,N,N-trimethyl chitosan (fig. 3).

By comparing the spectrum of powder chitosan (which is a polysaccharide, like the cellulose) with that of the standard sample, one can notice that, besides the C1s and O1s atoms, there are also N1s atoms (in the case of chitosan) in a proportion of 6.4% at.

The presence of N,N,N-trimethyl chitosan in the treated sample is confirmed in figure 3.c by two aspects:

- presence XPS spectrum in the treated sample, of the N1s atoms at the position 398, in a percentage of 1.23% (at);

- increase of the percentage of C1s atoms (from the position 283) at 83.35%, as compared to 74.90% in the untreated sample.

The performances of alkyl chitosans formed in the presence of NaH<sub>2</sub>PO<sub>2</sub> and MgCl<sub>2</sub> as catalysts of the cellulose cross-linking reaction are presented in table 2.

The data from table 2 confirm that N,N,N-trimethyl chitosan can be used as wrinkle-proofing agent, since its wrinkle-recovering angles (dry WRA, wet WRA) are bigger than those of the untreated cotton. The N,N,N-trimethyl chitosan wrinkle-proofing effects in the presence of sodium hypophosphite presence are smaller than when using MgCl<sub>2</sub> as catalyst of the cure reaction. This can be explained taking into account the preferential generation

of O-alkyl in the case of using MgCl<sub>2</sub>. Since in the presence of hypophosphite occur both an O-alkylation and an N-alkylation, the flexibility of the cross-linking (between cellulose and the wrinkle-proofing agent) obtained after cure is smaller, the wrinkle-recovering angles are also poorer. One should neglect neither the steric effect of the large volume of N-trimethyl groups from N,N,N-trimethyl chitosan, nor the presence of the positive charge which results in flexibility diminution. By comparing the N,N,N-trimethyl chitosan performances (WRA, take-up degree, effect's durability and yellowness) as wrinkle-proofing agent with those offered by chitosan (table 2), one can infer that the N,N,N-trimethyl chitosan confers better wrinkle-proofing effects than chitosan for each of the catalysts used in cross-linking. Moreover, after treatments with N,N,N-trimethyl chitosan, the samples had yellowness degrees (Y<sub>i</sub>) smaller, due to smaller degradations.

#### FTIR analyses of the samples treated with functionalized N,N,N-trimethyl chitosan

It has been proved that N,N,N-trimethyl chitosan has good wrinkle-proofing effects, even if it is a non-formaldehyde product. For these reasons, we have studied the effects of N,N,N-trimethyl chitosan derivatives resulted from their reaction with polyoles (ascorbic acid) of carboxylic acids of the type: caffeic acid, diclofenac, oxalic acid and butane tetracarboxylic acid. The reaction conditions were: contact time 15 min, temperature maintained at 100°C. The application on cellulose of these new agents through the pad-dry-cure technology (under the condition of high cure temperature of 140°C and the presence of NaH<sub>2</sub>PO<sub>2</sub> as catalyst) results in cellulose cross-linking.

We started from the idea that at least one of the functional groups of each enumerated poly-functional compounds (symbolized as HO-R-COOH) can establish an electrostatic (ionic) bond with N,N,N-trimethyl chitosan (symbolized as <sup>+</sup>TMCS-OH) of the following type: HOOC-(HO)R <sup>+</sup>TMCS-OH. These ionic compounds represent the linking bridge between the two neighboring macromolecular chains. Cellulose cross-linking with these products is based only on the ether or ester covalent bonds between the OH or COOH groups of the N,N,N-trimethyl chitosan functional derivatives and the primary OH group of cellulose.

The terms used in literature [11-15] are "cross-linking" and "ionic cross-linking". In the first case, the linking bridges between two neighboring macromolecular cellulose chains are of covalent type. In the second case, strong electrostatic forces are present either between previously cationized cellulose and an anionic wrinkle-proofing agent, or these electrostatic forces are established inside the cross-linking agent.

In this work, the cellulose cross-linking network is of ionic cross-linking and can be schematically represented like in figure 4, where the N,N,N-trimethyl chitosan compounds have been symbolized with HO-TMCS<sup>+</sup>, and

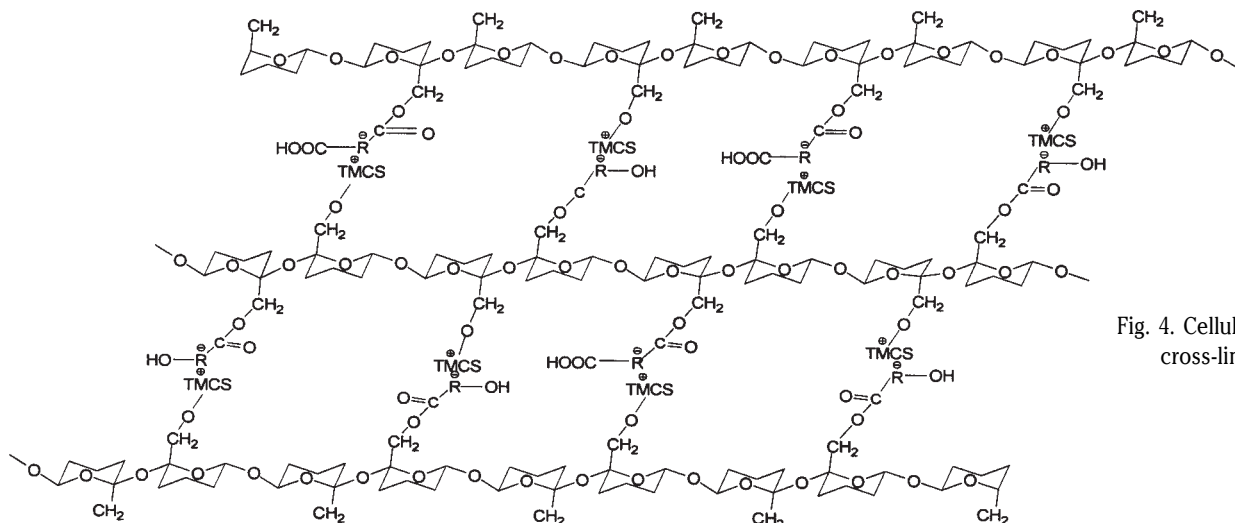


Fig. 4. Cellulose ionic cross-linking

any poly-functional agent used in functionalizing is symbolized with  $HOOC-R-OH$ .

In figure 4 one can notice that the linking bridges between two neighboring macromolecular cellulose chains are exactly the functionalized wrinkle-proofing agents. These have a dual character, determined by the covalent ionic nature of the chemical structure: they possess electric charge gained through functionalizing; they have enough free OH or COOH groups, able to interact with cellulose.

#### FTIR analysis of sample treated with N,N,N-trimethyl chitosan functionalized with a polyol

The ascorbic acid (AS) is a polyol which has 4OH groups in its composition. The scientific name of the ascorbic acid is 3,4-dihydroxy-5-(1,2-dihydroxy-ethyl) furan-2-one

The ascorbic acid participates in the chemical reaction with N,N,N-trimethyl chitosan in its ionic form derived as follows: the two hydroxyl (-OH) from the lower side of the double bond are enols. An enol loses a pair of electrons, thus becoming an oxoniium ( $=OH^+$ ) group, by creating a double bond with the carbon atom. Simultaneously, the carbon-carbon double bond (between enols) transfers electrons to form a double bond with the next carbon. To make room, the electrons of the carbonyl double bond are received by the carbonyl oxygen, in order to form an enolate. The oxoniium gets de-protonized in order to produce a carbonyl and this proton lost gives the ascorbic acid its acid character. The entire reaction is enol de-protonizing in order to form an enolate, where the negative charge of the resulted enolate is de-localized by the carbonyl system ( $C=O$ ) and the double bond ( $C=C$ ) (chemical reaction 5).

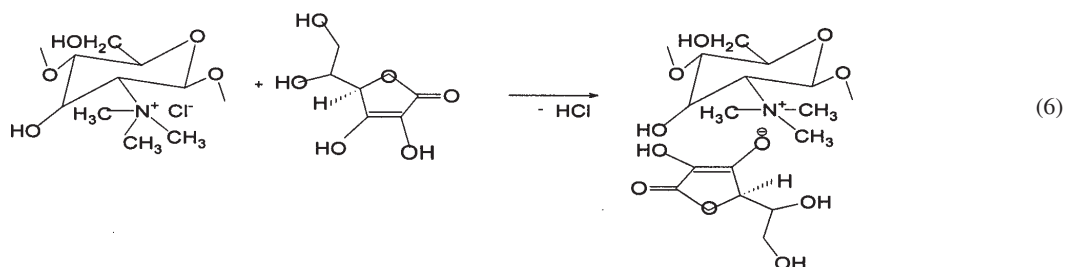
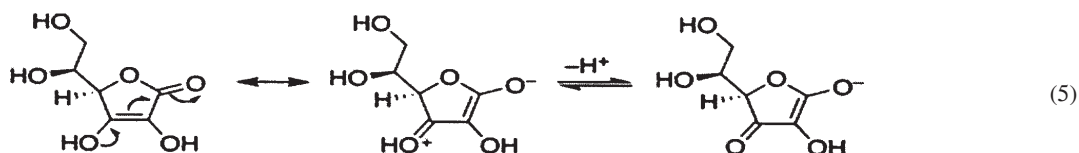
This de-localization makes the ion more stable and less prone to receive back its proton [16].

The possible chemical reaction between the ionic forms of the ascorbic acid and the cation from N,N,N-trimethyl chitosan is according to the chemical reaction (6).

The confirmation of N,N,N-trimethyl chitosan functionalizing with the ascorbic acid is given by the spectroscopic analysis performed in the IR range (fig. 5).

By comparing the spectra of the sample treated with chitosan (and  $NaH_2PO_4$  as catalyst), with that of the sample treated with chitosan and ascorbic acid (with  $NaH_2PO_4$  as catalyst), one can draw the following conclusions:

- the presence of  $(CH_3)_3N^+$  is confirmed by the increase of the peak at  $1633cm^{-1}$  [8] in the sample treated with trimethyl chitosan, but within this range also appears the absorption  $C=O$  stretch vibration); the  $C=C$  stretching vibration from the ascorbic acid overlaps around the same value ( $1640cm^{-1}$ ) (fig. 5a);
- the diminution of the peak from  $1539cm^{-1}$  (assigned to NH stretch) leads to the idea that N,N,N-trimethyl chitosan has less free  $NH_2$  groups, most of them being converted in alkylated groups;
- the participation of the OH group from the ascorbic acid in the hydrogen bond with the OH group from cellulose, results in the increase of the frequency of the in plane vibration of the O-H bond from  $1429cm^{-1}$ ;
- the increase of the peak at  $1368cm^{-1}$  (assigned to  $CH_3$  deformation vibration) confirms the methyl presence in the N,N,N -trimethyl chitosan;
- the decrease of the peaks from  $1158$  and  $1057cm^{-1}$  confirms the implication of the OH group from the ascorbic acid in the cellulose cross-linking reaction; the increase of the peaks from  $1200$  and  $1028cm^{-1}$  confirms the formation



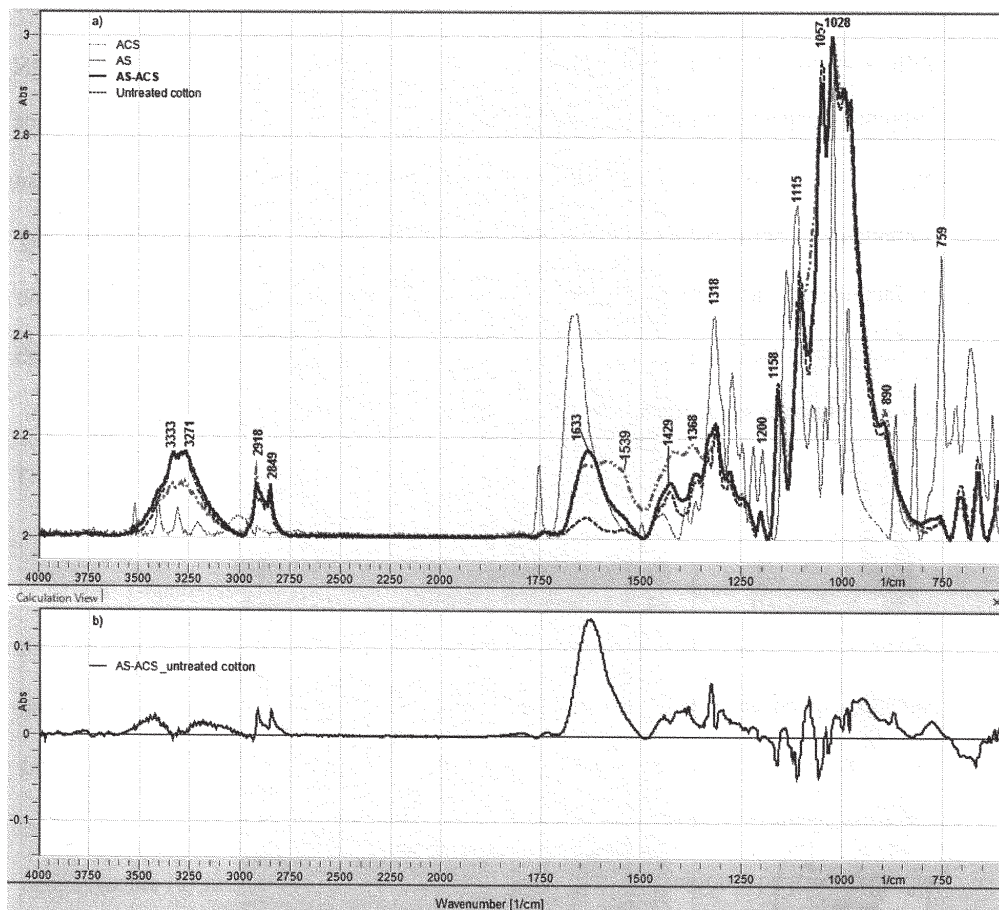
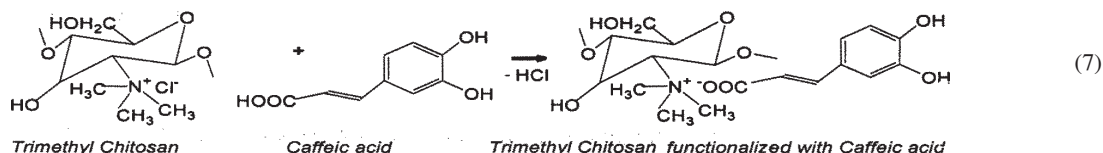


Fig. 5. FTIR spectra: a) overlapping spectra for the untreated (witness) cotton sample and samples treated with N,N,N-trimethyl chitosan without functionalizing (ACS) and functionalized with ascorbic acid (AS-ACS) respectively, and the spectrum of pure ascorbic acid (AS); b) subtraction spectra

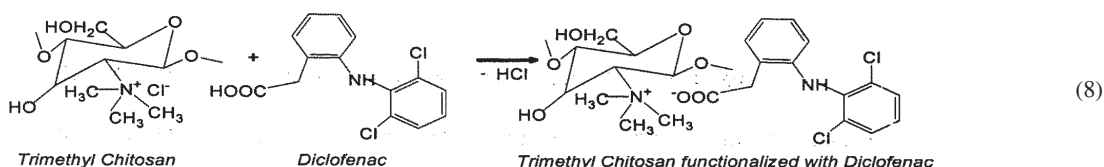
of an ether bridge between the ascorbic acid and cellulose, as well as between the primary OH group from N,N,N-trimethyl chitosan and cellulose.

#### FTIR analyses of samples treated with N,N,N-trimethyl chitosan functionalized with carboxylic acids

For N,N,N-trimethyl chitosan functionalizing carboxylic acids, one to four carboxylic groups were used, namely: caffeic acid, oxalic acid and butane tetracarboxylic acid.



This new product N,N,N-trimethyl chitosan functionalized with caffeic acid can make ether bridges with cellulose during the cure reaction.



Cotton treated with N,N,N-trimethyl chitosan functionalized with caffeic acid and diclofenac respectively presents the FTIR spectra from figure 6.

The presence of caffeic acid and diclofenac (which are two products of aryl carboxyl acid type) is confirmed by: the peak from 1640 $\text{cm}^{-1}$  assigned to C=O stretching; the decrease of the peaks from 3332 and 3261 $\text{cm}^{-1}$ , as a proof of the existence of free OH group; increase of the peaks

*Caffeic acid* is a hydroxycinnamic acid having the following functional groups: two OH groups; a phenolic ring and an acrylic group.

The COO<sup>-</sup> group from AC is the one which will preferably react with the N<sup>+</sup> group from N,N,N-trimethyl chitosan [17]. Pointing out the types of the specific functional groups, the chemical reaction between the caffeic acid and N,N,N-trimethyl chitosan can be written as in reaction (7):

*Diclofenac* is in fact 2-(2,6-dichloroanilino)phenyl acetic acid. In combination with N,N,N-trimethyl chitosan, it can confer wrinkle-proofing effects similar to chitosan. The diclofenac can react with N,N,N-trimethyl chitosan according to the reaction (8):

from 2911 and 2859 $\text{cm}^{-1}$  afferent to CH stretching; increase of the peaks from the range 950 - 900 $\text{cm}^{-1}$  afferent to OH out-of-plane deformation; increase of peaks near 1431 and 1300 $\text{cm}^{-1}$  (two bands) assigned to C-O stretching and O-H in plane deformation, coupled. One can notice in the both spectra the presence of N,N,N-trimethyl chitosan (the same explanation as for fig. 2). The cross-linking of

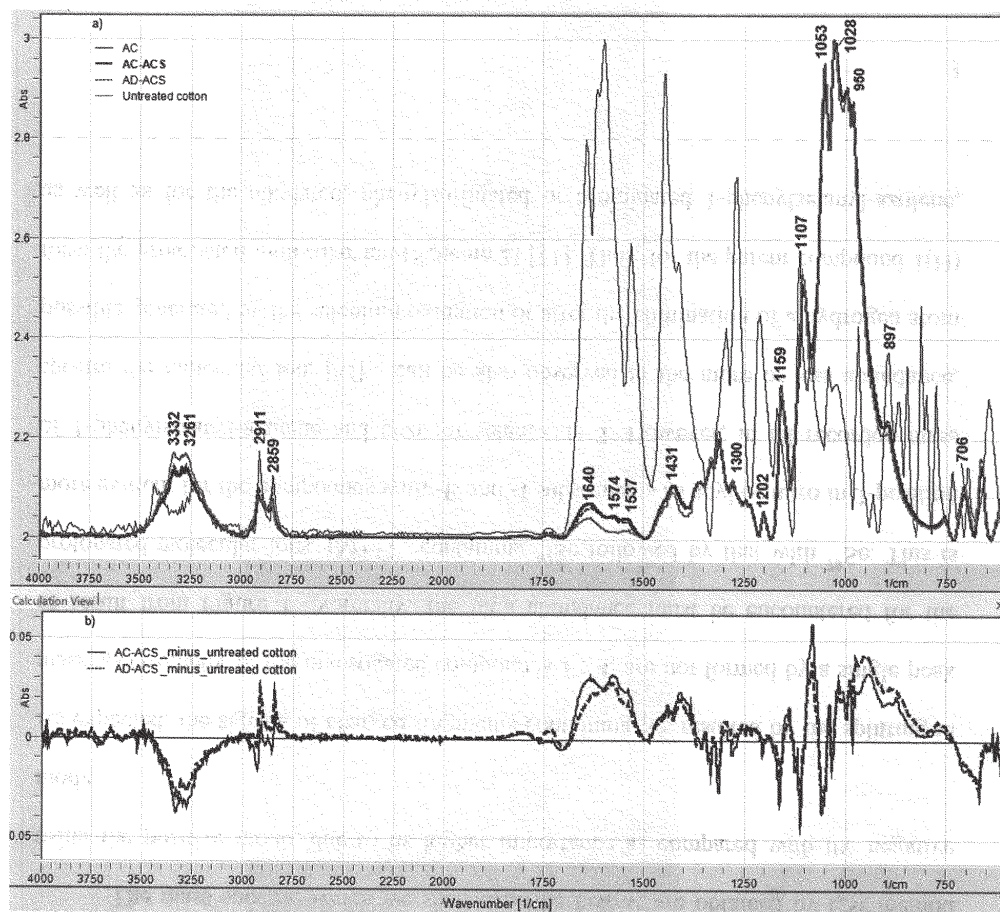
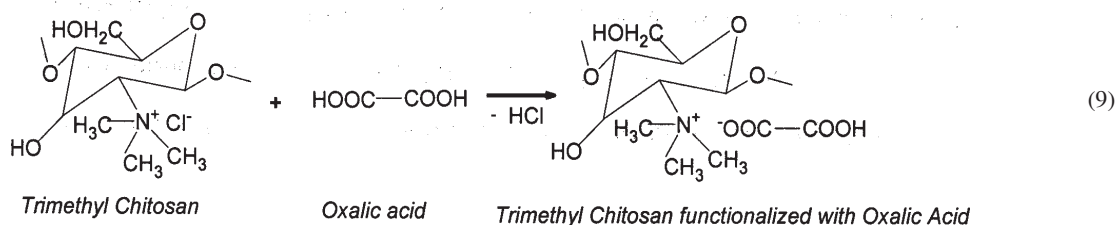


Fig. 6. FTIR spectra:  
 a) overlapping spectra for pure caffeic acid (AC), control sample (untreated cotton) and sample treated with N,N,N-trimethyl chitosan functionalized with caffeic acid (AC-ACS) and diclofenac (AD-ACS) respectively;  
 b) subtraction spectra

cellulose is confirmed by the increase of the peaks from 1159 and 1028 $\text{cm}^{-1}$ , assigned to C-O-C type ether bonds, between cellulose and the functionalized wrinkle-proofing agent.

*Oxalic acid* is a bifunctional compound, being a dicarboxylic acid. Any carboxyl group can form an ionic bond with the cationic group from N,N,N-trimethyl chitosan, see chemical reaction (9):



The FTIR spectra confirm the transformations produced by the oxalic acid on N,N,N-trimethyl chitosan (fig. 7).

Functionalizing of N,N,N-trimethyl chitosan with oxalic acid results in the following:

- increase of the peaks at 3331- 3271  $\text{cm}^{-1}$  as the result of the OH vibration from COOH group of the oxalic acid (positive values in fig. 7b);
- increase of the peaks from 2916- 2849  $\text{cm}^{-1}$  as the result of alkylation (positive values in fig. 7b);
- the peak at 1632 $\text{cm}^{-1}$  indicates the existence of C=O asymmetric vibration from a salt of carboxylic acid (ionic type wrinkle-proofing agent); the peaks near 1400 and 1300 $\text{cm}^{-1}$  are assigned to C=O symmetric vibration;
- the other COOH group of the oxalic acid, without electric charge, is involved in generation of ester bridges with cellulose, resulting in its crosslinking. The presence of these ester bonds is confirmed by the appearance of the peak from 1740 $\text{cm}^{-1}$  (C=O stretching vibration); increase of the peak at 1280 $\text{cm}^{-1}$  (assigned to C-O-C stretching)

and positive values (fig. 7b) in the range 3450-3271 $\text{cm}^{-1}$  (overtone of C=O stretching vibration);

- negative values (fig. 7b) around 1160, 1111, 1057  $\text{cm}^{-1}$  indicate a smaller number of secondary and primary OH groups respectively in the ionic compound, as the result of the more advanced cross-linking with the cellulose from cotton.

The ionic compound has available primary OH groups attached to C<sub>6</sub> of the pyranosic ring; these can interact with the primary OH groups from cellulose (considering the high temperature during the cure stage and the existence of an acid medium created by catalyst presence), eliminating the water and forming ether groups.

Cross-linking based on ether bonds is also proved by the positive values from 1200 and 1028  $\text{cm}^{-1}$  afferent to C-O-C asymmetric and symmetric stretching vibrations respectively.



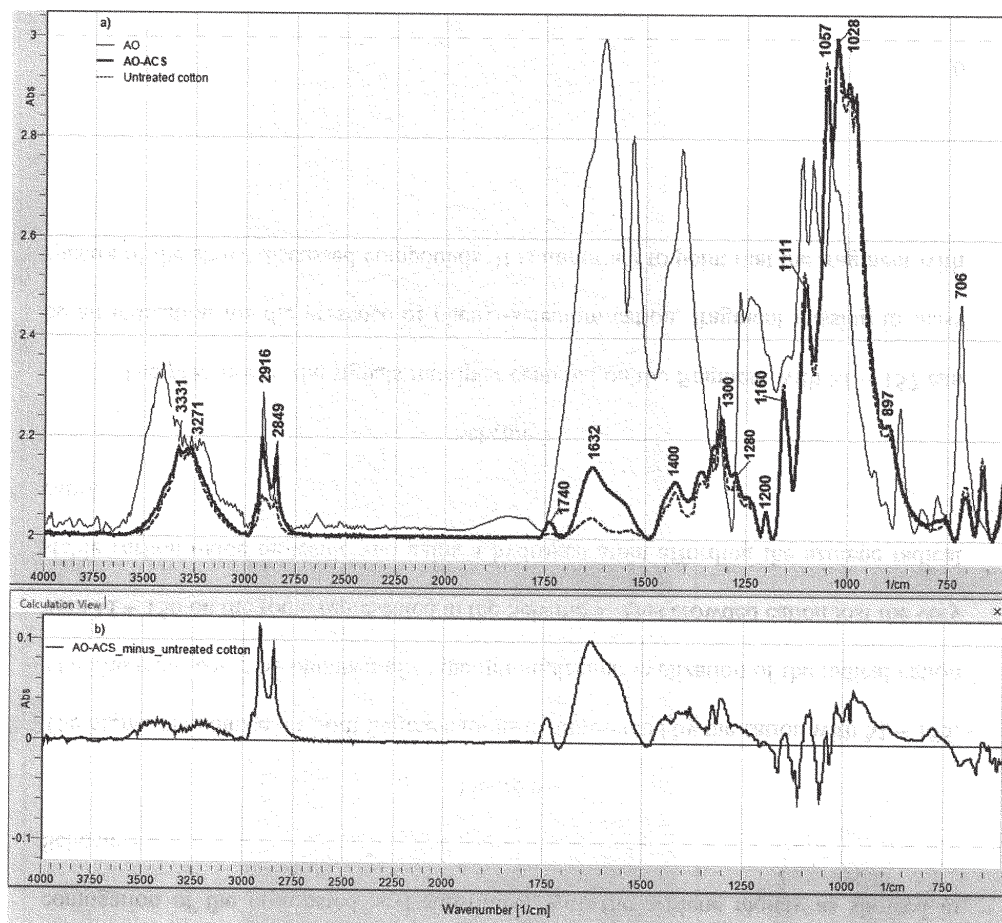
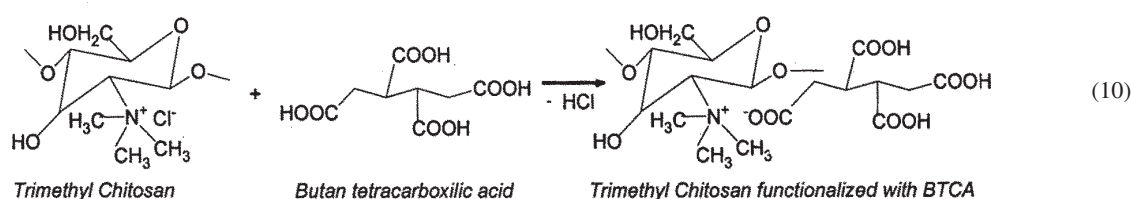


Fig. 7. FTIR spectra: a) overlapping spectra for pure oxalic acid (AO), control sample (untreated cotton) and sample treated with N,N,N-trimethyl chitosan functionalized with oxalic acid (AO-ACS); b) subtraction spectra

**Butane tetracarboxylic acid (BTCA):** the functionalizing of N,N,N-trimethyl chitosan with butane tetracarboxylic acid occurs according to the chemical reaction (10):



The spectrum of cellulose cross-linked with the functionalized agent of ionic type (N,N,N-trimethyl chitosan- butane tetracarboxylic acid- fig. 8) is characterized by:

- positive values within the range 1369- 1324  $\text{cm}^{-1}$  (fig. 8b), where absorption for C-H from  $\text{CH}_3$  umbrella deformation (m-w intensity) are recorded; these peaks confirm the presence of the alkylated type chitosan (N,N,N-trimethyl chitosan). The other characteristics of the trimethyl chitosan are also preserved (fig. 2);

- the presence of the butane tetracarboxylic acid is proved by:

- existence of a  $\text{COO}^-$  group involved in the electrostatic interaction with alkyl chitosan: 1632 $\text{cm}^{-1}$  (C=O asymmetric stretching vibration) and near 1427 and 1300 $\text{cm}^{-1}$  (C=O symmetric stretching vibration);

- existence of at least one  $\text{COOH}$  free group, able to form ester bonds with cellulose: 1734 $\text{cm}^{-1}$  (C=O stretching vibration); increase of the peak from 1280 $\text{cm}^{-1}$  (assigned to C-O-C stretching) and by the positive values (fig. 8b) within the range 3450- 3302 $\text{cm}^{-1}$  (overtone of C=O stretching vibration);

- possible intramolecular curing in butane tetracarboxylic acid and formation of groups specific for anhydrides ( $\text{O}=\text{C}-\text{O}-\text{C}=\text{O}$ ) that registers two bands (1734 and 1713  $\text{cm}^{-1}$ ), due to the C=O stretching vibrations. The C-O-C bond of

the anhydride is confirmed by the positives values (fig. 8b) afferent to the peaks of 1204 and 1026 $\text{cm}^{-1}$ .

The significant increase of C-H absorption from 2957-2886  $\text{cm}^{-1}$  range confirms the cellulose cross-linking with the ionic agent N,N,N-trimethyl chitosan with butane tetracarboxylic acid;

- two types of bonds are generated between the functionalized alkylation agent and cellulose, resulting in cellulose cross-linking: ether and ester bonds. Formation of ether bands (between the primary OH groups of cellulose and OH from alkylated chitosan) is confirmed by the positive values (fig. 8b) from 1204 and 1026 $\text{cm}^{-1}$ , afferent to the C-O-C asymmetric and symmetric stretching vibrations;

- the ester bonds are formed between the  $\text{COOH}$  group of butane tetracarboxylic acid and the OH group of another neighboring macromolecular cellulose chain. The presence of this ester bonds is confirmed by the appearance of the peak at 1734 $\text{cm}^{-1}$  (C=O stretching vibration), the increase of the peak at 1280  $\text{cm}^{-1}$  (assigned to C-O-C stretching) and the positive values (fig. 8b) within the range 3450 – 3302 $\text{cm}^{-1}$  (overtone of C=O stretching vibration).

The cotton treatment with functionalized derivatives of N,N,N-trimethyl chitosan (in the presence of  $\text{NaH}_2\text{PO}_4$  and at high cure temperature) results in good wrinkle-proofing effects, as one can see in figure 9 and in table 3.

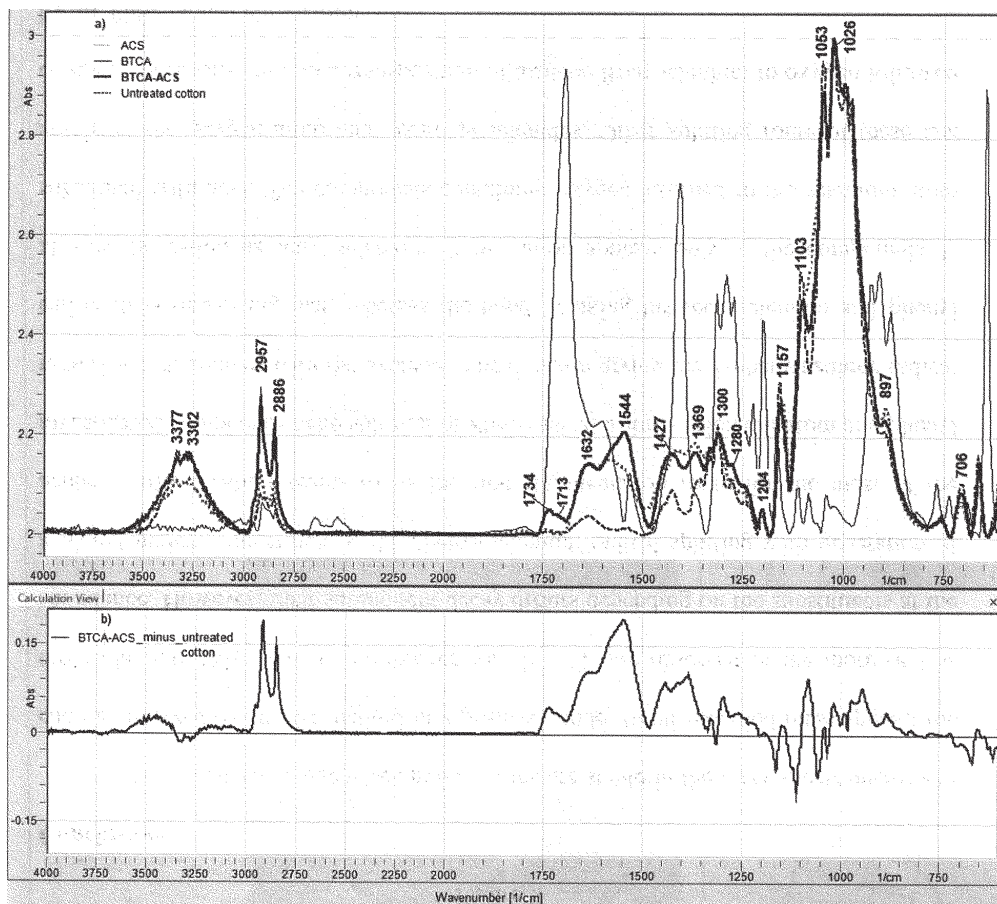


Fig. 8. FTIR spectra: a) overlapping spectra for butane tetracarboxylic (BTCA), control sample (untreated cotton) and sample treated with N,N,N-trimethyl chitosan unfunctionalized (ACS) and respectively functionalized with butane tetracarboxylic acid (BTCA-ACS); b) subtraction spectra

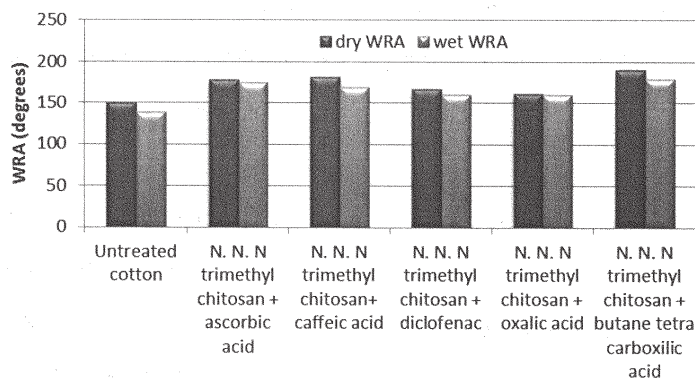


Fig. 9. Wrinkle recovering angle (WRA) values after treatments

Crt. No.	Wrinkle-proofing agents	Y <sub>P</sub> [%]	Effect durability [%]		YI
			Y <sub>P</sub> after 5 washings	Y <sub>P</sub> after 10 washings	
1.	Control sample	-	-	-	15.04
2.	chitosan+NaH <sub>2</sub> PO <sub>2</sub>	2,8	0.57	0.3	15.37
3.	N,N,N trimethyl chitosan+ NaH <sub>2</sub> PO <sub>4</sub>	6.01	3.61	2.44	13.86
4.	N,N,N trimethyl chitosan +ascorbic acid + NaH <sub>2</sub> PO <sub>4</sub>	2.45	2.34	0.98	15.01
5.	N,N,N trimethyl chitosan+caffeic acid+NaH <sub>2</sub> PO <sub>2</sub>	2.30	2.0	1.47	17.59
6.	N,N,N trimethyl chitosan +Diclofenac +NaH <sub>2</sub> PO <sub>2</sub>	1.67	1.06	0.7	15.4
7.	N,N,N trimethyl chitosan +oxalic acid+ NaH <sub>2</sub> PO <sub>2</sub>	3.58	2.81	0.83	16.41
8.	N,N,N trimethyl chitosan +butane tetracarboxylic acid+NaH <sub>2</sub> PO <sub>2</sub>	4.18	3.45	2.55	17.42

Table 3  
PERFORMANCES OF THE WRINKLE-PROOFING AGENTS

In all the studied cases, the wrinkle recovering angles are higher than those of the untreated sample.

The ionic character of any functionalized N,N,N-trimethyl chitosan compound will determine a bigger flexibility of the macromolecular chains [12, 18-21] and higher wrinkle recovering angles both in the case of dry or wet tested material.

The yield factors exceed 1.5%, yet the wrinkle-proofing effects are not permanent and their durability decreases through repeated washings. After 10 repeated washings, the wrinkle-proofing effect considerably diminishes as the

result of dislocation and removal of the wrinkle-proofing agent from cotton. Yet, this diminution is lower than in the case of samples only treated with chitosan [22-29].

After treating them with functionalized N,N,N-trimethyl chitosan, all the samples got slight yellowish shades, which confirms once more the realization of each chemical reaction between the cotton fabric and the ionic wrinkle-proofing agents.

The best performances as wrinkle-proofing agent belong to the N,N,N-trimethyl chitosan functionalized with butane tetracarboxylic acid, even if after treatment the yellowness index (YI) of the samples increased by 2 units.

## Conclusions

Based on alkylated chitosan, the ionic derivatives functionalized with N,N,N-trimethyl chitosan have good wrinkle-proofing effects. This can be explained through high chain flexibility, which determines good wrinkle-recovering angles. The FTIR and XPS spectra have proved the presence of the ionic wrinkle-proofing agents on the treated material, as well as the nature of the chemical bonds between them.

All products functionalized with a polyol (ascorbic acid) or carboxylic acids (caffeic acid, diclofenac, oxalic acid and butane tetracarboxylic acid) led to wrinkle recovery angles higher than the samples treated with unmodified chitosan or than the standard. In all cases the wrinkle recovery angles values were better on dry samples than on wet samples.

The most efficient catalyst was  $\text{NaH}_2\text{PO}_4$  that gave the opportunity for training of both the N-alkyl chitosan and O-alkyl chitosan. The sustainability of the effects vary with the strength of the link made between cotton and wrinkle-proofing agent. From this point of view, samples taken from the recipe with catalyst  $\text{NaH}_2\text{PO}_4$  have obtained higher degrees of take-up and final laundering does not lead to a significant reduction in mass, so the effect is good.

The yellowness of the samples treated with N, N, N-trimethyl chitosan is not significantly affected.

The best performances as wrinkle-proofing agent belong to the N,N,N-trimethyl chitosan functionalized with butane tetracarboxylic acid.

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