Effects of Chitosan Grafting onto Cotton Fabric Pretreated with a Tetrol

VASILICA POPESCU[1]*, IOAN GABRIEL SANDU[2], ECATERINA VASLUIANU[1], ION SANDU[3,4], LILIANA ROZEMARIE MANEA[1], CRISTINE CAMPAGNE[5,6]

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

[2] Gheorghe Asachi Technical University, Faculty of Material Science and Engineering, 64 Mangeron Blv., 700050, Iasi, Romania

[3] Alexandru Ioan Cuza University, ARHEOINVEST Interdisciplinary Platform, 11 Carol I, Corp G demisol, 700506, Iasi, Romania

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

[5] University Lille Nord de France, F-59000 Lille, France

[6] ENSAIT, GEMTEX, F-59100 Roubaix, France

The pretreatment of the cotton cloth with a tetrol, characterized by a high affinity for fats and oils resulted in its hydrophilization. The big concentrations of tetrol and the temperature of 160°C (from the curing stage) make possible the formation of ether bridges with cellulose. The chitosan grafting onto cellulose support pretreated with tetrol is possible because the primary OH groups of chitosan can react with the OH groups of tetrol and/or cellulose, generating other ether bridges. The modifications generated by chitosan grafting have been confirmed by Fourier Transform infrared analyses (FTIR), X-ray photoelectron spectroscopy (XPS) and by the following quantitative effects: take-up degree, yellowness index, durability of grafting (by tinctorial method: dyeing with dyestuffs from two classes: acid and direct), color measurements, absorption by capillarity, dry and wet WRA, and tensile strength.

Keywords: chitosan, grafting, FTIR, wrinkle-proofing, absorption by capillarity.

Chitosan is obtained through the process of chitin deacetylating (in highly alkaline medium), being considered a linear amino-polysaccharide consisting of 20% β1,4-linked N-acetyl-D-glucosamine and approximately 80% β1,4-linked D-glucosamine. It is a natural polymer named 2-Amino-2-deoxy-(1→ 4)-β-D- glucopyranan, Poly-(1,4β-D-glucopyranosamine) [1]. Chitosan is a bio-compatible, bio-degradable, antibacterial polyelectrolyte, with a large variety of applications: water clarification, filtration, food-processing, surgical dressing, biosensors, tissue engineering and controlled release in both pharmaceutics and agriculture fields [2]. Chitosan can be successfully used in textile wrinkle-proofing. In the specialty literature there are reports on the good wrinkle-proofing effects accomplished with chitosan applied directly on the cotton fabric [3, 4]. The disadvantage of using chitosan as wrinkle-proofing agent is that it results in poor water absorbing capacities [5]. In time, numerous scientists tried to eliminate this shortcoming. They increased the anionic charge of cellulose by treating it with various anionic agents: perchloric acetic acid [6-7], BTCA [8-10]. The cellulose functionalized in this way reacted with cationized chitosan (by dissolution in acetic acid), giving good wrinkle-proofing results, but the water absorbing capacity was not improved significantly.

In this work we have tested the effects acquired by chitosan grafting onto a cellulose support pretreated with a poly-functional agent. The pretreatment is performed with the Tetronic 701 [11] compound. This is a tetrol with a big affinity for fats and oils, having the balance HLB = 7. At small concentration, Tetronic 701 determines the removal of wax from cotton and the decrease of pectine amount, resulting in excellent cotton cleaning. At large concentrations, Tetronic 701 forms ether bridges between cellulose and chitosan [12]. Both the stage of pre-treatment with Tetronic 701, and the stage of grafting with chitosan were carried out based on pad-dry-cure technology. The effects produced by Tetronic 701 and chitosan in equal concentrations (3-15%) were tested. The effects generated by increasing chitosan concentrations were also determined in the conditions of using 15% tetrol and different pad-dry-cure parameters (catalyst type, time, temperature). The modifications generated by chitosan grafting onto the support pretreated with Tetronic 701 were confirmed by Fourier Transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS) analyses, and by the following quantitative effects: take-up degree, yellowness index, dry and wet WRA, durability of grafting (by tinctorial method: dyeing with dyestuffs from two classes: acid and direct), tensile strength and absorption by capillarity.

Experimental part

Materials and methods

The 100% cotton fabric obtained from the IASITEX SA/ Romania Company was pre-treated with Tetronic 701. Tetronic 701 is the commercial name for a product based on Ethylenediamide tetrakis (ethoxylate-block-propoxylate) tetrol [12]; purchased from Aldrich Company. Chitosan (highly viscous) was purchased from Fluka, and the dyestuffs (C.I. 45380 and C.I. 22120) from Merck Company. Their chemical structures are presented in table 1.

Tetronic 701 is in fact ethylenediamine tetrakis (ethoxylate-block-propoxylate) tetrol, i.e. superficial active agent (surfactant) with poly(ethylene oxide)/poly (propylene oxide), linear blocks anchored on the molecule of a diamine situated in the molecule central position [11]. Tetronic 701 is an amphoteric surface active agent that contains both hydrophilic and lipophilic groups, having a

* email: vpopescu65@yahoo.com

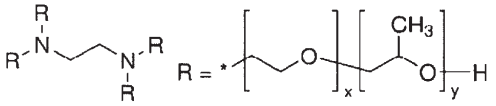
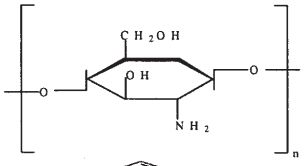
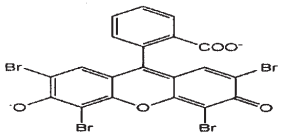
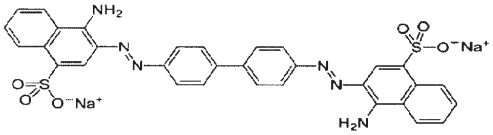
Name	Structures
Tetronic 701	
Chitosan	
Eosin Y C.I. 45380	
Congo Red C.I. 22120	

Table 1
CHEMICAL STRUCTURES OF THE UTILIZED PRODUCTS

high affinity for fats, oils, wax. Tetronic 701 was chosen with the goal to create a better cleaned surface by wax removal from cotton. This tetrol is able to operate as a linking bridge for the future products to be grafted [12]. The utilized chitosan is of highly viscous type, with 78% deacetylation degree.

Mode of operation

The treatments with chitosan were planed so that to find for each stage of pad-dry-cure technology the parameters that determine the highest effects of wrinkle-proofing, durability, minimum yellowness and resistance loss. Therefore the samples 1-4 were realized using identical concentrations of Tetronic 701 and of chitosan. All the 5-12 samples were made with 15% Tetronic 701, because this concentration led to the best water absorbing effects, also creating wrinkle-proofing effects. For the samples 1-14, the variable parameters were as follows:

- chitosan concentration (3, 9, 12.5 and 15%);
- catalyst type ($MgCl_2$ and NaH_2PO_2 in concentration of 3%);
- padding time (3 - 10 min);
- drying time /temperature (3 min/ 100°C);
- curing time (3-10 min);
- curing temperature (160 and 180°C).

The treatment conditions are presented in table 2.

Methods and analyses

IR Spectroscopy analysis

The ATR- FTIR analysis was carried out to reveal the chitosan presence onto the cotton fabric supports pretreated with Tetronic 701, as the result of the process of grafting. FT-IR analysis was carried out on a Multiple Internal Reflectance Accesory (SPECAC, SUA) with ATR KRS-5 crystal of thalium bromide – iodide, having 25 reflexions and the investigation angle of 45 degrees. This accessory device was attached to the Spectrophotometer FTIR IRAffinity-1, Shimadzu (Japan), the spectra registration was realized with 250 scans in the 1800-600cm^{-1} range. After the registration, the absorption spectra have been electronically superposed (using the LabCognition 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).

	Tratament I* **Pad I-dry I-cure I**	**Tratament II Pad II-dry II-cure II**						
Crt. no.	Padding I with Tetronic701 (%)	Padding II with chitosan (%)	Catalyst type (3%)	Padding duration (min.)	drying (°C)	Drying time (min.)	Curing temperature (°C)	Curing duration (min.)
W	**Witness**	-	-	-	-	-	-	-
1	3	3	$MgCl_2$	3	100	3	160	3
2	9	9	$MgCl_2$	3	100	3	160	3
3	12.5	12.5	$MgCl_2$	3	100	3	160	3
4	15	15	$MgCl_2$	3	100	3	160	3
5	15	3	$MgCl_2$	3	100	3	160	3
6	15	9	$MgCl_2$	3	100	3	160	3
7	15	12.5	$MgCl_2$	3	100	3	160	3
8	15	15	$MgCl_2$	3	100	3	160	3
9	15	15	NaH_2PO_2	3	100	3	160	3
10	15	15	$MgCl_2$	6	100	3	160	3
11	15	15	$MgCl_2$	10	100	3	160	3
12	15	15	$MgCl_2$	6	100	3	160	6
13	15	15	$MgCl_2$	6	100	3	160	10
14	15	15	$MgCl_2$	3	100	3	180	3

**treatment I conditions: padding I with Tetronic 701 and 3% catalyst –drying (100°C, 3 min.)-curing (160°C, 3 min.)*

Table 2
CONDITIONS OF 100% COTTON FABRIC TREATMENT WITH CHITOSAN

Take –up degree (Y_P)

The take-up degree Y_p was determined using the relation (1):

$$Y_P = 100 \cdot (W_a - W_b)/W_b \quad [\%] \quad (1)$$

where:

Y_p = take-up degree;

W_a = cotton mass before wrinkle-proofing;

W_b = cotton mass after wrinkle-proofing.

Yellowness index

Yellowness index 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. Yellowness index was determined by using the Spectroflash SF300/Datacolor Spectrophotometer and the ASTM Method E313-73.

Durability of treatment effects highlighted by tinctorial method

Testing the strength of the link between fabric pretreated with Tetronic 701 and grafted with chitosan can be done by determining the losses after a number of cycles of washings (5-10) [13] or by the method of tinctorial. We have chosen to show the method tinctorial to prove that chitosan remains covalently bound to the pretreated cotton fabric even under severe conditions of treatment (high temperature required for the dyeing process).

Dyeing tests were made with two dyes from two different classes: acid dye class - Eosin Y(Acid Red 87, CI 45380) and direct dye class: Congo Red (C.I 22120). The choice of these classes of dyes was made taking into account the affinity they have with two partners present in any sample treated: tetrol and chitosan.

The dyeings of the samples treated with chitosan with Eosin Y (Acid Red 87) were carried out only after having first been carried out a operation acidification (acetic acid, *p*H = 4.5) for 30 min at 20°C. This step was necessary to protonate nitrogen atoms existing in chitosan, thus giving the treated cellulose, cationic character. Intensity type electrostatic interactions, the attraction is reflected in strength color values (K/S), which can justify the effects generated by grafting with chitosan.

Congo Red dye was performed by the classical procedure in neutral. Dyeing parameters were: temperature 90°C for 90 min.

Wrinkle recovering angles (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 angles as the average of 10 measurements along both the warp and the weft directions.

Tensile strength of the treated samples

Tensile strength determinations were carried out in the weft and warp direction using the apparatus ZWICK ROELL 2005 Germany 2008, according to the standard test DIN EN 13934-1.

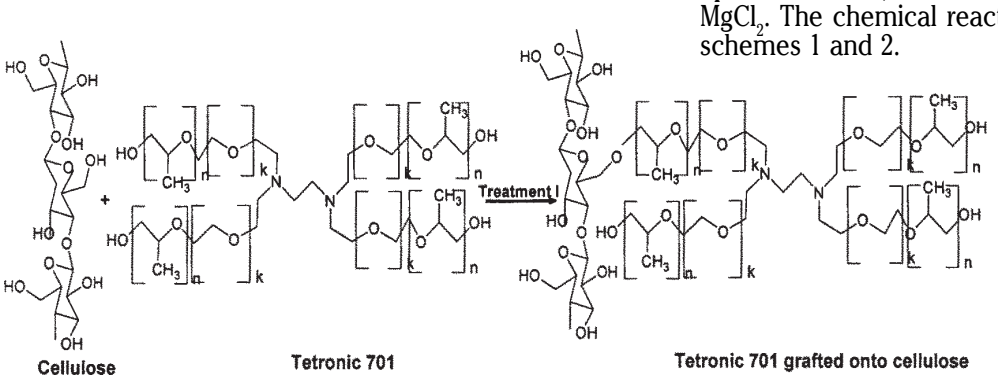
Water absorption through capillarity

The samples treated with tetrol had the following dimensions: 25x200mm. The 0.2% Eosin Y solution was poured in the apparatus vat up to the indicated mark. The samples were fixed in their upper end from the support from the top of the apparatus, while the other end was immersed in the solution from the vat till 30mm depth. The level up to which the solution rose on the material during each 5 min interval was measured during one hour. Twelve measurements were carried out for each sample, until the rise level became constant. The capillarity absorption was tested on 30 samples, because two identical specimens were used for each sample.

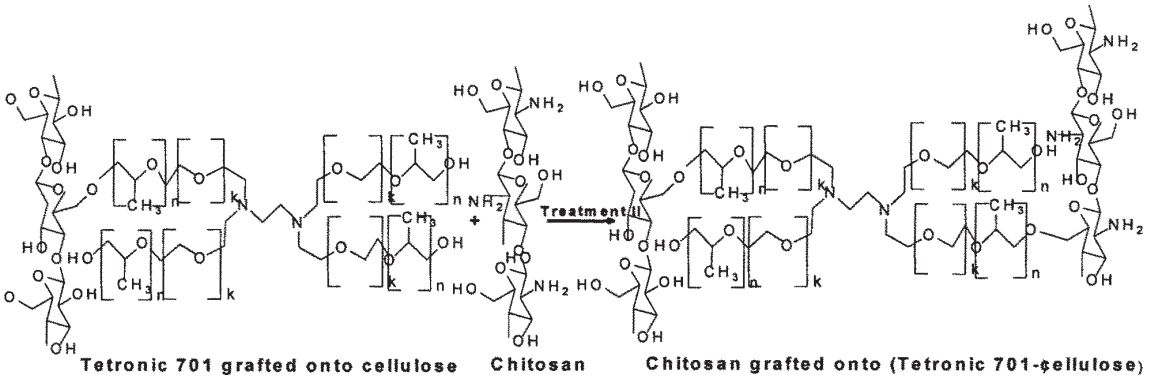
Results and discussions

Mechanism

The main functional groups of chitosan are the OH group attached to the C no. 6, and the amine group attached to the C no. 2 [14]. The cellulose pretreated with Tetronic 701 also includes at most three OH groups coming from Tetronic 701 structure. These groups are responsible for condensation reaction (i.e. water removal) and generation of new ether bridges with chitosan; yet, these reactions are only possible under certain conditions during the curing operation: 160°C, 3 min time and the presence of a catalyst, $MgCl_2$. The chemical reactions can be described by the schemes 1 and 2.



Scheme 1



Scheme 2

The chitosan presence in the new samples is testified by the spectroscopic analyses (FTIR and XPS) and by the tinctorial method: dyeing with acid dye - Eosin Y and dyeing with direct dye- Congo Red.

Spectroscopic analyses

ATR-FTIR analysis

We compared in Figure 1 the spectra of a sample treated only with Tetronic 701 (as a witness sample), with those of a sample subject to both a pretreatment with Tetronic 701 and a treatment with chitosan. At the same time, we overlapped the spectrum corresponding to powder chitosan. The spectrum of the sample pretreated with Tetronic 701 and grafted with CS indicates the preservation of the cellulose support pretreated with Tetronic 701, but one can also notice the presence of vibrations characteristic to chitosan (Fig. 1a and 1b), namely: 3336 $cm^{-1}$for O-H, NH_2 asymmetric and symmetric stretchings:1647cm^{-1} for NH deformation, amide II; 1547cm^{-1} for N-H bending of NH_2 (detail from fig. 1b); 1258cm^{-1} is a combination of N-C-O stretching, amide IV and OH bending; 1159cm^{-1} overlapping asymmetric bridge oxygen (C-O-C) stretching with CN stretching; 1105-1027cm^{-1} overlapping C-O stretching of C_3-OH with CN stretching; 706cm^{-1} for NH, Wagging (broad peak). The peaks from 1200 and 1027cm^{-1} (C-O asymmetric and symmetric stretchings) confirm the accomplishment of an ether bond between the terminal OH groups of Tetronic 701 and the primary OH groups of chitosan.

XPS analysis

The XPS spectroscopic analysis indicates the presence of Tetronic 701 product and of chitosan in the treated samples. In figure 2, the de-convolutions obtained after performing the XPS spectroscopic analyses confirm the realization of a chemical bond between the cotton pretreated with Tetronic 701 and then treated with chitosan.

By comparing the XPS results corresponding to the untreated sample with those of chitosan powder (Table 3), one can notice that, besides the C1s and O1s atoms, in the case of chitosan also appear N1s atoms, in a proportion of 6.5% atoms. The chitosan presence in the treated samples is confirmed by two aspects:

- presence in the XPS spectrum of the sample pretreated with Tetronic 701 and grafted with chitosan, of the N1s atoms at the position 400.0, in a percentage of 2.6% (atom concentration);
- increase of the percentage of C1s atoms (from the position 283) to 76.10%, as compared to 73.60% in the untreated sample.

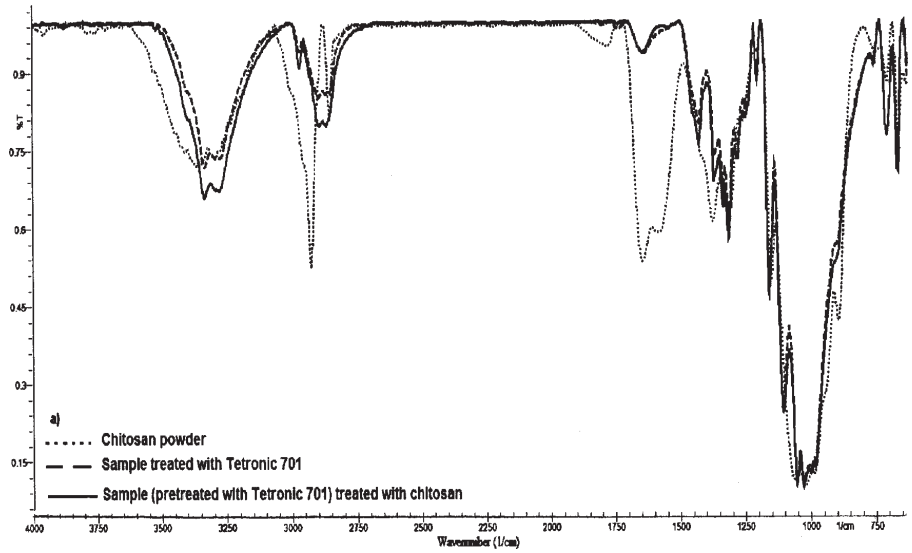


Fig. 1a

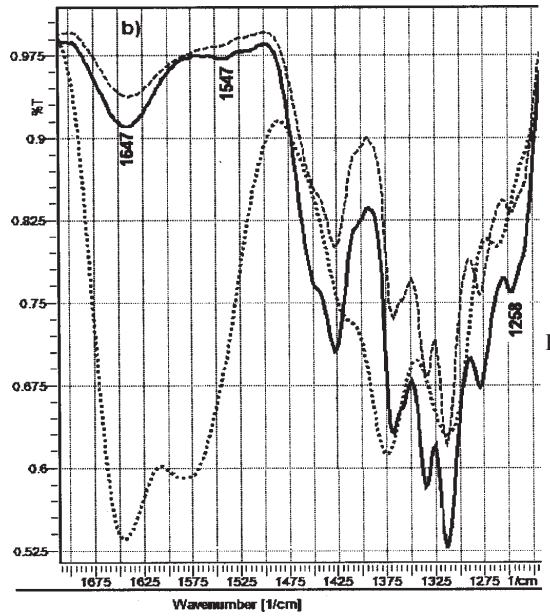


Fig. 1b

Fig. 1. FTIR spectra: a) spectra overlapping; b) detail from 1700-1200cm^{-1} range

Take-up degree (Y_P) and yellowness index (YI)

The passage of chitosan from the treatment solution to the textile material functionalized with Tetronic 701 can be appreciated by means of the take-up degree (Y_P) and the yellowness index (YI). The values obtained for Y_P and YI are presented in Table 4 (the code of each sample is the same as in table 2).

The treatment conditions significantly influence both the take-up degree and the yellowness index. For instance, the samples 1-4 (realized with equal concentrations of Tetronic 701 and chitosan) took up the lowest quantities of substances from the padding through: as the quantities of substances from the padding through, the take-up degree also decreased, and the yellowness index decreased. This fact confirms the eco-friendly character of chitosan; any treatment performed with chitosan does not worsen the degree of whiteness, on the contrary, the higher the chitosan concentration, the poorer the yellowish shade acquired after the treatment (samples 5-8). As the chitosan is colorless and it is disposed on the external surface of the cotton fiber, it will determine an increase of the light reflection, therefore a better degree of whiteness and/or a poorer yellowness.

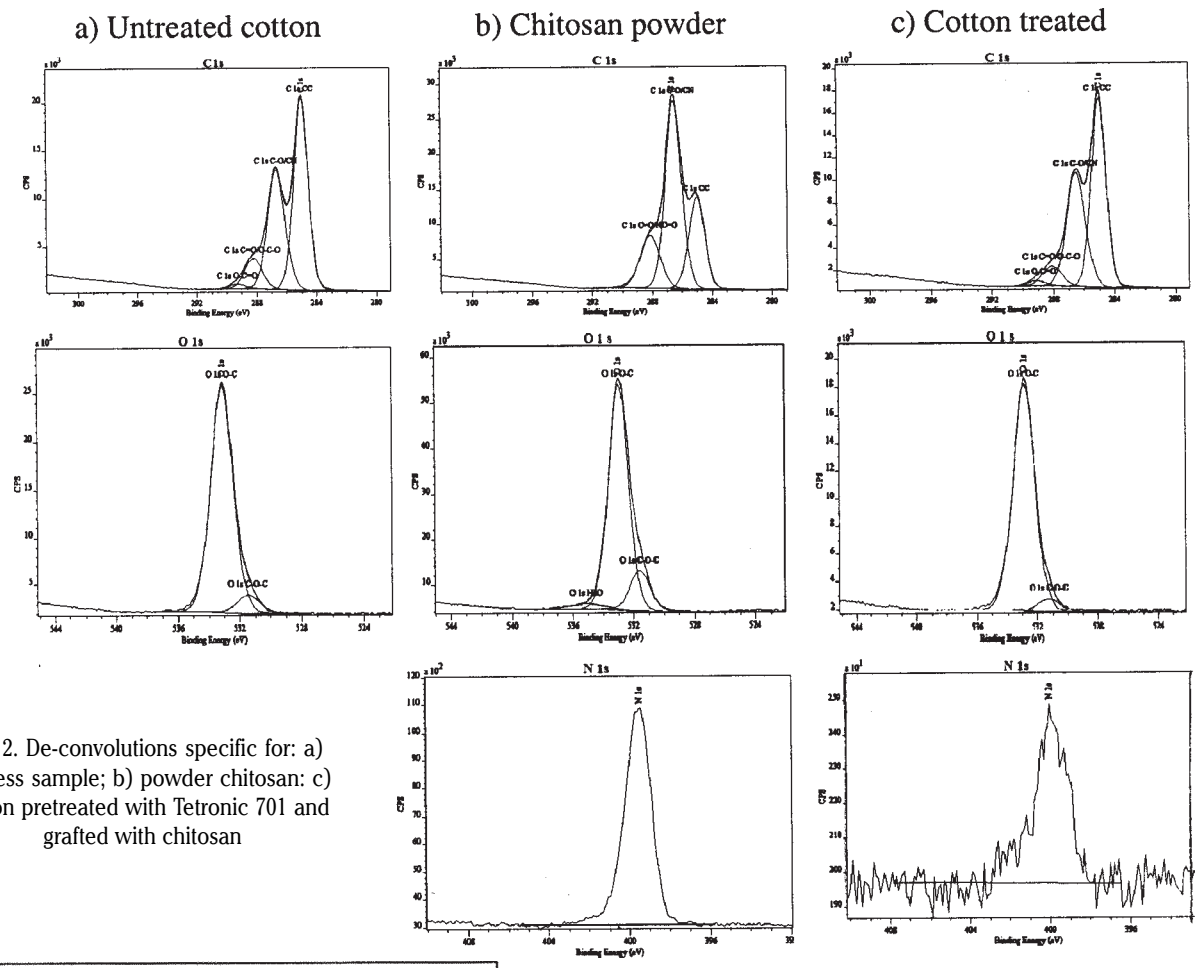


Fig. 2. De-convolutions specific for: a) witness sample; b) powder chitosan: c) cotton pretreated with Tetronic 701 and grafted with chitosan

Sample	Name	Position	Atoms Concentration (%)
Untreated cotton	C1s	285.0	73.6
	O1s	533.1	26.4
Chitosan powder	C1s	286.6	60.8
	O1s	533.0	32.7
	N1s	399.5	6.5
(Cotton+ Tetronic701)+ Chitosan	C1s	285.0	76.1
	O1s	532.9	21.3
	N1s	400.0	2.6

Table 3
RESULTS OF THE XPS ANALYSES

Crt. No.	Padding I with Tetronic 701 (%)	Padding II with chitosan (%)	Catalyst type	Padding time/drying time/curing time (min.)	Take–up degree Y_P (%)	Yellowness index YI
W	**Witness**	-	-	-	-	11,58
1.	3	3	$MgCl_2$	3/3/3	5.30	16.95
2	9	9	$MgCl_2$	3/3/3	8.76	15.59
3	12.5	12.5	$MgCl_2$	3/3/3	8.67	14.22
4	15	15	$MgCl_2$	3/3/3	10.01	10.46
5	15	3	$MgCl_2$	3/3/3	13.97	11.35
6	15	9	$MgCl_2$	3/3/3	11.92	10.66
7	15	12.5	$MgCl_2$	3/3/3	13.20	10.20
8	15	15	$MgCl_2$	3/3/3	16.84	8.46
9	15	15	NaH_2PO_2	3/3/3	16.13	7.35
10	15	15	$MgCl_2$	6 /3/3	14.41	10.07
11	15	15	$MgCl_2$	10/3/3	14.99	19.29
12	15	15	$MgCl_2$	6 /3/6	15.07	20.39
13	15	15	$MgCl_2$	6 /3/10	13.11	21.75
14	15	15	$MgCl_2$/180°C	3/3/3	11.37	24.53

Table 4
VALUES OF THE TAKE-UP DEGREE AND YELLOWNESS INDEX

Under more severe treatment conditions (maximum chitosan concentration (15%) and smaller impregnation, and/or curing times (6-10 min)), one can notice, besides a poorer taking-up of substances, (comparative to samples 8 and 9) a worsening of the whiteness degree, manifested through a marked yellowness (samples 10-13). The poorest results were registered for the sample 14 that was made at the highest curing temperature (180°C).

Samples Codes*	*Witnesses*	dE*	dL*	da*	db*	dC*	dH*
1	cotton+3% Tetronic 701	22.41	-16.107	-15.581	-0.305	-14.819	4.822
2	cotton+9% Tetronic 701	22.76	-15.261	-16.877	-0.118	-16.002	5.399
3	cotton+12.5% Tetronic 701	23.46	-15.382	-17.516	2.679	-15.599	8.405
4	cotton+15% Tetronic 701	22. 24	-14.908	-16.36	2.105	-14.96	6.949
5	cotton+15% Tetronic 701	21.71	-14.646	-15.41	4.397	-13.209	9.087
6	cotton+15% Tetronic 701	23.02	-14.308	-17.62	3.831	-15.453	9.295
7	cotton+15% Tetronic 701	25.34	-18.622	-16.80	3.637	-14.78	8.778
8	cotton+15% Tetronic 701	20.74	-10.145	-17.97	2.101	-16.463	7.522
9	cotton+15% Tetronic 701	21.38	-13.800	-15.86	5.148	-13.333	10.054
10	cotton+15% Tetronic 701	21.24	-12.170	-16.76	4.947	-14.208	10.178
11	cotton+15% Tetronic 701	21.44	-12.357	-16.50	5.892	-13.569	11.091
12	cotton+15% Tetronic 701	21.36	-11.273	-18.06	1.281	-16.645	7.241
13	cotton+15% Tetronic 701	23.60	-13.163	-19.50	1.910	-17.944	7.874
14	cotton+15% Tetronic 701	22.48	-14.185	-17.42	0.696	-16.461	6.761

* Samples Codes are same as in Table 2

Table 5
CHROMATIC CHARACTERISTICS OF THE SAMPLES DYED WITH EOSIN Y

Durability of the treatment effects highlighted by tinctorial method

The tinctorial method demonstrates the way of chitosan bonding on the samples pretreated with Tetronic 701. The FTIR analysis confirms the realization of the ether bridges between Tetronic 701 and chitosan, i.e. the terminal OH groups of Tetronic 701 react with the chitosan primary OH groups in the presence of an acid medium realized by means of the catalyst; it is known that this metallic salt ($MgCl_2$) generates HCl due to high temperatures during the cure stage. In this relation, the chitosan presence can be demonstrated by means of the tinctorial method, as the amine groups from chitosan can serve as dyeing centers for any acid dye, after a previous protonation.

The tinctorial tests were performed by using two dyes: an acid dye, Eosin Y (Acid Red 87, C.I. 45380) and a direct dye, Congo Red (C.I.22120) in neutral medium.

Dyeing with Eosin Y (Acid Red 87, C.I. 45380)

At the beginning of dyeing process, all the samples treated with chitosan (and pretreated with Tetronic 701) suffered an operation of acidulation with acetic acid (*p*H = 4.5) for 30 min at 20°C. This stage was necessary in order to protonate the amine groups from chitosan, conferring the treated cellulose a cationic character. Dyeing with Eosin Y of the treated and protonated samples is possible due to the electrostatic attraction between the positive groups from the treated textile (acquired at the level of the N atom from the amine group of chitosan) with the negative groups (COO^- and O^-) from the acid dye (table 5).

Table 5 presents chromatic characteristics for the 14 samples pretreated with Tetronic 701 and grafted with Chitosan. Data were presented separately, according to witnesses they have.

The colorimetric characteristics of the treated samples (with Tetronic 701 in the first stage and with chitosan in the second stage) and dyed with Eosin Y are highlighted in Table 5.

For the data from table 5, the color differences were examined by using a Spectroflash SF 300 type Data Color spectrophotometer. The color differences **dE*** were estimated from the values of **dL***, **dC***, **db***, **da*** and **dH***, where: **dE*** is color differences between the examined sample and the witness, i.e. the distance between their positions in the CIELAB space; **dL*** is brightness difference; **dC*** is saturation difference; **da** and **db** represent chromatic parameters; **dH*** is shade difference [15-23].

In table 5 one can easily notice if the samples are brighter (**dL** > 0) or darker (**dL** < 0) than the witness, as well as the sample hue, (appreciated from the position as reported to the **da** (red-green) and **db** (yellow-blue) axes.

Luminosity differences for the samples treated and dyed with 2% Eosin Y are negative (**dL*** < 0 in table 5), which explains the completion of the reaction of covalent bonding of wrinkle-proofing agent (chitosan) with the samples treated with Tetronic 701. All the samples dyed with Eosin Y are less bright than the witness, as they were dyed more intensely than this.

The **dC*** < 0 values indicate that Eosin Y is not a pure dyestuff; it is non-unitary, has a lower saturation, being based on two components: a red one and a yellow one. The chromatic parameters **da*** and **db*** indicate the color variation toward green (through the negative values for **da*),** and a higher tendency toward yellow (though the positive values of **db***). The positive values of **dH*** show that all the samples have slight yellow hues as compared to the witness, yet, they have stronger hues toward green than the witness (because **da*** <0), therefore one can say that the yellow hue is less pronounced [24-30]. Therefore, after dyeing the samples treated with Tetronic 701 and Chitosan, one can get "darker red less yellow hues".

The treatment efficiency is revealed by the colour strength (K/S) of the 14 samples produced under the condition of modifying the following parameters:

- equal concentration of chitosan and Tetronic 701, used in the two treatments for the samples 1-4 results in the increase of K/S (*samples have **dL** < 0*);
- the increase of chitosan concentration (3-15%) on the samples 5-8 pretreated with 15% Tetronic 701, under the condition of $MgCl_2$ utilization as catalyst results in the increase of the color intensity (they have ***dL** < 0*);
- the treatment with 15% chitosan on the sample pretreated with 15% Tetronic 701, but in the presence of NaH_2PO_3 as catalyst (sample 9) leads to a higher K/S than for the identical sample treated in the presence of $MgCl_2$;
- changing the padding time (samples 10-11) and curing time (for the samples 12 and 13, when the concentrations

Nr. crt.	Witness	dE*	dL*	da*	db*	dC*	dH*
1	cotton+3% Tetronic 701	6,728	-0.367	3.231	5.891	5.715	3.531
2	cotton+9% Tetronic 701	6.562	-1.291	2.662	5.857	5.207	3.780
3	cotton+12.5% Tetronic 701	7.789	-0.189	3.661	6.873	6.578	4.167
4	cotton+15% Tetronic 701	5.683	-1.454	2.252	5.011	4.407	3.280
5		7.265	1.520	4.782	5.254	6.715	2.318
6		6.638	-0.323	3.347	5.724	5.712	3.367
7		6.428	0.446	4.134	4.903	5.979	2.319
8		5.951	0.091	3.584	4.750	5.426	2.444
9		6.057	2.024	4.142	3.92	5.509	1.498
10		5.905	-1.434	2.939	4.917	4.951	2.881
11		6.155	-1.505	2.610	5.367	4.896	3.412
12		7.253	-0.204	3.596	6.295	6.220	3.726
13		6.164	-2.340	1.660	5.456	4.129	3.934
14		7.886	-3.511	2.748	6.505	5.604	4.297

Table 6
CHROMATIC CHARACTERISTICS OF THE SAMPLES DYED WITH CONGO RED

of the treatment substances were 15% Tetronic 701 and 15% chitosan respectively) results in higher values of K/S than when the treatment time was of 3 min.

By comparing the K/S values of the samples 14 and 8 (produced under identical conditions of concentrations and treatment time, but increasing the curing temperature at 180°C for the sample 14), one can notice that the sample 14 has higher K/S values; this fact indicates the need to avoid the utilization of the temperature of 180°C in the future treatments because leads to smaller take-up degrees and higher yellowness index (table 4), even if the dL<0.

Dyeing with Congo Red

In table 6 are presented the data for the chromatic characteristics of the samples dyed with Congo Red.

The table 6 highlights the following aspects:

- samples 1-4 are darker than the corresponding witnesses;

- samples 5-8 have smaller color intensities K/S; therefore they are lighter than the witness (*sample treated only with 15% Tetronic 701*). These samples were realized through pretreatment with a constant concentration of Tetronic 701 (namely 15%), but with increasing chitosan concentrations (3-15%). Ether bridges are formed through the covalent bonding of chitosan with Tetronic 701, their number increasing with the increase of chitosan concentration;

- the involvement of OH groups from Tetronic 701 in the interaction with primary OH groups of chitosan results in the diminution of the number of OH groups (*from the molecule of Tetronic 701 product)* available to realize hydrogen bonds with the direct Congo Red dye. In these cases, the color intensities are smaller that those of the witness sample. Yet, as the chitosan concentration increases from 3 to 15%, the sample luminosity diminishes, also demonstrating the involvement of the secondary OH groups from chitosan in the dyeing process.

- the utilization of hypophosphite as catalyst results in cellulose partial crosslinkings. The presence of these reticulation cross-linking lines determines the decrease of the number of OH groups able to interact with the SO_3H groups from the dye. For this reason, the sample 9 will be brighter than the witness, i.e. its color is lighter;

- samples 10 -14 have higher K/S values than the witness, because the increase of the parameters (padding time, curing time and temperature) results accordingly in taking-up bigger amounts of substances, therefore a more intense dyeing.

As one can notice in table 6, the samples that have **dL*** < 0 are darker than the witness, while those that have **dL*** > 0 are brighter than the witness.

The data from table 6 indicate large colour differences between the witness and the treated samples, considering the high values of **dE*.** The positive values of **da*** and **db*** indicate that color variation turns to red and respectively yellow, while **dC* > 0** indicates the unilateral character of the Congo Red dye. The positive values for the hue difference **dH*** indicate that all the samples are more yellow than the witness, namely they have less blue than the witness. Therefore, after dyeing the samples treated with Tetronic 701 and Chitosan, darker redder yellow hues are obtained.

Absorption by capillarity

The phenomenon of capillary rise has been followed during a determined time interval, and sample characterization was done by drawing the curves of capillary rise (fig. 3), working according to the indications from literature [12].

Figure 3 indicates the cumulated rises of the height of the liquid column along one hour (from 5 to 5 minutes). It is thus revealed that the capillary absorption is performed with different rates during the studied time interval, and that there is a stationary tendency to the end of the 60 minute testing interval. The highest values were obtained for the witness sample (W). Irrespective of the utilized catalyst, all the samples treated with chitosan (1-14) show a poorer liquid absorption, this fact proving the hydrophobic character of chitosan.

Wrinkling recovering angle, WRA

The wrinkle recovering angles were determined for both dry and wet samples (fig. 4).

By analyzing the data from figure 4, one can notice that:

- all the samples treated with chitosan lead to wrinkle recovering angles bigger than that of the witness, which recommend it as a good wrinkle-proofing agent;

- dry and wet WRA of the samples pretreated with Tetronic 701 and grafted with chitosan are bigger than those of the samples only treated with 15% Tetronic 701;

- WRA values are bigger for the dry samples than for the wet samples [31];

- increasing concentration of chitosan results in increasing WRA;

- the increase of the padding and/or curing times lead to the increase of the wrinkle recovering angles. But, these severe conditions determine sample yellowing (see the YI values in the Table 2) as the result of degradation, therefore they should be avoided. The effects generated by both substances and working conditions are best shown off by the tensile strength values for the treated samples.

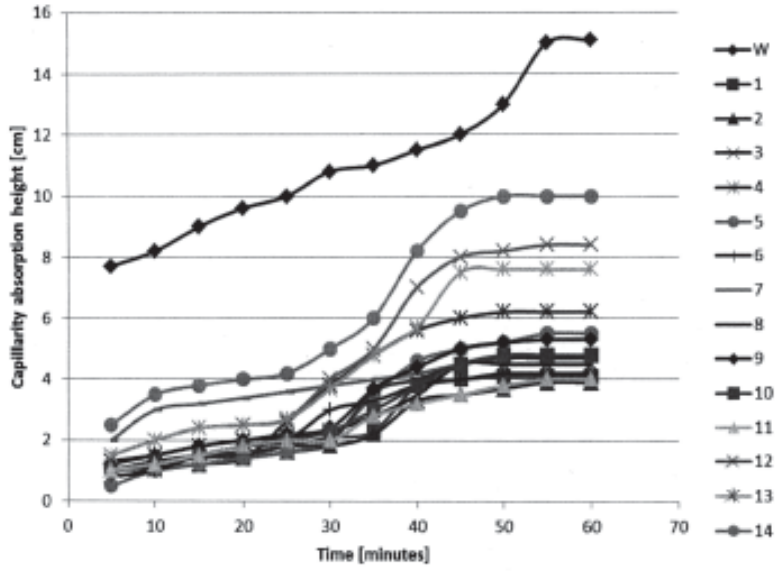


Fig. 3. Capillary rise after the treatment with Chitosan

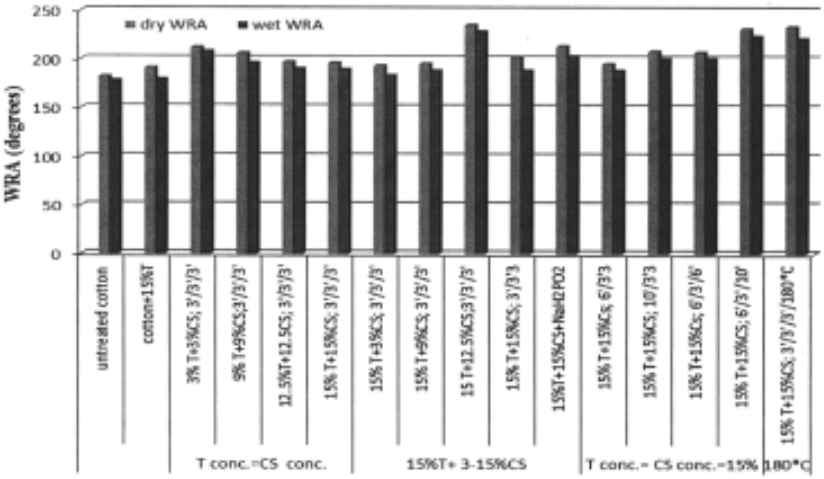


Fig. 4. WRA values for the samples pretreated with Tetronic 701 and then grafted with Chitosan

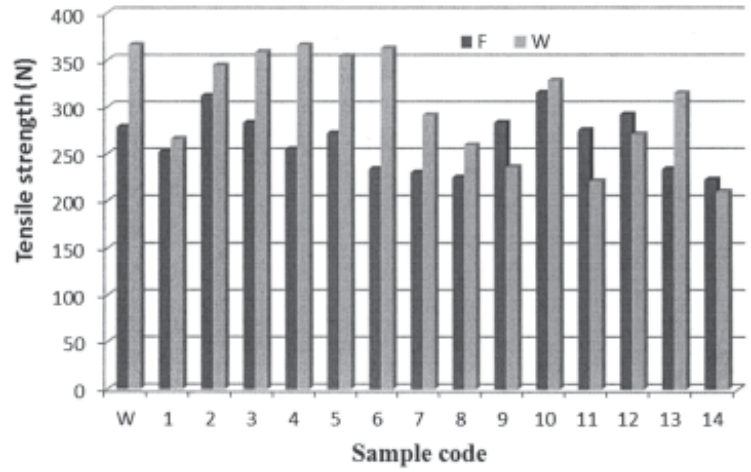


Fig. 5. Tensile strength value on weft (F) and warp (W) directions (*sample code:* is the same as in table 2 and W is the witness)

Tensile strength

Most of the samples treated with chitosan have a slightly smaller tensile strength than the witness sample (fig. 5). The small losses of the tensile strength can be explained as follows: under the action of the tensile force, the lines from the yarn slide until they get equally distributed on all the yarn elements, thus resisting to extreme force. Yet, crosslinking occurs, the sliding ceases such that the external force, especially the tensile force, no longer acts equally along all the yarn elements, resulting in successive breakings. In the end, the yarn tensile strength is smaller. The crosslinking generally appears when the padding and curing conditions respectively are more severe (higher times and temperatures).

The tensile strength loss is more significant only for the samples realized on weft direction.

In figure 5 one can notice that some samples (*especially on warp direction*) have equal or higher values than the witness, due to chitosan utilization (samples 2 and 3) and the big padding times (samples 10 and 11). Perhaps chitosan acts like a binder for all the component elements of the fabric (fibers/yarns), which makes the textile act as a single whole that opposes a higher resistance when subject to an external force.

The action of maintaining large padding times, cumulated with the increase of the curing time or temperature do not result in a better tensile strength; the effect is quite opposite (see samples 11, 13 and 14).

Even if it does not improve the wettability, chitosan can be used in the future research, as it is an eco-friendly product and produces big wrinkle-recovering angles, cumulated with small losses of the tensile strength, therefore good wrinkle-proofing effects.

Conclusions

Spectroscopic (FTIR and XPS) analyses confirm the chitosan covalent bonding on the cellulose support pretreated with Tetronic 701. The durability of the effects of chitosan grafting is confirmed by the tinctorial method; dyeing with an acid dye, unspecific for cotton, is possible due to the chitosan presence in the treated samples, even under severe dyeing conditions (100°C for 60 min). The protonation of the chitosan NH_2 groups (at the beginning of dyeing) confers positive charges to the grafted textile support. This can be easily dyed with acid dyes, based on ionic interactions. Dyeing with Congo Red direct dye confirms the involvement of the terminal OH groups from Tetronic 701 in the ether bridges formed after curing, with the OH primary groups from chitosan. The decrease of the number of free OH groups from Tetronic results in stronger luminosity of the dyed samples. The accomplishment of grafting was also confirmed by the increase of the take-up degree as the chitosan concentration increased. For a constant Tetronic 701 concentration (15%) and increasing chitosan concentrations (3-15%), the yellowness index decreased, thus confirming the presence of chitosan as a colorless film on the treated support, which determines the increase of the reflected light, therefore of the degree of white. The water absorbing capacity, WRA and the tensile strength change are depending on the treatment conditions. The chitosan presence determines the diminution of the water absorbing capacity, even if the pretreatment with Tetronic 701 produced samples more hydrophilic than the witness. The resistance loss is smaller due to chitosan, which acts as a binder for the yarns/fibers from the treated textile. The tensile strengths are slightly smaller than that of the witness sample on the weft direction, except for the samples 2, 3, 10 and 12. WRA increases with the increasing chitosan concentration.

Acknowledgement: This paper was acomplished 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.

References

1.RAMAPRASAD, A.T., RAO, V., SANJEEV, G., RAMANANI, S.P., SABHARWAL S., Synthetic Metals, **159**, 2009, p. 1983.
2.SANTOS, C. SEABRA, P. VELEIRINHO, B. DELGADILLO I., LOPES da SILVA J.A. European Polymer Journal, **42**, 2006, p. 3277
3.VERMA, M., KHAMBRA, K., YADAV, N., SINGH, R., International Journal of Textile and Fashion Technology, **3**, no.4, 2013.
4.CAN, Y., AKAYDIN, M., TURHAN, Y., AY, E., Indian Journal of Fibre & Textile Research, **34**, no.6, 2009, p 183.
5.IVANOVA, N.A., PHILIPCHENKO, A.B., Applied Surface Science, **263**, 2012, p. 783.
6.ILIESCU, E., POPESCU, V., RADU, D. C, Symposium with International Participation "Scientifically Research - A bridge for European Integration", Arad, 3-4 November, 2004, p.89
7.KAMIDE, K., Cellulose and Cellulose Derivatives, Elsevier, 2005, 652 p.
8.SCHRAMM, C., RINDERER ,B., BOBLETER, O., Textile Chemist and Colorist, **29**, no.9, 1997, p. 37
9. Yang, H., Yang, C.Q., Journal of Fire Science, **25**, 2007, p. 425.
10. Mao, Z., Yang, C.Q., Journal of Applied Polymer Science, **81**, 2001, p.2142.
11.PAPAY, A.G., MATTHEWS, B.W., THOMAS, A.S., Lubricating oil compositions of improved rust inhibition, Patent US3,928,219/Dec. 23, 1975.
12.RADU, C.D., PARTENI, O., BORHAN, O., VASLUIANU, E., SANDU, I., Rev. Chim. (Bucharest), **65**, no. 5, 2014. p. 534.
13.POPESCU.V., MURESAN, E.I., GRIGORIU, A.M., Carbohydrate Polymers, **86**, no.2, 2011, p. 600.
14.MOURYA, V.K., INAMDAR, N.N., React. Funct. Polym., **68**, no. 6, 2008, p. 1017.
15.PUSCAS, E.L., RADU, D.C., Introducere in cunoasterea si masurarea culorii, Ed. Dosoftei, Iasi, 1997, p.154.
16.PUSCAS, E.L., Colour theory and measurement, Ed. Rotaprint, Iaşi, 1983, p.167.
17.WARDMAN, R.H., An update on numerical problems in colour physics, Rev. Prog. Coloration, **24**, 1994, p. 55.
18.RADU, C. D., Colour measurement, Ed. Rotaprint, Iaşi, 2004, p.61.
19.SANDU, I., SANDU, I.C.A., SANDU, I.G., Colorimetry in Art, Ed. Corson, Iasi, 2002.
20.SCHANDA, J., Colorimetry, Wiley-Interscience John Wiley & Sons Inc., 2007, p. 56.
21.SANDU, I.C.A., LUCA, C., SANDU, I., Rev. Chim. (Bucharest), **51**, 2000, p. 532.
22.SANDU I., LUCA C., SANDU I.C.A., CIOCAN, A., SULITANU, N., Rev. Chim. (Bucharest), **52**, 2001, p. 485.
23.SANDU, I.C.A., LUCA, C., SANDU, I., POHONTU, M., Rev. Chim. (Bucharest), **52**, no. 7-8, 2001, p.409.
24.BERCU, E., DIACONESCU, R.M., RADU, C.D., POPESCU, V., European J. of Sci. and Theology, **8**, 2012, p.235.
25.SCARLET, R., MANEA, L.R., SANDU, I., MARTINOVA, L., CRAMARIUC, O., SANDU, I.G., Rev.Chim. (Bucharest), **63**, no. 7, 2012, p. 688.
26.SCARLET, R., MANEA, L.R., SANDU, I., CRAMARIUC, B., SANDU, A.V., Rev.Chim. (Bucharest), **63**, no. 8, 2012, p. 777.
27.ATODIRESEI G.V., SANDU, I.G., TULBURE, E.A., VASILACHE, V., BUTNARU, R., Rev. Chim. (Bucharest), **64**, no. 2, 2013, p. 165.
28.BERCU, E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., Mat. Plast., **50**, no. 3, 2013, p.215.
29.BERCU, E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., ALDEA, H.A., Mat. Plast., **49**, no. 4, 2012, p.270.
30.RADU, C.-D., BERCU, E., SANDU, I., FOIA, L.G., Mat. Plast., **51**, no.1, 2014, p. 104.
31.ILIESCU, E., NAGY, G., POPESCU, V., Finisarea superioara a materialelor textile, Vol I, Nesifonabilizarea, Ed. Tehnopress, Iasi, 2004, p. 191

Manuscript received: 13.02.2014