

The Influence of Non-selective Oxidation on Differently Pre-treated Cotton Yarns Properties

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Differently pre-treated cotton yarns were subjected to non-selective oxidation with perchloric acid and the effects of pre-treatment processes on oxidation were studied through functional groups quantity, and degradation through mechanical properties and degree of polymerization. Different pre-treatments include, different scouring (with alkali, alkaline and acid pectinase), mercerization-different scouring as well as different scouring-mercerization. The quantity of functional groups was studied by measuring carboxyl groups with methylene blue and calcium-acetate methods and aldehyde groups with iodine and tetrazolium (TTC) methods. Pre-treatment processes affect the degree of elimination of non-cellulosic components of cotton and have strong influence on oxidation process. The non-selective oxidation of enzymatic scoured cotton with perchloric acid has introduced carboxyl and aldehyde groups without serious degradation of cotton yarns, confirmed by only 15 % decreasing of tensile strength and 8 % decreasing of degree of polymerization.

Keywords: oxidation, cotton, degradation, carboxyl groups, functionalization.

1. INTRODUCTION

Cellulose is the largest and most widely used polysaccharide with ability to absorb moisture, with high thermal stability, good biocompatibility, relatively low cost and good mechanical properties. Modification of cellulose is an interesting route for preparing new polymers with specific properties. It may be obtained either by physical methods or chemical means. Physical methods are mechanical, thermal, plasma, laser, corona etc. The chemical methods are divided on chemical modification of polymers and application of chemicals (biopolymers). Chemical modifications are oxidation, treatments with enzymes, graft copolymerization, mercerization, esterification etc. [1]. The oxidation of cellulose is a typical method for modification under mild aqueous condition where introduction of aldehyde or carboxylic groups can be easily done by different chemicals, controlling pH, temperature, treatment time as well as state of the starting cellulose. Oxidation can be done on primary (at C-6) or secondary hydroxyl groups (at C-2 and C-3) and can be selective or non-selective. Selective oxidation is achieved with K- or Na-periodate, TEMPO or PINO [2–4], while non-selective with HClO₄, permanganate, hypochlorites and hydrogen peroxide [5].

Hydrogen peroxide, sodium hypochlorite and sodium periodate have been studied for different kind of textile materials like cotton gauze compresses, cotton knitted bandage and unwoven textile of viscose/PES which were preliminary alkaline scoured by 14 % NaOH [5]. Higher aldehyde groups were accounted for cotton gauze, followed by knitted bandages and unwoven textile independent of used oxidizing agent, providing that the structure of the cotton textile material is very important. The highest quantity of aldehyde groups was found on

oxidized cellulose by sodium periodate, followed by hypochlorite and peroxide. Periodate oxidation leads to the highest depolymerization and cause significant degradation [6]. Oxidized native cotton fibres with TEMPO showed a minimum increase of fineness, substantial decrease of tensile strength and a higher amount of carboxyl groups [7] with substantial decrease in DP [8].

Oxicellulose serve as useful intermediates for cellulose based materials that can adsorb some chemicals such as metals, proteins, polymers and dyes and are widely used in pharmaceuticals, drug and gene delivery, food industry, cosmetic products, polymer composites and metal absorbent [9]. Obtained dialdehyde celluloses can be used to immobilize proteins, drugs or hormones [10] or amino polysaccharides by reaction with their amino functional groups.

Oxidation of cotton, commonly is applied after conventional pre-treated processes such as scouring, bleaching or mercerization [5, 6]. In traditional alkaline scouring cuticle is completely removed and cotton can be degraded through oxicellulose formation. Enzymatic scouring with pectinase, through its selective action, breaks down the pectin in the cuticle and thereby assists the removal of waxes, proteins and other non-cellulose components. Mild working conditions and selective action avoid degradation of cotton [11].

Previous worldwide researches were mainly focused on analysis of charge on oxidized cotton prepared under more aggressive conditions, so, less attention has been given to oxidation of cotton pre-treated under mild conditions named as a „green” treatment which protects the fiber structure as well as environment.

Our previous research works, were mainly focused on evaluating the changes on cotton surface and non-cellulosic components after different „green” pre-treatments [12, 13]. Different pre-treatment conditions have strongly influenced the surface charge on cotton fiber, reduced the non-

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cellulosic components, but they were still detected at the fiber surface [12, 13].

The goal of this paper is to investigate the influence of different pre-treatment processes on the non-selective oxidation of cotton with perchloric acid including different scouring (with alkali, alkaline and acid pectinase), mercerization and different scouring as well as different scouring and mercerization. Quantity of carboxyl and aldehyde group as well as the degradation were studied on oxidized cotton yarns and compared to un-oxidized.

2. EXPERIMENTAL DETAILS

2.1. Materials

Piled, ring-worsted cotton yarn with linear density of 30 x 2 tex spun with 330 twists/m was supplied by VETEX AD Veles, Macedonia.

2.2. Treatment methods

Raw and mercerized cotton yarns (as hanks) were scoured by alkaline, alkaline pectinase and acid pectinase scouring.

Mercerization was done on Jäegli hank mercerization equipment by rolling the hanks in 23.5 % NaOH solution and 1 g/dm³ Subitol MEZ-N (CHT-Germany), wetting agent at 18 °C. Next, the hanks were extended by application of tension to the original length, rinsed with hot (80 °C) and cold (20 °C) water for 1 min under tension, neutralized and rinsed, and dried at 20 °C.

Alkaline scouring was done using 3.2 g/L NaOH in presence of 2 ml/L Cotoblanc HTD-N anionic surfactant (CHT) and 1 ml/l Kemonecer NI nonionic surfactant (Kemo-Croatia), 16.6 : 1 LR, at 100 °C for 60 min.

Alkaline pectinase scouring was done using 0.666 g BioPrep 3000L per kg material, 16.6 : 1 LR, containing 0.15 g/L Na₃PO₄ (pH 9) in the presence of 1 ml/L Kemonecer NI at 55 °C for 30 min. Then, 0.4 g/L EDTA was added to the scouring bath and the temperature raise to 90 °C for 15 min to stop enzymatic activity.

Acid pectinase scouring was done with 0.625 g NS 29048 per kg material, 16.6 : 1 LR, in acetic buffer (pH 4), in the presence of 1 ml/L Kemonecer NI, at 45 °C for 30 min. After that, 0.8 g/L EDTA was added and the temperature was raised to 90 °C for 15 min to stop enzymatic activity. After all used types of scouring yarns were rinsed at 90 °C for 10 min at 70 °C for 10 min, and once with cold water to full neutralization.

Demineralization was done with 0.01 M HCl, 35 : 1 LR, at 20 °C for 120 min. Yarns were rinsed five times with cold water for 15 min. After demineralization yarns were oxidized without drying. Oxidation was done with 1 M HClO₄, 35 : 1 LR, at 20 °C for 12 h. Yarns were rinsed five times with cold water for 15 min and dried at room temperature.

Sample codes and linear densities of the used yarns are given in Table 1.

2.3. Testing methods

Determination of carboxyl groups by Methylene blue adsorption (MB) was carried out according to Fras L. et al. [6].

Determination of carboxyl groups by Ca-acetate method [14]. A 1 g sample was added in 100 ml distilled water and 60 ml 0.25 M Ca-acetate solution, and 12 h treatment at room temperature with frequent shaking were done facilitated completion of the interchange: complexometric titration method (EDTA). 25 ml of the calcium-acetate solution were titrated with 0.1 M EDTA, using eriochrom black T at pH 10 by the addition of 5 ml (NH₄Cl + NH₄OH) buffer. The quantity of carboxyl groups is calculated using equation:

$$COOH(mmol/g) = \frac{(V_a - V_b) \cdot C}{m}, \quad (1)$$

where V_b is the consumption of titrating reagent (EDTA) for the sample (ml); V_a is the consumption of titrating reagent (EDTA) for the blank sample (ml); C is the concentration of the titrating reagent (mol/l); m the weight of sample (g).

Neutralization titration method (NaOH). 25 ml of the calcium-acetate solution were titrated with 0.01 M NaOH, using thymol blue indicator. The quantity of carboxyl groups is calculated using equation:

$$COOH(mmol/g) = \frac{\frac{160}{25} \cdot 0.01 M \cdot V(NaOH)}{m}, \quad (2)$$

where 0.01 M is the concentration of NaOH; V is the volume (ml) of NaOH solution used for titration; m is the weight of oxidized or un-oxidized cotton yarns (g).

Table 1. Codes and linear densities of the differently pre-treated cotton yarns

Codes	Differently pre-treated cotton yarns	Linear density (tex)
R	Raw	58.36
SA	Scoured with NaOH	58.10
SB	Scoured with BioPrep 3000 L	59.39
SN	Scoured with NS 29048	57.37
MSA	Mercerized, scoured with NaOH	58.35
MSB	Mercerized, scoured with BioPrep 3000 L	57.46
MSN	Mercerized, scoured with NS29048	58.52
SAM	Scoured with NaOH and mercerized	58.75
SBM	Scoured with BioPrep 3000 L and mercerized	59.71
SNM	Scoured with NS 20948 and mercerized	57.80

Determining the aldehyde groups by modified iodine method (I). 0.08 g sample was suspended in a solution of 30 cm³ 0.008 M NaOH and 10 cm³ 0.001 M J₂ solution. After standing 3 h at room temperature with frequent shaking, 25 cm³ portion of the solution, 15 cm³ 0.3 M HCl were titrated with 0.0075 M Na₂S₂O₃·5H₂O, using starch as indicator.

Aldehyde groups by tetrazolium method (TTC) were measured according to Strlic and Pihlar [15]. Presented results for carboxyl and aldehyde groups are mean values of 3 measurements at confidence level of 95 %.

Tensile strength (F), elongation (ε) and work of rupture (A) were carried out according to EN ISO 2062 1995 (2009) on Tinus Olsen (SDL ATLAS) using test speed of 100 mm/min and gauge length of 300 mm. Presented results are the mean values of 20 measurements at confidence level of 95 %.

Degree of polymerization (DP) was determined viscosimetrically after dissolving the sample in EWNN (sodium salt of ferric tartaric acid) [6].

All investigated parameters were analyzed by main effects analysis of variance (ANOVA), considering the oxidation (variable A), course of pre-treatment (variable B) and type of scouring (variable C) using STATISTICA 6 program.

3. RESULTS AND DISCUSSION

3.1. Analysis of functional groups on un-oxidized differently pre-treated cotton yarns

Oxidation is performed to produce cellulose derivate for specific applications. Pre-treatment processes of cotton are very important and may be crucial regarding its further oxidation. The results of analyzed surface residues through dyeing with different dyes published in our previous publications [12, 13] are given in Table 2, and the quantity of aldehyde and carboxyl groups before oxidation, obtained by method used in this work, is given in Table 3. Cotton yarns were dyed with direct and reactive dyes for determination of cellulosic purity and oil red, methylene blue (basic dye) and bemaclide blue (acid dye) for determination of waxes, pectin and proteins, respectively (Table 2). The highest degree of cellulose purity and the lowest value of waxes were obtained on cotton yarns after alkaline scouring; higher quantity of wax and pectin residues were found on alkaline pectinase scoured and the highest quantity of wax and pectin residues on acid pectinase scoured yarns (Table 2). In traditional alkaline scouring proteins are hydrolyzed to lower molecular weight components while waxes are saponified and emulsified. This process is followed with the lowest quantity of aldehyde and carboxyl groups, obtained by all used methods providing that the impurities are completely removed (Table 3). During enzymatic scouring, pectinases break down the pectin from the cuticle and thereby assist in removing of waxes, protein and other non-cellulosic components. As a result of mild working conditions and selective action of enzymes, part of the non-cellulosic residues, such as waxes, pectin and proteins remained on the cotton surface decreasing L_{OR}^* , L_{MB}^* and L_{BB}^* values (Table 2). Polygalacturonic acid is a main component of pectin. It contains carboxyl groups responsible for increased values of carboxyl groups on enzymatic scoured yarns (Table 3). The same examination was confirmed by Canal M. J at al. [16]. Acid pectinase scoured yarns has a higher quantity of carboxyl groups than alkaline pectinase scoured (Table 3). Acid pectinase acts in acid media promoting Ca^{2+} ions removal and producing higher quantity of carboxyl groups compared to scouring in alkaline media with alkaline pectinase [17].

Mergerized cotton yarns, independent of course of pre-treatment, have the same trend for aldehyde and carboxyl groups as scoured. SA has the lowest quantity of aldehyde and carboxylic groups followed by SB and SN (Table 3). The results from main effects ANOVA analysis confirmed that type of scouring has a significant influence on quantity of aldehyde and carboxyl groups to all courses of pre-treatment, while course of pre-treatment does no (Table 4).

The exception is only aldehyde groups determined by iodine method where course of pre-treatment has a significant influence.

Table 2. L^* values of differently pre-treated cotton yarns dyed with Siriuslichtblau FGG 200 % (Direct), Bezactiv blau HE-RM (Reactive) Oil red O (Dye for waxes), Methylene blue (Cationic dye for pectin) and Bemacid blau GLF 200 % (Acid dye for protein) [12, 13]

Differently pre-treated cotton yarns	L_{dir}^*	L_{reac}^*	L_{OR}^*	L_{MB}^*	L_{BB}^*
SA	52.945	48.397	56.47	66.51	77.22
SB	52.537	48.287	52.24	60.58	74.40
SN	52.405	48.504	51.83	58.19	74.41
MSA	46.424	37.560	62.81	68.37	77.76
MSB	44.999	35.573	57.14	63.94	73.12
MSN	45.178	37.165	50.73	59.55	72.98
SAM	46.461	34.784	64.99	68.55	77.62
SBM	44.921	34.810	60.27	66.12	75.73
SNM	43.710	35.123	56.53	62.62	75.69

Table 3. Carboxyl and aldehyde groups quantity of differently pre-treated cotton yarns determined with MB, EDTA and NaOH, I and TTC methods

Differently pre-treated cotton yarns	COOH, mmol/kg			CHO, mmol/kg	
	MB	EDTA	NaOH	I	TTC
SA	12.7	15	49.6	18.4	17.2
SB	19.4	20	61.6	23.1	18.2
SN	21.9	20	62.4	50.2	22.4
MSA	10.1	15	50	34.4	15.7
MSB	24.5	23.5	57.6	36.2	18.5
MSN	26.2	25	60.8	55.9	20.6
SAM	12.7	15	51.2	55.9	17.5
SBM	14.7	20	59.8	70.0	18.6
SNM	16.9	25	62.2	76.6	20.9

Iodine method is usually used for determination aldehyde groups and fine structure [18, 19]. The compositions of solutions in both cases are the same, but reaction conditions are different. In the case of aldehyde group determination, iodine acts with aldehyde groups and transform them to carboxyl [20]. In the case of fine structure (accessibility) determination, three-iodine ions form monolayer film, and therefore can be used for specific internal surface area determination [18].

Table 4. Evaluated p-values for significance of course of pre-treatment and type of scouring for all investigated properties

Variables	COOH			CHO	
	MB	EDTA	NaOH	I	TTC
Course of pre-treatment (p_B)	0.267	0.260	0.224	0.003	0.329
Type of scouring (p_C)	0.055	0.010	0.000	0.013	0.004

Note: p-values in bold indicate significant influence on the variables on investigated properties.

In our case iodine reacted with aldehyde groups, but probably, also made monolayer film inside the cotton fiber surface.

In our previous investigation mercerization index by FTIR-ATR (MI), monolayer capacity (MLC) and moisture

regain (MR) on the same yarns were determined [11]. The results showed that differently scoured-mercerized yarns have higher MI, MLC and MR than mercerized-differently scoured.

High coefficients of correlation were found between L_{OR}^* , L_{MB}^* and L_{BB}^* with MB, EDTA, NaOH and TTC, and also between L_{dir}^* and L_{reac}^* with iodine (Table 5). L_{OR}^* , L_{MB}^* and L_{BB}^* are methods for determination the wax, pectin and protein residues on the cotton surface, while iodine method for internal surface and accessibility determination. MB, EDTA, NaOH and TTC are methods that could be used mainly for surface functional groups determination (surface functionalization) while iodine method for surface as well as internal fiber functionalization.

Table 5. Coefficients of correlation between L^* values of cotton yarns dyed with different dyes and quantity of carboxyl and aldehyde groups

	MB	EDTA	NaOH	I	TTC
L_{OR}^*	-0.770	-0.605	-0.689	-0.142	-0.677
L_{MB}^*	-0.822	-0.684	-0.839	-0.088	-0.836
L_{BB}^*	-0.948	-0.809	-0.774	-0.039	-0.618
L_{dir}^*	-0.059	-0.045	-0.097	-0.687	-0.072
L_{reac}^*	0.064	-0.274	0.052	-0.647	0.126

3.2. Analysis of functional groups on oxidized differently pre-treated cotton yarns

3.2.1. Analysis of carboxyl groups

Differently pre-treated yarns were further oxidized with perchloric acid and the results of carboxyl groups obtained with different methods are present in Table 6. Oxidized yarns keep the same behaviour of increase of MB values as un-oxidized (Table 6). Oxidized SA has the lowest value of MB, followed by oxidized SB and SN. This trend could be observed for all courses of pre-treatment. Although enzymatic scoured-oxidized yarns have higher MB values than alkaline scoured-oxidized, when scoured-oxidized yarns are compared with unoxidized, alkaline scoured-oxidized (in all courses of pre-treatment) have higher percentage of increasing of MB values than enzymatic scoured-oxidized. 20 %, 60 % and 35 % have increased MB values on SA-, MSA- and SAM-oxidized yarns respectively, compared to unoxidized. For comparison, MB values increased 10 % on enzymatic scoured and oxidized, 15 % on mercerized-enzymatic scoured and oxidized and about 25 % on enzymatic scoured-mercerized and oxidized yarns. Higher percentage of increased MB value on SA oxidized yarns (in all courses of pre-treatment) is due to completely removed cuticle and completely available cellulose surface for oxidation.

Main effects ANOVA analysis (Table 7) showed that beside oxidation and type of scouring, course of pre-treatment have significant influence on MB values. While quantity of carboxyl groups of alkaline scoured yarns (oxidized and non-oxidized) are very similar in all courses of pre-treatment, quantity of carboxyl groups of enzymatic scoured yarns (oxidized and non-oxidized) differ on courses of pre-treatment. The highest values of MB have mercerized-differently scoured yarns, followed by differently scoured and differently scoured-mercerized.

Our previous results showed that significant changes occurred in cuticle structure and composition during mercerization [13]. The altered cuticle allows its different behaviour during scouring resulting in higher quantity of residual carboxyl groups and different behaviour during oxidation. That is why differently scoured-mercerized yarns have lower amount of carboxyl groups than mercerized-differently scoured [12, 13].

Table 6. Carboxyl groups quantity of differently pre-treated (S) and oxidized (O) cotton yarns determined with MB, EDTA and NaOH methods

Differently pre-treated cotton yarns	MB, mmol/kg		EDTA, mmol/kg		NaOH, mmol/kg	
	S	O	S	O	S	O
SA	12.7	15.2	15	35	49.6	52.6
SB	19.4	20.6	20	40	61.6	63.8
SN	21.9	24.6	20	40	62.4	72.1
MSA	10.1	16.1	15	35	50	54.6
MSB	24.5	28.5	23.5	45	57.6	62.9
MSN	26.2	30.8	25	45	60.8	72.4
SAM	12.7	17.1	15	35	51.2	53.7
SBM	14.7	18.8	20	37.5	59.8	61.7
SNM	16.9	21.0	25	37.5	62.2	68.6

Table 7. Evaluated p-values for significance of oxidation, course of pre-treatment and type of scouring for all investigated properties

Variables	COOH			CHO	
	MB	EDTA	NaOH	I	TTC
Oxidation (p _A)	0.0159	0.0000	0.0002	0.0208	0.0002
Course of pre-treatment (p _B)	0.0119	0.0347	0.8151	0.0002	0.0309
Type of scouring (p _C)	0.0002	0.0001	0.00000	0.0006	0.0052

Note: p-values in bold indicate significant influence on the variables on investigated properties.

Carboxyl groups obtained by complexometric titration (EDTA) are increased in all cases after oxidation. Enzymatic scoured yarns (independent of courses of pre-treatment) have higher quantity of carboxyl groups than alkaline (Table 6). After oxidation the highest increase of carboxyl groups was registered on mercerized-differently scoured, followed by differently scoured and differently scoured-mercerized yarns. Main effects ANOVA analysis showed that oxidation, course of pre-treatment and type of scouring have significant influence on carboxyl groups determined by EDTA (Table 7).

Quantity of carboxyl groups of differently pre-treated yarns before and after oxidation obtained by calcium-acetate method using neutralization titration (NaOH) is shown in Table 6. The results of carboxyl groups determined by this method are similar with the results determined by MB and EDTA methods.

3.2.2. Analysis of aldehyde groups

Quantity of aldehyde groups of differently pre-treated yarns after oxidation obtained by iodine and TTC methods are present in Table 8. In all courses of pre-treatments the lowest quantity of aldehyde groups determined by iodine method was found on SA, followed by SB and the highest on SN. This trend has the same behavior as the carboxyl

groups after oxidation. Unlike carboxyl groups, the quantity of aldehyde groups determined by iodine method decreased after oxidation with HClO₄. The main reason is probably conversion of aldehyde to carboxylic groups in presence of HClO₄.

Tetrazolium method showed that oxidized yarns possessed increased quantity of aldehyde groups.

Table 8. Aldehyde groups quantity of differently pre-treated (S) and oxidized (O) cotton yarns determined with (I) and (TTC) methods

Differently pre-treated cotton yarns	I, mmol/kg		TTC, mmol/kg	
	S	O	S	O
SA	18.4	19.7	17.2	22.8
SB	23.1	25.4	18.2	29.2
SN	50.2	47.8	22.4	29.1
MSA	34.4	29.1	15.7	18.6
MSB	36.2	30.0	18.5	24.4
MSN	55.9	48.8	20.6	23.2
SAM	55.9	42.2	17.5	19.7
SBM	70.0	43.3	18.6	22.9
SNM	76.6	51.6	20.9	21.4

The highest value of TTC has SB, followed by SN and SA. The trend is the same in all courses of pre-treatment. Although aldehyde groups of oxidized yarns determined by iodine methods decreased, the increase of aldehyde groups determined by TTC is a result of high sensitivity of the TTC method. Our previous results of TTC, on the same yarns oxidized with KIO₄, are 9 – 12 time higher than un-oxidized (in the process of publishing). On the other hand, aldehyde groups of KIO₄ oxidized yarns, measured with iodine method, increased to max 2.7 times. It confirms the sensitivity of TTC.

Main effects ANOVA analysis also confirm that oxidation, course of pre-treatment and type of scouring have significant influence on aldehyde groups obtained by iodine and TTC methods (Table 7).

3.3. Mechanical properties and degree of polymerization

The results from the effect of oxidation on the mechanical properties are given in Table 8. Increased tensile strength of alkaline scoured yarns, in all courses of pre-treatment, was a result of increased inter fiber friction. Remained non-cellulosic components on the enzymatic scoured cotton decreased inter fiber friction and therefore they have lower tensile strength than alkaline scoured cotton [21].

Oxidation of differently pre-treated yarn decrease tensile strength. Alkaline scoured yarns have higher degree of degradation (higher decrease of tensile strength) than enzymatic scoured. The completely removed cuticle on alkaline scoured yarns did not protect cellulose from perchloric acid attack. Perchloric acid destroyed cellulose chain, and therefore decreased the tensile strength.

The works of rupture of alkaline scoured yarns are, again, higher than on enzymatic scoured. Although the work of rupture decreased after oxidation, the changes are mainly lower than on tensile strength. Maximum 15 % lower tensile strength and 13 % lower work of rupture after oxidation confirmed negligible degradation of oxidized cotton yarns.

The degree of oxidative degradation of cellulose was followed by the degree of polymerization before and after oxidation. DP was measured on scoured yarns (Table 10). The higher DP on enzymatic scoured yarns than alkaline is due to the mild scouring conditions. Oxidized yarns have the same trend of DP as un-oxidized. Although the oxidation with perchloric acid decreases DP, the decreasing is around 8 %. These results are consistent to the results of Fras L. et al. [6].

It confirmed previously discussion of mechanical properties, that oxidation of cellulose with perchloric acid is non-aggressive, and is very good method for improving functionality of cotton.

Table 9. Tensile strength, elongation and work of rupture of differently pre-treated cotton yarns before (S) and after (O) oxidation

Differently pre-treated cotton yarns		Fs, N	Fo, N	ΔF, %	es, %	eo, %	Δε, %	As, mJ	Ao, mJ	ΔA, %
R	M ± ME	7.8 ± 0.18			6.6 ± 0.18			66.5 ± 2.69		
	Cv (%)	4.96			6.81			8.65		
SA	M ± ME	9.3 ± 0.30	8.3 ± 0.31	-10.7	10.1 ± 0.31	9.3 ± 0.39	-7.9	90.2 ± 4.16	78.5 ± 3.54	-12.9
	Cv (%)	6.86	7.89		6.52	9.06		9.87	9.65	
SB	M ± ME	7.9 ± 0.15	7.2 ± 0.18	-8.9	9.4 ± 0.32	9.8 ± 0.25	4.2	73.7 ± 2.85	68.4 ± 2.90	-7.2
	Cv (%)	4.62	5.38		7.31	5.50		9.55	9.04	
SN	M ± ME	7.7 ± 0.24	7.1 ± 0.25	-7.8	9.6 ± 0.25	9.3 ± 0.35	-3.1	70.4 ± 3.25	66.0 ± 2.50	-6.2
	Cv (%)	6.68	7.55		5.58	7.98		9.86	8.08	
MSA	M ± ME	16.0 ± 0.41	14.3 ± 0.42	-10.6	7.7 ± 0.23	8.0 ± 0.29	3.9	120.7 ± 5.49	114.4 ± 4.50	-5.2
	Cv (%)	5.92	6.19		6.30	7.87		9.73	9.26	
MSB	M ± ME	14.9 ± 0.55	12.6 ± 0.40	-15.4	6.8 ± 0.25	7.8 ± 0.21	14.7	102.1 ± 4.05	101.1 ± 4.36	-1.0
	Cv (%)	7.98	6.74		9.08	5.74		9.20	9.23	
MSN	M ± ME	12.7 ± 0.46	11.2 ± 0.33	-11.8	7.5 ± 0.24	7.0 ± 0.22	-6.7	97.1 ± 4.70	92.4 ± 4.19	-4.8
	Cv (%)	7.65	6.23		6.91	6.81		10.35	9.68	
SAM	M ± ME	16.1 ± 0.49	15.2 ± 0.55	-5.6	5.3 ± 0.24	6.4 ± 0.22	20.7	99.0 ± 4.42	87.3 ± 2.41	-11.8
	Cv (%)	6.52	7.66		9.68	7.49		9.54	9.00	
SBM	M ± ME	13.9 ± 0.40	13.7 ± 0.24	-1.4	6.6 ± 0.24	7.0 ± 0.20	6.1	92.6 ± 3.90	82.0 ± 3.38	-11.4
	Cv (%)	6.71	3.79		6.64	7.15		8.36	8.79	
SNM	M ± ME	14.8 ± 0.42	14.4 ± 0.45	-2.7	5.5 ± 0.21	6.4 ± 0.26	16.4	94.0 ± 3.95	92.2 ± 4.50	-1.9
	Cv (%)	6.09	6.68		8.13	8.72		8.99	9.89	

Note: M – mean value; ME – margin of error; Cv – coefficient of variation

Table 10. Degree of polymerization of differently pre-treated (S) and oxidized (O) cotton yarns

Type of pre-treatment	DP	
	S	O
SA	1222.5	1121.4
SB	1647.4	1529.9
SN	1346.3	1259.9

4. CONCLUSION

As a result of measured properties and as a result of discussions, following conclusions can be made:

Type of scouring processes of cotton yarns have significant influence on the quantity of carboxyl and aldehyde groups before non-selective oxidation with perchloric acid, while course of pre-treatment does no. Alkaline scoured cotton yarns (in all courses of pre-treatment) have the lowest quantity of carboxyl and aldehyde groups followed by alkaline pectinase and acid pectinase scoured.

Quantity of carboxyl and aldehyde groups on differently pre-treated and oxidized cotton yarns significantly depends of oxidation, course of pre-treatments and type of scouring. In terms of course of pre-treatment, the highest quantity of carboxyl groups has mercerized-differently scoured, followed by differently scoured and differently scoured-mercerized oxidized cotton.

15 % lower tensile strength, 13 % lower work of rupture as well as 8 % lower DP after oxidation confirms that oxidation with perchloric acid is good method for improving functionality on cotton fibers without its significant degradation.

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