

Cationization of waste cotton fabric - the influence on mechanical properties

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In this paper, the influence of cationization on the mechanical properties of waste cotton fabrics was investigated. Prior to determination of the mechanical properties, the efficiency of the cationizing agent was researched. Since the waste material was used, and its active groups are blocked, it was questionable whether it could be cationized. Therefore, waste cellulosic material, optically bleached and printed cotton fabrics, leftovers after tailoring process, were cationized during the mercerization process under laboratory conditions with high performance 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride and more ecologically acceptable cationizing agents. Based on the zeta potential it was found that waste materials, optically bleached and printed cotton cloth, were cationized. Testing the tensile properties of cationized materials confirmed improved strength and elongation, enabling the "filter" to be produced by the needle-punch process. Application of such filter would have multiple benefits for textile industry – textile waste recycling and waste waters purification, which directly have positive influence to environment protection.

Key words: cationization, textile waste from tailoring process, tensile properties

1. Introduction

The textile and garment industry, other than waste waters, generates waste from tailoring and sewing processes. For that reason this paper deals with the investigation of the cationization during mercerization of waste cellulose material which could be used as an added value material, a "filter" in wastewater treatment systems.

Cationization is a modification of cotton cellulose under alkaline condi-

tions based on the blocking mechanism of the -OH group, resulting in cellulose ethers [1-10]. The beginning of the research of cationized cotton with the aim of improving dyeing ties to M. Rupin, who processed cotton with a 40% solution of epoxypropyl trimethyl ammonium chloride [1]. In the 1990s detailed research of cotton modification with other cationic agents began, for the purpose of investigating the better exhaustion of anionic dyes in dyeing and printing

with direct, reactive and acid dye-stuff, and its fastness afterwards. Studies of quaternary ammonium compounds for cationization of cotton cellulose were investigated in papers [2-5]. They developed cotton cationization using 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride (CHPTAC) and 2,3-epoxypropyl trimethyl ammonium chloride (EPTAC) in aftertreatment to improve the dyeing and printing process [2-5]. Grancarić A.M. et al. and Tar-

buk A. et al. [6-8] have developed a technological process for the application of these compounds during mercerization process. With the well-known properties achieved by mercerization, increasing adsorptivity, strength and gloss [9-13], cationization during the mercerization process additionally change the charge of cotton cellulose, thereby completely changing the dye-cellulose and surfactant system [6-8, 14-17]. Finally, the modified cotton material of positive charge [7] is obtained. Other cationic reactive polyammonium compounds [14-16] can be used for cationizing cotton.

Since cationised bleached cotton has high adsorptivity for anionic agents, and could be used as a filter for wastewaters purification [7], the idea of using waste cellulosic material for the same cationization process was generated.

2. Eksperimental

2.1. Material, agents/auxiliaries and treatments

From tailoring process of company „DM TEKSTIL KROJAČKI OBRT“, Ozalj, two waste cellulosic fabrics were obtained (tailoring leftovers of 25 cm width):

- 1) Optical brightened fabric (OB)
 - weave: plain 1/1;
 - 100 % cotton;
 - application: hospital cloth and beddings;
 - mass per unit area: 190 g/m²;
 - finess warp/weft: 36/34 tex;
- 2) Printed fabric (TI)
 - weave: flannel;
 - 100 % cotton;
 - application: beddings;
 - mass per unit area: 165 g/m²;
 - finess warp/weft: 27,5/70 tex.

The following agents were used for cationization: 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC, Sigma Aldrich), and CHT-Bezema cationic reactive polyammonium compounds: Rewin OS and Rewin DWR. The Rewin DWR (cationic character, pH 3-4, yellow clear liquid) is used as aftertreatment

agent to improve the washing fastness of reactive dyes on cellulose fibers. It is applied at pH 7.5-8 at 40 °C in a concentration of 3-4% at m.m. [18]. Rewin OS (cationic character, pH 4-5, clear light yellow liquid) is used as aftertreatment agent for improving the washfastness of direct dyeings and for finishing color catching cloths. For the difference of Rewin DWR, Rewin OS is applied to alkaline medium (at pH 10).

Waste cotton fabrics are cationized during mercerization process according to [7]. The cationization was carried out on a jigger continuous by speed of $v = 2$ m/min with extension 0% at temperature of 20 °C. 12 passages were performed through a bath containing: 24% NaOH and 5 g/l Subitol MLF (Bezema) - anionic wetting agent. Then the alkali fabric is treated for 12 passages in the bath containing 50 g/l of cationizing agent and left for 24 h in a closed system. Afterwards, hot rinsing with distilled water at 80-90 °C, 2x cold rinsing with distilled water, neutralization with 5% CH₃COOH, and a series of cold rinsings in distilled water was performed until neutral pH was reached, and than air dried.

In Tab.1 labels and treatments are listed.

Tab.1 Labels and treatments

Label	Treatment
OB	Optical brightened waste cotton fabric
TI	Printed waste cotton fabric
...-DWR	Cationization with Rewin DWR
...-OS	Cationization with Rewin OS
...-CHPTAC	Cationization with CHPTAC

2.2. Methods

Zeta potential. Zeta potential was measured on Electrokinetic Analyzer, EKA (Anton Paar) by streaming potential method in dependance of pH of electrolyte 0.001 M KCl using moveable stamp cell.

Mechanical fabric properties. Warp and weft count, mass per unit area and tensile properties of waste cotton fabrics after cationization were determined by standard methods.

Warp and Weft Count Noven fabric density by was determined according to ASTM D3775-07 *Standard Test Method for Warp (End) and Filling (Pick) Count of Woven Fabrics*.

Mass per unit area, m of cotton waste farics was determined according to ISO 3801:1977 *Textiles -- Woven fabrics -- Determination of mass per unit length and mass per unit area*.

Breaking force (F_p, F_o) and breaking elongation (ϵ_p, ϵ_o) in warp and in weft direction were determined according to ISO 13934-1:2013 *Textiles -- Tensile properties of fabrics -- Part 1: Determination of maximum force and elongation at maximum force using the strip method* using Tensolab, MESDAN-LAB. Conditions: sample size 200 mm x 50 mm; gauge length 100 mm; constant speed of 100 mm/min; pretension of 2 N.

3. Results and discussion

This paper deals with the cationization of waste textile cellulose material from tailoring process: a fabric printed with reactive dyes and optically brightened fabric. The effect of cationization was evaluated by the zeta potential determination. The results are presented in Tab.2 and in Fig.1.

From the results of the zeta potential measurement it is evident that the printed fabric was poorly cationized.

Tab.2 Zeta potential (ζ) of waste optical brightened (OB) and printed (TI) cotton fabric before and after cationization at pH 10, and iso-electric point (IEP)

Sample	OB		TI	
	$\zeta_{pH 10}$ [mV]	IEP	$\zeta_{pH 10}$ [mV]	IEP
Before	-22.5	<2.5	-18.5	2.5
...-DWR	-6.6	4.9	-17.0	2.7
...-OS	-4.0	4.8	-15.7	3.1
...-CHPTAC	-10.9	3.4	-17.1	2.8

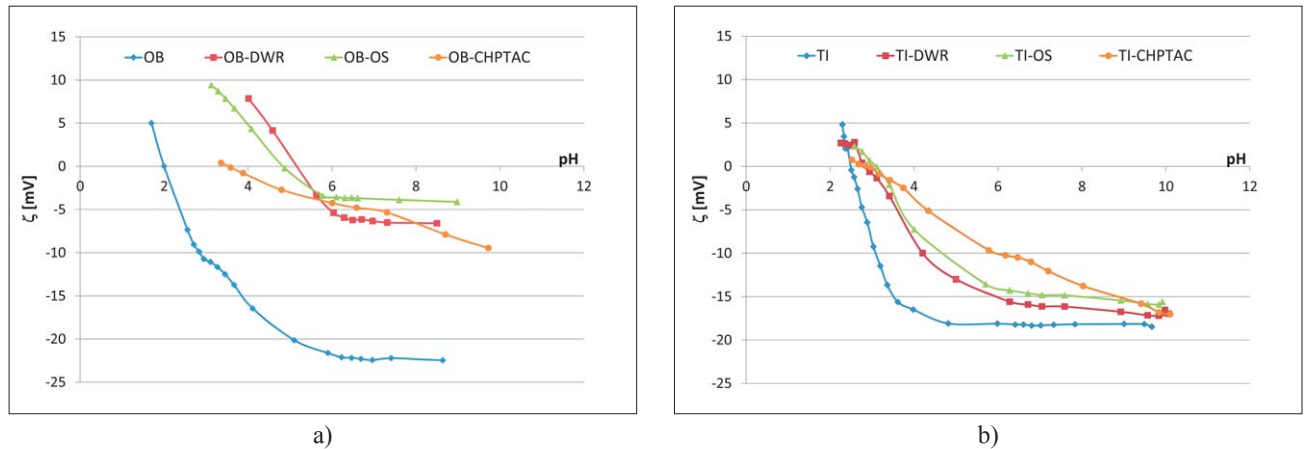


Fig.1 Zeta potential (ζ) of waste cotton fabric before and after cationization in dependence of pH of electrolyte 0.001 M KCl: a) optical brightened (OB) and b) printed (TI) fabric

An increase of the zeta potential from -18 to -16 mV can be observed, as well as the shift of the isoelectric point (IEP) from 2.5 to 3.1. However, unlike cotton in standard fabric [7] which in the same conditions of cationization can show positive values, the cationized printed fabric did not result in such high values. The reason for that are occupied active groups with covalently bound reactive dyes, so the number of available active groups was low for bonding of cationization agents. On the other hand, the results of the electrokinetic potential of optically brightened cotton fabrics indicate the satisfactory

effects of cationization. Optical brightening agents are bonded by hydrogen bonds and van der Waals forces, and usually release in wet processing, making available active groups for bonding of cationization agent. Therefore, the zeta potential of cationized optical brightened waste cotton fabric shows values greater than -11 mV at pH 10, and above -6 mV at pH 6.5. The shift of IEP to 4.9 is noticeable. It should be noted that the better effects of cationization have proved to be reactive polyammonium compound Rewin DWR and Rewin OS than a short-chain CHPTAC compound that gives

the best results in systems using standard bleached cotton. This may be because these compounds are intended for use in aftertreatment, eg. after dyeing and/or printing with direct/reactive dyes.

After confirming the successful cationization of waste cotton fabrics, the influence of cationization to their mechanical properties was investigated: fabric count, mass per unit area, and tensile properties through breaking force and elongation. First, the results of cationized optical brightened waste cotton fabric were given, than for the printed one, and finally a conclusion has been made

Tab.3 Density (warp and weft yarn count) of optical brightened waste cotton fabric before and after cationization

Sample	Fabric density - warp				Fabric density - weft			
	No [cm ⁻¹]	σ	CV [%]	Δ No [%]	Np [cm ⁻¹]	σ	CV [%]	Δ Np [%]
OB	25.8	1.14	4.45	0.00	23.6	0.84	3.52	0.00
OB-DWR	29.6	1.14	3.85	15.63	25.8	0.84	3.24	7.75
OB-OS	31.8	1.30	4.10	24.22	26.8	1.30	4.87	11.19
OB-CHPTAC	32.2	0.84	2.60	25.78	28.6	1.14	3.99	16.78

*No – average number per cm; σ - standard deviation; CV – variation coefficient

Tab.4 Mass per unit area m [g/m²] of optical brightened waste cotton fabric before and after cationization

Sample	m [g/m ²]	σ	CV [%]	Δm [%]
OB	192.40	3.51	1.82	0.00
OB-DWR	213.80	4.09	1.91	10.01
OB-OS	225.80	2.28	1.01	14.79
OB-CHPTAC	235.20	2.17	0.92	18.20

* m - average mass per unit area [g/m²]; σ - standard deviation; CV – variation coefficient

taking into account both cationized waste cotton fabrics.

Analyzing the mechanical properties of cationized optical brightened waste cotton fabric, from the results of the fiber count shown in Tab.3, mass per unit area shown in Tab.4, the increase in all values can be seen. The reason for this is that in all wet treatments, especially in merceriza-

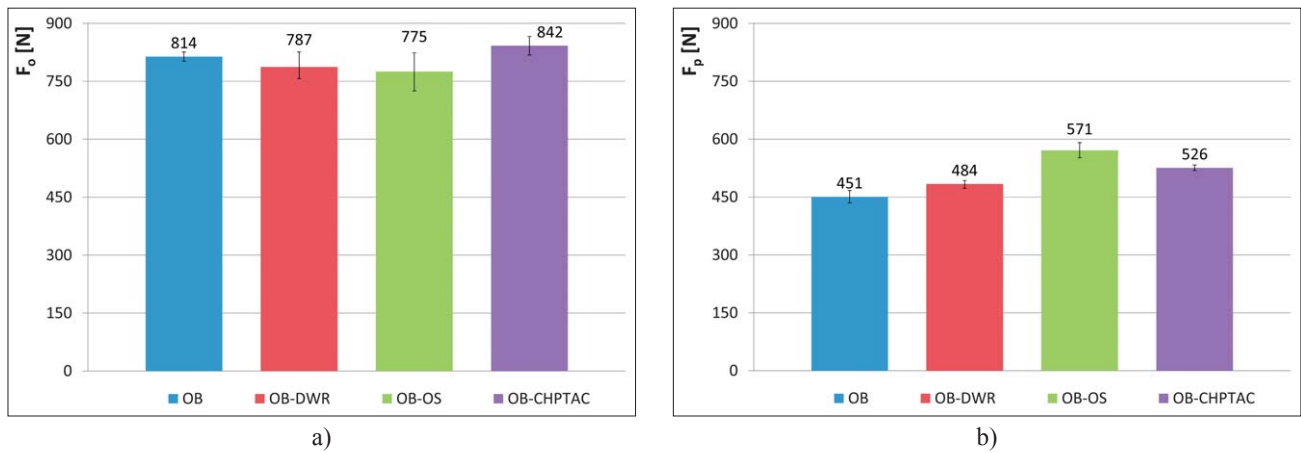


Fig.2 Breaking force of optical brightened waste cotton fabric before and after cationization: a) warp direction (F_0), and b) weft direction (F_p)

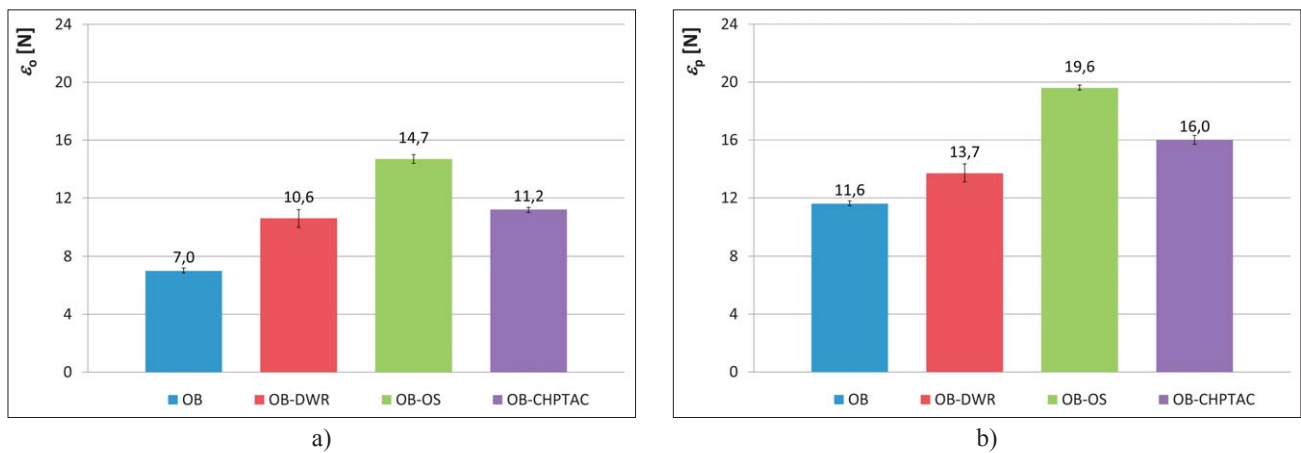


Fig.3 Breaking elongation of optical brightened waste cotton fabric before and after cationization: a) warp direction (ϵ_0), and b) weft direction (ϵ_p)

Tab.5 Density (warp and weft yarn count) of printed waste cotton fabric before and after cationization

Sample	Fabric density - warp				Fabric density - weft			
	No [cm ⁻¹]	σ	CV [%]	Δ No [%]	Np [cm ⁻¹]	σ	CV [%]	Δ Np [%]
TI	19.1	0.55	2.87	0	16.2	1.1	6.76	0
TI-DWR	25.5	0.98	3.82	25.16	21.2	0.84	3.95	23.58
TI-OS	32.3	0.64	1.99	40.90	26.3	0.61	2.33	38.50
TI-CHPTAC	33.5	0.95	2.84	43.05	27.5	0.98	3.55	41.13

*No - average count per cm; σ - standard deviation; CV - variation coefficient

tion, swelling of cellulosic materials causes the shrinkage of fabric after drying. Since cationization was performed during mercerisation and the agent is embedded in the structure, it can be seen that in the case of application of CHPTAC, a short chain agent, the swelling was the highest resulting in the greatest increase in yarn count and surface mass.

Tab.6 Mass per unit area m [g/m²] of printed waste cotton fabric before and after cationization

Uzorak	m [g/m ²]	σ	CV [%]	Δ m [%]
TI	165.80	2.95	1.78	0.00
TI-DWR	225.00	3.81	1.69	26.31
TI-OS	283.80	1.30	0.46	41.58
TI-CHPTAC	293.00	4.69	1.6	43.41

*m - average mass per unit area [g/m²]; σ - standard deviation; CV - variation coefficient

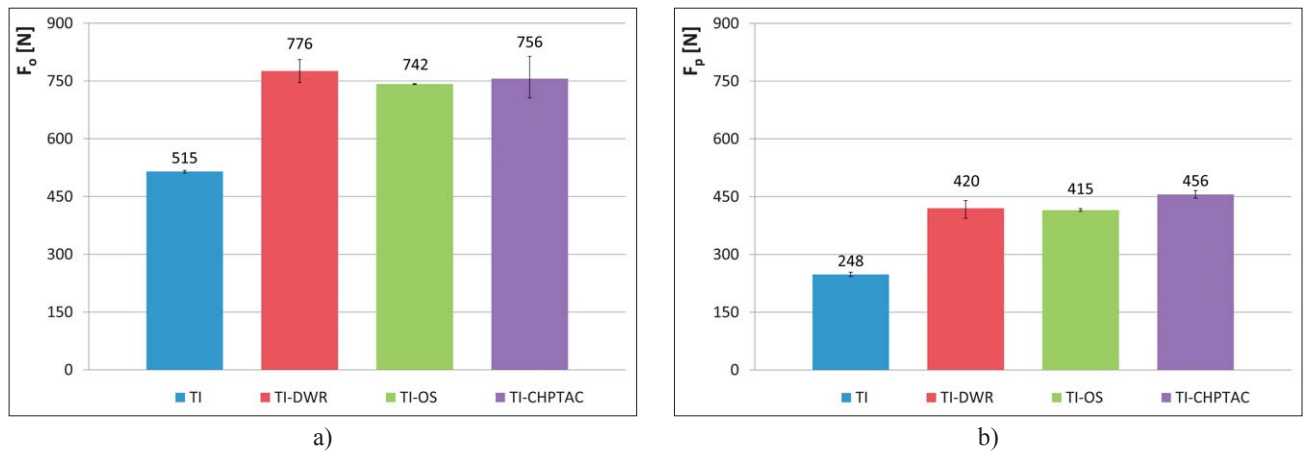


Fig.4 Breaking force of printed waste cotton fabric before and after cationization: a) warp direction (F_0), and b) weft direction (F_p)

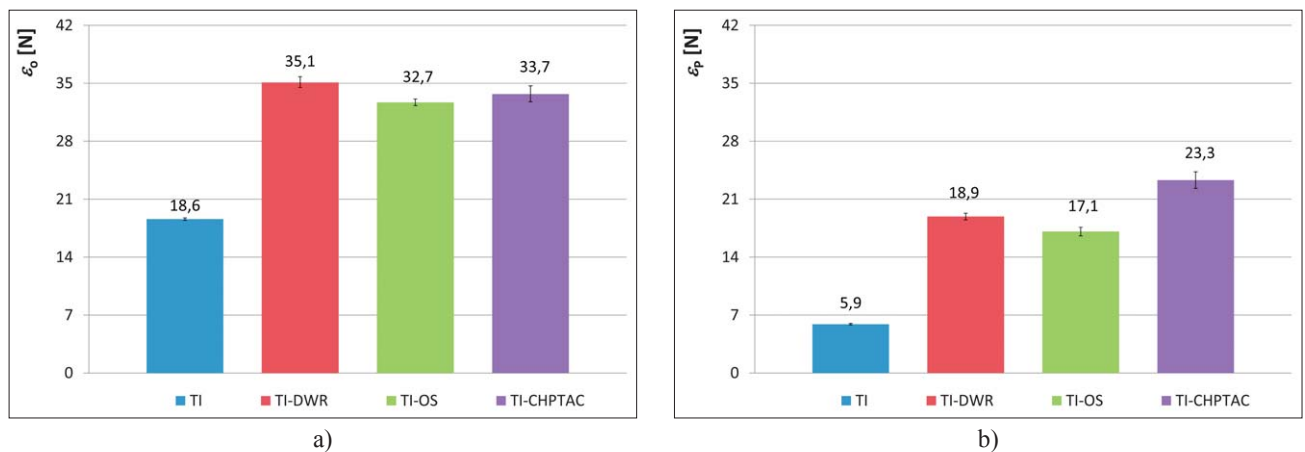


Fig.5 Breaking elongation of printed waste cotton fabric before and after cationization: a) warp direction (ϵ_0), and b) weft direction (ϵ_p)

The results shown in Fig.2 and 3 of the force and elongation at the break of the optical brightened waste cotton fabric, measured by warp and weft direction, indicate an improvement in the mechanical properties. The reason for the increase of the breaking force is in increasing the yarn count (number of threads), as well as the change of the cellulose crystal lattice from cellulose I into cellulose II, whereby rotation of chains causes the formation of new bonds. Best results have been achieved by the of reactive polyammonium compound Rewin OS.

The analysis of the mechanical properties of printed waste cotton fabric after cationization, similar changes were observed as for optical brightened one. There is a noticeable increase in yarn count and increase in

mass per unit area after cationization (Tab.5 and 6).

The reason for this is the cotton fabric shrinkage which increases the number of threads per unit length in all directions, and therefore increasing the mass per unit area. Comparing the cationization agents, the most effective has been shown 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC), with the effect of both fabrics having the largest increase in mass per unit area and number of threads (yarn count). It should be noted that this property is more pronounced in printed waste cotton fabrics, where the increase in mass per unit area is noted as 77%, from 165 to 293 g/m².

The results of the breaking force and elongation on the warp and weft direction shown in Fig.4 and 5, indicate

similar phenomena for the printed waste cotton fabrics after cationization as for the optical brightened ones.

Improved mechanical properties are more pronounced in printed fabrics. The breaking force in the printed fabric is increased by more than 50% due to all three compounds used, whilst the increase for the optical brightened one is slightly lower. There is also a noticeable increase in breaking elongation in warp and weft direction. The reason for this is the cationization process that allows swelling in all direction (3D swelling). Since the cellulose structure has changed, there is an increase in breaking force and elongation.

4. Conclusion

In this paper the possibility of modification – cationization of waste cot-

ton fabrics from tailoring process was investigated. The influence of cationization process to waste cotton fabric mechanical properties, primarily strength, was researched to allow the production of "filter" by the needle-punch process. For this purpose, two waste cotton fabrics, one printed with reactive dye, and the other optical brightened, were cationized during mercerization process with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride and cationic auxiliaries of CHT-Bezema, reactive polyammonium compounds Rewin OS and Rewin DWR.

It was found that both waste cotton fabrics – printed and optically brightened one can be cationized, with improved tensile properties, which is a good basis for making a "filter" by the needle-punch process. Considering the adsorption of anionic surfactants and reactive dyes [17], the cationized optically brightened waste cotton fabric would be a good raw material for the production of waste.

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References:

- [1] Lewis D. M., K. A. McIlroy: The Chemical Modification of Cellulosic fibers to Enhance Dyeability, *Review of Progress in Coloration* 27 (1997), 5-17
- [2] Hauser P. J., A. H. Tabba: Improving the Environmental and Economic Aspects of Dyeing Cotton, *Coloration Technology* 117 (2001) 5, 282-288
- [3] Cannon K. M., P. J. Hauser: Color Assessment of Cationic Cotton Dyed with Fiber Reactive Dyes, *AATCC Review* 3 (2003) 5, 39-40
- [4] Hashem M., P.J. Hauser, B. Smith: Reaction Efficiency for Cellulose cationization using 3-Chloro-2-Hydroxypropyl Trimethyl Ammonium Chloride, *Textile Research Journal* 73 (2003) 11, 1017-1023
- [5] Hashem M.: Development of a One-stage Process for Pretreatment and Cationization of Cotton Fabric, *Coloration Technology* 122 (2006) 3, 135-144
- [6] Grancarić A.M., A. Tarbuk, T. Dekanić: Elektropozitivan pamuk; *Tekstil* 53 (2004.) 2, 47-51
- [7] Tarbuk A., A.M. Grancarić, M. Leskovic: Novel cotton cellulose by cationization during the mercerisation process - Part 1: Chemical and morphological changes, *Cellulose* 21 (2014) 3; 2167-2179.
- [8] Tarbuk A., A.M. Grancarić, M. Leskovic: Novel cotton cellulose by cationization during mercerisation - Part 2: Interface phenomena; *Cellulose* 21 (2014) 3; 2089-2099.
- [9] Marsh J. T.: *Mercerising*; Chapman & Hall Ltd., London 1951.
- [10] Soljačić I., M. Žerdik: Osnovi mercerizacije pamuka (Basis of cotton mercerization), *Tekstil* 17 (1968.) 6, 495-518
- [11] Žerdik M., I. Soljačić: Studij proces mercerizacije (Study of mercerization process), *Tekstil* 18 (1969.) 2, 99-114
- [12] Soljačić I. i sur.: O mercerizaciji pamuka (About mercerization process), *Tekstil* 36 (1987.) 3, 123-130
- [13] Dinand E. et al.: Mercerization of Primary Wall Cellulose and its Implication for the Conversion of Cellulose I to cellulose II; *Cellulose* 9 (2002); 7-18
- [14] Tarbuk A., A. M. Grancarić, A. Majcen le Mareschal: Kationiziranje celuloznih materijala – mogućnost primjene u sustavima za pročišćavanje voda (Cationization of cellulosic materials – possible application in wastewaters system), *Tekstil* 61 (2012.) 7-12, 346-348
- [15] Tarbuk A., A. M. Grancarić: Interface Phenomena of Cotton Cationized in Mercerization, Chapter 6 in *Cellulose and Cellulose Derivatives: Synthesis, Modification and Applications, Part I: Cellulose Synthesis and Modification*; Ed. Ibrahim H. Mondal, New York : Nova Science Publishers, 2015, 103-125
- [16] Ristić N. et al.: Interface Phenomena and Dyeability with Reactive Dyes of Cationized Cotton, *Industria Textila* 65 (2014) 4, 220-227
- [17] Vunderl M., J. Marković: Kationiziranje otpadnog celuloznog materijala – mogućnost pročišćavanja otpadne vode (Cationization of cellulosic textile waste – possibility for waste waters purification), student research for Rectorovu prize, University of Zagreb Faculty of textile technology, june 2017
- [18] CHT-Bezema: Rewin DWR. Technical leaflet, CHT R. BEILICH GMBH, Sept 2009
- [19] CHT-Bezema: Rewin OS. Technical leaflet, CHT R. BEILICH GMBH, Nov 2013