Kationiziranje otpadne pamučne tkanine - utjecaj na mehanička svojstva

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U ovom radu istražen je utjecaj kationiziranja na mehanička svojstva otpadnih pamučnih tkanina, uz prethodno utvrđivanje učinkovitosti sredstva za kationiziranje. Budući da se radi o otpadnom materijalu kojem su aktivne skupine blokirane, bilo je upitno može li ga se uopće kationizirati. U tu svrhu otpadni celulozni materijal, optički bijeljena i tiskana pamučna tkanina, okrajci iz šivaonice, kationizirane su tijekom postupka mercerizacije u laboratorijskim uvjetima s visokoučinkovitim 3-kloro-2-hidroksipropil-trimetil amonijevim kloridom te ekološki prihvatljivijim trgovačkim sredstvima za kationiziranje. Na temelju zeta potencijala je utvrđeno da su otpadni materijali, optički bijeljena i tiskana pamučna tkanina, kationizirani. Ispitivanjem vlačnih svojstava kationiziranih materijala, utvrđena je poboljšana čvrstoća i prekidno istezanje, čime bi se omogućila izrada filtra postupkom iglanja. Primjena ovakvog filtra bila bi od višestruke koristi za tekstilnu industriju - zbrinjavanje otpadnog tekstila i pročišćavanje otpadnih voda, čime bi se pozitivno utjecalo i na zaštitu okoliša.

***Ključne riječi**: kationiziranje, otpadni tekstilni materijal iz šivaonice, čvrstoća, prekidno istezanje, broj niti*

1. Uvod

Tekstilna i odjevna industrija, osim otpadnih voda, generira otpad iz krojnica i šivaonica, koji je neophodno zbrinjavati. Upravo se zbog toga ovaj rad bavi istraživanjem kationiziranja otpadnog tekstilnog celuloznog materijala tijekom mercerizacije koji bi se kao materijal dodane vrijednosti mogao primijeniti kao „filtar“ u sustavima za pročišćavanje otpadne vode.

Kationiziranje je modifikacija pamučne celuloze u alkalnim uvjetima mehanizmom blokade hidroksilnih (–OH) skupina, pri čemu nastaju eteri celuloze [1-10]. Početak istraživanja kationiziranog pamuka sa svrhom poboljšanja bojadisarskih svojstava veže se uz M. Rupina koji je obrađivao pamuk sa 40 % otopinom epoksipropil-trimetil amonijevog klorida [1]. Početkom 1990-ih započela su detaljna istraživanja na problematici modifikacije pamuka s drugim kationskim sredstvima sa svrhom pronalaženja boljeg iscrpljenja anionskih bojila u bojadisanju i tisku s direktnim, reaktivnim i kiselim bojilima te postojanosti obrada u oplemenjivanju. Istraživanja kvarternih amonijevih spojeva za kationiziranje celuloze pamuka provodili su istraživači u radovima [2-5]. Razvili su kationiziranje pamuka uz primjenu 3-kloro-2hidroksipropil-trimetil amonijevog klorida (CHPTAC) i 2,3-epoksipropil-trimetil amonijevog klorida (EPTAC) u naknadnoj obradi za poboljšanja procesa bojadisanja i tiska [2-5]. A.M. Grancarić i sur. te A. Tarbuk i sur. [6-8] razvili su tehnološki postupak primjene navedenih spojeva tijekom mercerizacije. Uz unaprijed poznata svojstva koja se postižu mercerizacijom, povećanje adsorptivnosti, čvrstoće i sjaja [9-13] kationiziranjem tijekom procesa mercerizacije, dodatno se mijenja naboj celuloze pamuka, čime se u potpunosti mijenja sustav bojilo-celuloza i tenzid-celuloza [6-8, 14-17]. U konačnici dobiva se modificirani pamučni materijal pozitivnog naboja [7]. Za kationiziranje pamuka mogu se koristiti i druga sredstva na bazi kationskih reaktivnih poliamonijevih spojeva [14-16].

S obzirom da kationizirani čisti pamuk ima visoku adsorptivnost za anionska sredstva, te na mogućnost upotrebe kao filtra za pročišćavanje otpadnih voda [7], nametnula se ideja kationiziranja otpadnih celuloznih materijala za jednake primjene.

2. Eksperimentalni dio

2.1. Materijal, sredstva i postupci obrade

Iz šivaonice „DM TEKSTIL KROJAČKI OBRT" dobivene su dvije vrste otpadne pamučne tkanine (okrajci širine 25 cm):

1) optički bijeljena tkanina (OB)
   - vez: platneni 1/1,
   - 100 % pamuk,
   - namjena: za operacijsko i posteljno rublje,
   - površinska masa: 190 g/m^2,
   - duljinske mase pređe osnova/potka: 36/34 tex,

2) tiskana tkanina (TI)
   - 100 % pamuk,
   - namjena: za posteljno rublje,
   - vez: flanel,
   - površinska masa: 165 g/m^2,
   - duljinske mase pređe osnova/potka 27,5/70 tex.

Za kationiziranje su korištena sljedeća sredstva: 3-kloro-2-hidroksipropil trimetil-amonijev klorid (CHPTAC, Sigma Aldrich), te kationski reaktivni poliamonijevi spojevi tvrtke CHT-Bezema: Rewin OS i Rewin DWR. Sredstvo Rewin DWR (kationski karakter, pH 3-4, žuta prozirna kapljevina) se koristi za oplemenjivanje tekstila sa svrhom poboljšanja postojanosti obojenja u mokrom i postojanosti obojenja na pranje, prilikom uporabe reaktivnih bojila na celuloznim vlaknima. Primjenjuje se pri pH 7,5-8 na 40 °C u koncentaraciji 3-4 % na m.m. [18]. Rewin OS (kationski karakter, pH 4-5, svijetložuta prozirna kapljevina) se koristi za oplemenjivanje celuloznih vlakana sa svrhom poboljšanja postojanosti obojenja na pranje nakon bojadisanja direktnim bojilom, te za oplemenjivanje funkcionalnih maramica za hvatanje bojila (tzv. Color catcher). Za razliku od Rewin DWR, Rewin OS se primjenjuje u alkalnom mediju (pH 10).

Okrajci pamučne tkanine kationizirani su tijekom mercerizacije prema [7]. Kationiziranje je provedeno na džigeru kontinuirano brzinom od *v* = 2 m/min uz rasteg 0 % pri temperaturi 20 °C. Provedeno je 12 prolaza kroz kupelj koja sadrži: 24 % NaOH i 5 g/l Subitol MLF (Bezema) - anionsko sredstvo za kvašenje. Potom je zalužena tkanina obrađivana u 12 prolaza u džigeru u kupelji koja je sadržavala 50 g/l sredstva za kationiziranje. Slijedilo je 24-satno odležavanje u zatvorenom sustavu. Nakon odležavanja uslijedilo je vruće ispiranje destiliranom vodom temperature 80-90 °C, 2x hladno ispiranje destiliranom vodom, neutralizacija sa 5 % CH_3COOH, te niz hladnih ispiranja destiliranom vodom do neutralnog pH i sušenje na zraku.

U tab.1 navedene su oznake i obrade uzoraka.

Tab.1 Oznake i obrade uzoraka

Oznaka	Obrada
OB	Optički bijeljena pamučna tkanina
TI	Tiskana pamučna tkanina
-DWR	Kationiziranje s Rewin DWR
-OS	Kationiziranje s Rewin OS
-CHPTAC	Kationiziranje s CHPTAC

2.2. Mjerne metode

Zeta potencijal. Zeta potencijal mjeren je tehnikom potencijala strujanja u ovisnosti o pH vrijednosti elektrolita 0,001 M KCl na elektrokinetičkom analizatoru EKA tvrtke Anton Paar, primjenom pomične ćelije (tzv. movable stamp cell).

Mehanička svojstva tkanine. Gustoća tkanine (broj niti u smjeru osnove i broj niti u smjeru potke), površinska masa i vlačna svojstva tkanine utvrđeni su nakon kationiziranja prema standardnim metodama.

Gustoća tkanine (br. niti osnove i potke po 1 cm) određena je prema ASTM D3775-07 *Standard Test Method for Warp (End) and Filling (Pick) Count of Woven Fabrics*.

Površinska masa *m* pamučnih tkanina određena je vaganjem prema HRN ISO 3801:2003 *Tekstil - Tkanine - Određivanje mase po jedinici duljine i mase po jedinici površine*.

Prekidna sila (F_p, F_o) i prekidno istezanje (ε_p, ε_o) u smjeru osnove i u smjeru potke izmjereni su prema HRN EN ISO 13934-1:2008 *Tekstilije - Vlačna svojstva plošnih tekstilija - 1. dio: Određivanje maksimalne sile i istezanja pri maksimalnoj sili metodom trake* na dinamometru Tensolab, MESDAN-LAB. Uvjeti određivanja prekidne sile i prekidnog istezanja su: dimenzije uzorka 200 mm x 50 mm; razmak među stezaljkama 100 mm; brzina istezanja 100 mm/min; predopterećenje 2 N.

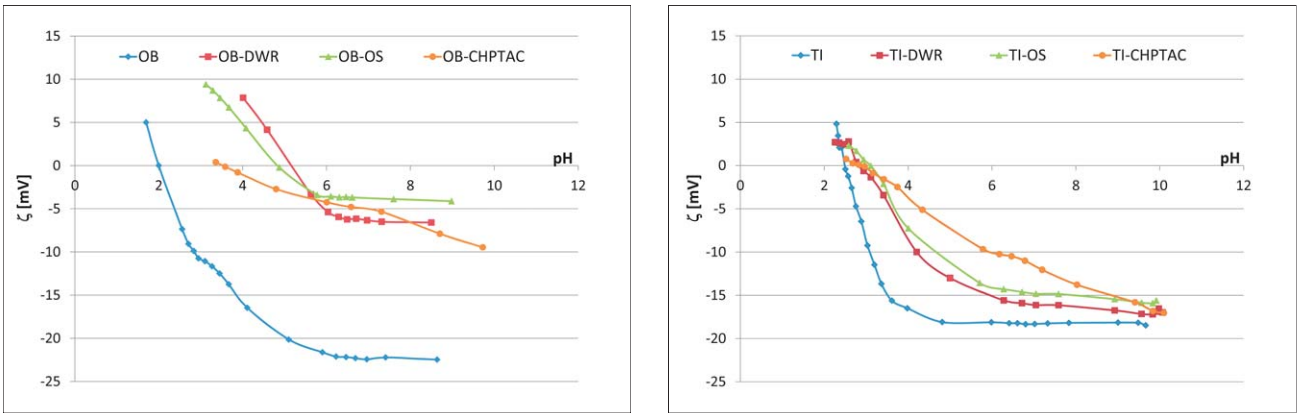
3. Rezultati i rasprava

U radu je provedeno kationiziranje otpadnog tekstilnog celuloznog materijala iz šivaonice: tkanina tiskana reaktivnim bojilom i optički bijeljena tkanina. Učinak kationiziranja provjeren je mjerenjem zeta potencijala. Rezultati su prikazani u tab.2 i na sl.1.

Iz rezultata mjerenja elektrokinetičkog potencijala vidljivo je da se tiskana tkanina slabo kationizirala.

Tab.2 Zeta potencijal (ζ) optički bijeljene (OB) i tiskane (TI) pamučne tkanine prije i nakon kationiziranja na pH 10 i izoelektrična točka (IEP)

Uzorak	OB		TI	
	$\zeta_{pH\ 10}$ [mV]	IEP	$\zeta_{pH\ 10}$ [mV]	IEP
prije obrade	-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



a) b)

Sl.1 Zeta potencijal (ζ) pamučne tkanine prije i nakon kationiziranja u ovisnosti o pH elektrolita 0.001 M KCl: a) optički bijeljene (OB), b) tiskane (TI)

Može se uočiti povećanje zeta potencijala s -18 na -16 mV i pomak izoelektrične točke (IEP) s 2,5 na 3,1. Za razliku od pamuka u standardnoj tkanini [7], koji u istim uvjetima kationiziranja pokazuje gotovo pozitivne vrijednosti, na tiskani pamuk se kationsko sredstvo nije moglo vezati u tolikoj mjeri zbog zauzetih aktivnih mjesta kovalentno vezanim reaktivnih bojila. S druge strane, rezultati elektrokinetičkog potencijala optički bijeljenih tkanina potvrđuju zadovoljavajuće učinke kationiziranja. Optička bjelila vežu se vodikovim vezama i van der Waalsovim silama, te se ispiru u pranju i u mokrim obradama, čime se oslobađaju dostupne skupine za vezivanje kationskog sredstva. Zeta potencijal pri pH 10 ima vrijednosti više od -11 mV, a pri pH 6,5 iznad -6 mV. Vidljiv je pomak IEP na 4,9. Valja istaknuti da su bolje učinke kationiziranja pokazala reaktivna poliamonijeva sredstva Rewin DWR i Rewin OS nego kratkolančani spoj CHPTAC koji u čistim sustavima daje najbolje rezultate. Razlog tomu može biti što su navedena sredstva namijenjena primjeni u naknadnoj obradi nakon bojadisanja i/ili tiska direktnim/reaktivnim bojilima.

Nakon potvrde uspješnog kationiziranja otpadnih pamučnih tkanina, istražen je utjecaj kationiziranja na promjene njihovih mehaničkih svojstava: konstrukcijska svojstva tkanine, površinsku masu tkanine, te prekidnu silu i prekidno istezanje. Najprije su analizirani rezultati za kationiziranje optički bijeljene tkanine, potom za tiskane, te je na kraju donesen zaključak uzevši u obzir obje otpadne pamučne tkanine.

Analizirajući mehanička svojstva modificirane otpadne optički bijeljene pamučne tkanine nakon kationiziranja iz rezultata za gustoću tkanine, odnosno broja niti osnove i potke prikazanih u tab.3 te površinske mase u tab.4 jasno je uočljiv porast svih vrijednosti. Razlog tomu je što u svim mokrim obradama, posebice u mercerizaciji dolazi do bubrenja celuloznih materijala što nakon sušenja dovodi do skupljanja tkanine. Budući da je kationiziranje rađeno tijekom mercerizacije i sredstva se ugrađuju u strukturu, može se uočiti da je u slučaju kratkolančanog spoja CHPTAC bubrenje bilo najjače i zato upravo ova tkanina

Tab.3 Gustoća optički bijeljene pamučne tkanine prije i nakon kationiziranja u smjeru osnove i potke

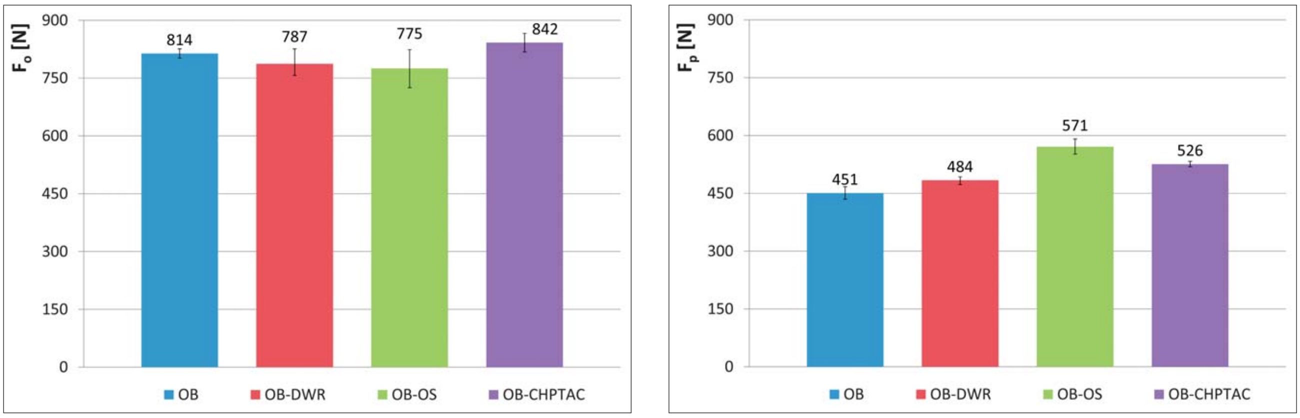
	Gustoća tkanine po osnovi				Gustoća tkanine po potki			
Uzorak	**No [cm⁻¹]**	**σ**	**CV [%]**	**ΔNo [%]**	**Np [cm⁻¹]**	**σ**	**CV [%]**	**ΔNp [%]**
OB	25,8	1,14	4,45	0,00	23,6	0,84	3,52	0,00
OB-DWR	29,6	1,14	3,85	15,63	25,8	0,84	3,24	7,75
OB-OS	31,8	1,30	4,10	24,22	26,8	1,30	4,87	11,19
OB-CHPTAC	32,2	0,84	2,60	25,78	28,6	1,14	3,99	16,78

*No - srednja vrijednost broja niti osnove po cm; σ - standardna devijacija; CV - koeficijent varijacije

Tab.4 Površinska masa m [g/m²] optički bijeljene pamučne tkanine prije i nakon kationiziranja

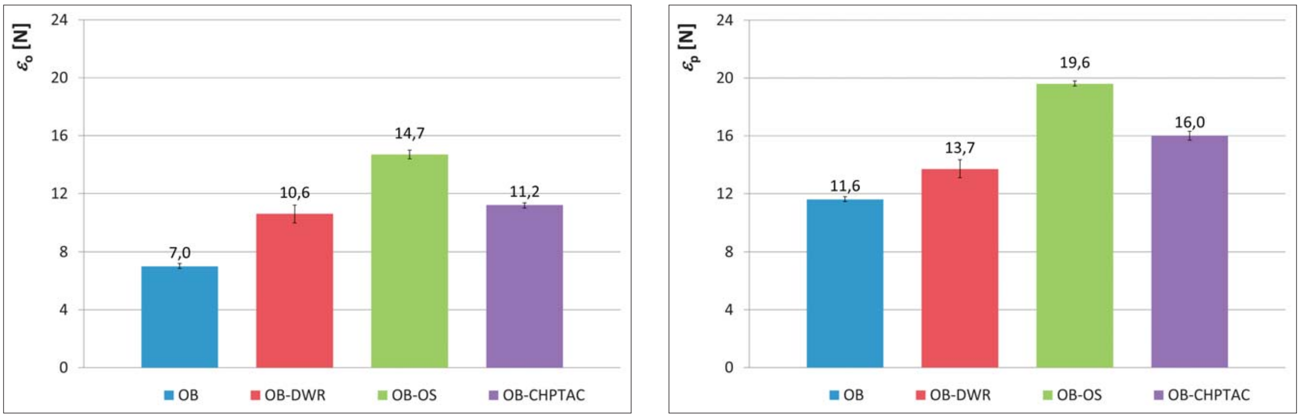
Uzorak	**m [g/m²]**	**σ**	**CV [%]**	**Δm [%]**
OB	192,40	3,51	1,82	0,00
OB-DWR	213,80	4,09	1,91	10,01
OB-OS	225,80	2,28	1,01	14,79
OB-CHPTAC	235,20	2,17	0,92	18,20

*m - srednja vrijednost površinske mase [g/m²]; σ - standardna devijacija; CV - koeficijent varijacije



a) b)

Sl.2 Prekidne sile optički bijeljene pamučne tkanine prije i nakon kationiziranja: a) po osnovi (F_o), b) po potki (F_p)



a) b)

Sl.3 Prekidno istezanje optički bijeljene celulozne tkanine prije i nakon kationiziranja: a) po osnovi (ε_o), b) po potki (ε_p)

Tab.5 Gustoća tiskane bijeljene pamučne tkanine prije i nakon kationiziranja u smjeru osnove i potke

	Gustoća po osnovi				Gustoća po potki			
Uzorak	**No [cm^{-1}]**	**σ**	**CV [%]**	**ΔNo [%]**	**Np [cm^{-1}]**	**σ**	**CV [%]**	**ΔNp [%]**
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 - srednja vrijednost niti osnove po cm; σ - standardna devijacija; CV - koeficijent varijacije

Tab.6 Površinska masa m [g/m^2] tiskane pamučne tkanine prije i nakon kationiziranja

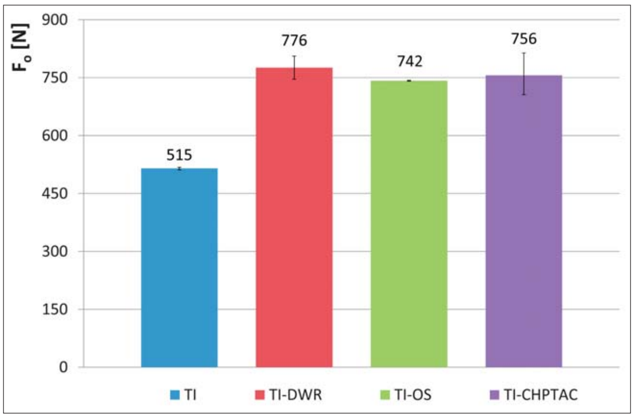
Uzorak	**m [g/m^2]**	**σ**	**CV [%]**	**Δm [%]**
TI	165,80	2,95	1,78	0,00
TI-DWR	225,00	3,81	1,69	26,31
TI-OS	283,80	1,30	0,46	41,58
TI-CHPTAC	293,00	4,69	1,6	43,41

* m - srednja vrijednost površinske mase [g/m^2]; σ - standardna devijacija; CV - koeficijent varijacije

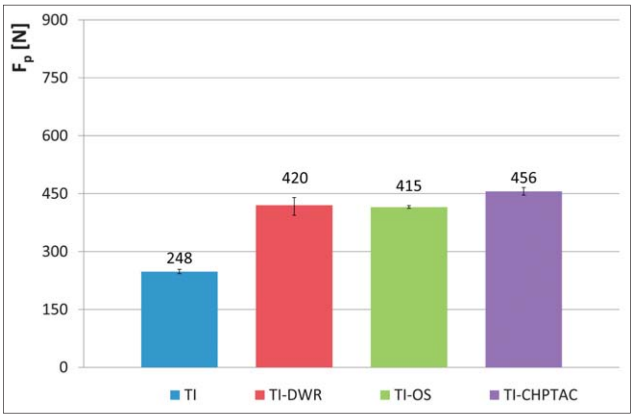
ima najveće povećanje gustoće tkanine (broja niti u smjeru osnove i potke) i površinske mase.

Rezultati prekidne sile i prekidnog istezanja optički bijeljene tkanine po osnovi i po potki, prikazani na sl. 2 i 3, pokazuju poboljšanje mehaničkih svojstava. Razlog povećanju prekidne sile je u povećanju gustoće tkanine (broja niti), kao i promjena kristalne rešetke iz celuloze I u celulozu II pri čemu rotacije lanaca uvjetuju stvaranje novih veza. Najboljim se pokazala primjena reaktivnog poliamonijevog spoja Rewin OS.

Analizom mehaničkih svojstva modificirane otpadne tiskane pamučne tkanine nakon kationiziranja uočavaju se slične promjene kao kod optički

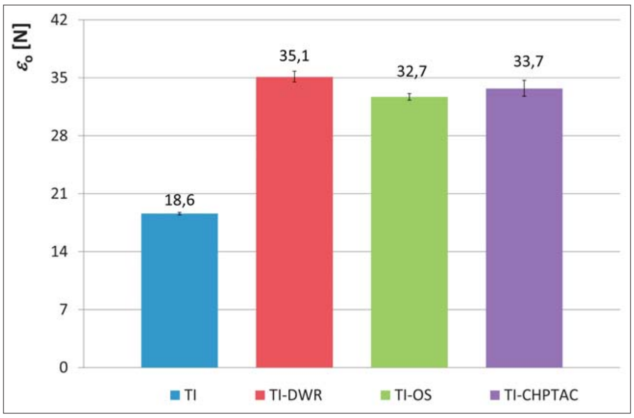


a)

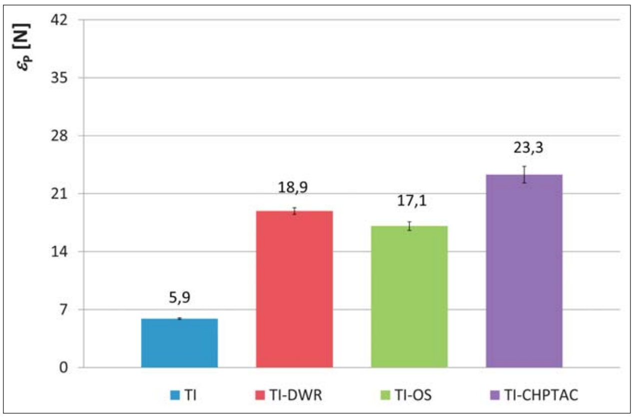


b)

Sl.4 Prekidne sile tiskane pamučne tkanine prije i nakon kationiziranja: a) po osnovi (F_o), b) po potki (F_p)



a)



b)

Sl.5 Prekidno istezanje tiskane pamučne tkanine prije i nakon kationiziranja: a) po osnovi ($\boldsymbol{\varepsilon}_o$), b) po potki ($\varepsilon_p$)

bijeljene. Uočljiv je porast broja niti te porast površinske mase u kationiziranju (tab. 5 i 6).

Razlog tomu je skupljanje pamučne tkanine, čime se povećava broj niti po jedinici dužine u svim smjerovima, a time i površinska masa. Uspoređujući sredstva za kationiziranje, najučinkovitijim se pokazao 3-kloro-2-hidroksipropil trimetilamonijev klorid (CHPTAC), čijim djelovanjem obje tkanine imaju najveće povećanje mase i broja osnovinih i potkinih niti. Valja istaknuti da je ovo svojstvo naglašenije kod tiskane tkanine, te se bilježi povećanje površinske mase za čak 77 %, sa 165 na 293 g/m^2.

Rezultati prekidne sile (F_{op}) i prekidnog istezanja (ε_{op}) po osnovi i po potki tiskane tkanine prikazani na sl.4 i 5 ukazuju na slične učinke kao i kod optički bijeljene.

Poboljšanje mehaničkih svojstava je naglašenije kod tiskane tkanine. Prekidna sila kod tiskane tkanine povećava se više od 50 % kod svih triju obrada, dok je kod optički bijeljene nešto manja. Uočljiv je i značajan porast prekidnog istezanja, i po osnovi i po potki. Razlog tomu je postupak kationiziranja koji omogućava bubrenje u slobodnom stanju. Budući da je došlo do promjene strukture celuloze, dolazi do povećanja prekidne sile i prekidnog istezanja.

4. Zaključak

U radu je istražena mogućnost modificiranja-kationiziranja otpadnih pamučnih tkanina iz šivaonice sa svrhom utvrđivanja mehaničkih svojstava, prije svega čvrstoće kako bi se omogućila izrada filtra postupkom iglanja. U tu svrhu odabrane su dvije otpadne tkanine, jedna tiskana reaktivnim bojilom, a druga optički bijeljena, koje su kationizirane tijekom mercerizacije s 3-kloro-2-hidroksipropil trimetil amonijevim kloridom i kationskim pomoćnim sredstvima tvrtke CHT-Bezema, reaktivnim poliamonijevim spojevima Rewin OS i Rewin DWR.

Utvrđeno je da se otpadna optički bijeljena i tiskana pamučna tkanina mogu kationizirati, pri čemu se poboljšavaju vlačna svojstva, što je dobra osnova za izradu filtra postupkom iglanja. Uzevši u obzir istraživanja adsorpcije anionskih tenzida i reaktivnih bojila [17], kationizirana otpadna optički bijeljena pamučna tkanina bila bi dobra sirovina za izradu filtara za pročišćavanje otpadne vode, u prvom redu tekstilne industrije.

Autori se zahvaljuju tvrtki "DM TEKSTIL KROJAČKI OBRT" Ozalj na doniranim uzorcima otpadnih tkanina, tvrtki CHT-Bezema na doni-

ranim pomoćnim sredstvima, te Sveučilištu u Zagrebu na financijskim potporama istraživanju „Primjena kationiziranih celuloznih materijala“ (TP5-16), 2016. voditeljice doc. dr. sc. A. Tarbuk, te „Funkcionalizacija i karakterizacija tekstilnih materijala za postizanje zaštitnih svojstava“, 2017. voditeljice doc. dr. sc. S. Flinčec Grgac.

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SUMMARY

Cationization of waste cotton fabric - the influence on mechanical properties

J. Marković, M. Vunderl, K. Grgić, A. Tarbuk

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

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Kationisierung von Baumwollgewebeabfällen - der Einfluss auf mechanischen Eigenschaften

In dieser Arbeit wird der Einfluss der Kationisierung auf die mechanischen Eigenschaften von Baumwollgewebeabfällen untersucht. Vor der Bestimmung der mechanischen Eigenschaften wurde die Wirksamkeit des Kationisierungsmittels untersucht. Da das Abfallmaterial verwendet wurde und seine aktiven Gruppen blockiert wurden, war es fraglich, ob es kationisiert werden könnte. Daher wurden zellulosisches Abfallmaterial, optisch gebleichte und bedruckte Baumwollstoffe sowie Schneidereireste während des Mercerisierungsverfahrens unter Laborbedingungen mit Hochleistungs-3-Chlor-2-hydroxypropyltrimethylammoniumchlorid und ökologisch verträglicheren Kationisierungsmitteln kationisiert. Aufgrund des Zeta-Potentials wurde festgestellt, dass Abfälle, optisch gebleichter und bedruckter Baumwollstoff, kationisiert wurden. Die Prüfung der Zugfestigkeitseigenschaften kationisierter Materialien bestätigte verbesserte Festigkeit und Bruchdehnung, wodurch der 'Filter' durch den Vernadelungsprozess hergestellt werden könnte. Die Anwendung eines solchen Filters hätte mehrere Vorteile für die Textilindustrie - das Recycling von Textilabfällen und die Reinigung von Abwässern, was sich unmittelbar positiv auf den Umweltschutz auswirkt.

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 conditions 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 begun, for the purpose of investigating the better exhaustion of anionic dyes in dyeing and printing with direct, reactive and acid dyestuff, 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 Tarbuk 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 washfastnessof direct dyeings and for finishing coulor 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% CH_3COOH, and a series of cold rinsings in distilled water was performed until neutral pH was reached, and than air dryed.

In Tab.1 labels and treatments are listed.

Tab.1 Labels and treatments

Label	Treatment
OB	Optical brigthened 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.

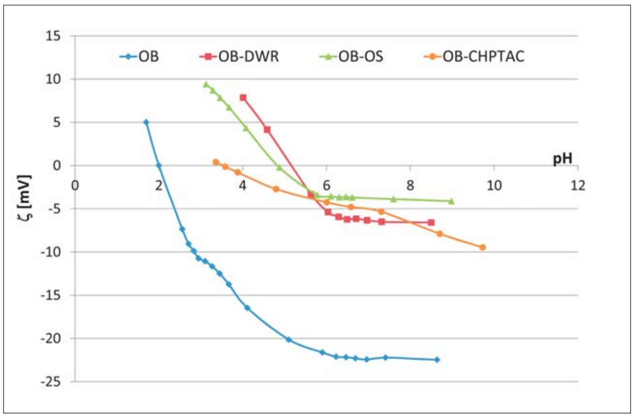
3. Results and discussion

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

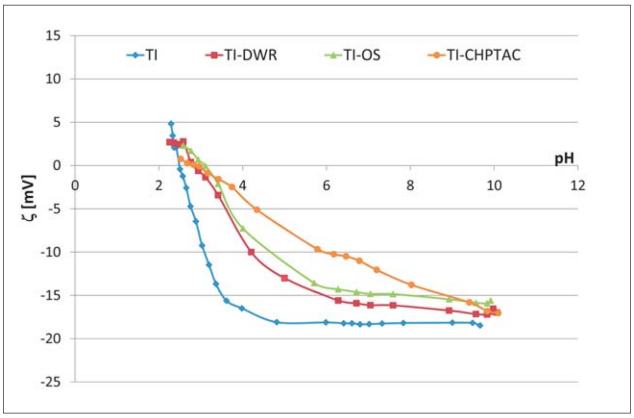
From the results of the zeta potential measurement it is evident that the printed fabric was poorly cationized.

Tab.2 Zeta potential (ζ) of waste optical brigthened (OB) and printed (TI) cotton fabric before and after cationization at pH 10, and isoelectric 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



a)



b)

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 brigthened (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 occupated 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 taking into account both cationized waste cotton fabrics.

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

	Fabric density - warp				Fabric density - weft			
Sample	**No [cm^{-1}]**	**σ**	**CV [%]**	**ΔNo [%]**	**Np [cm^{-1}]**	**σ**	**CV [%]**	**ΔNp [%]**
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

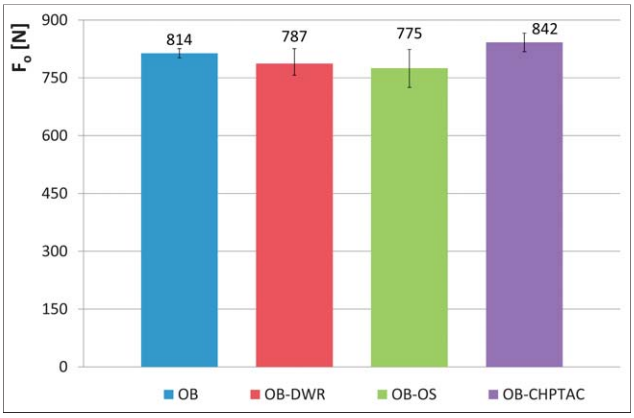
*No – average number per cm; σ - standard deviation; CV – variation coefficient

Tab.4 Mass per unit area *m* [g/m^2] of optical brightened waste cotton fabric before and after cationization

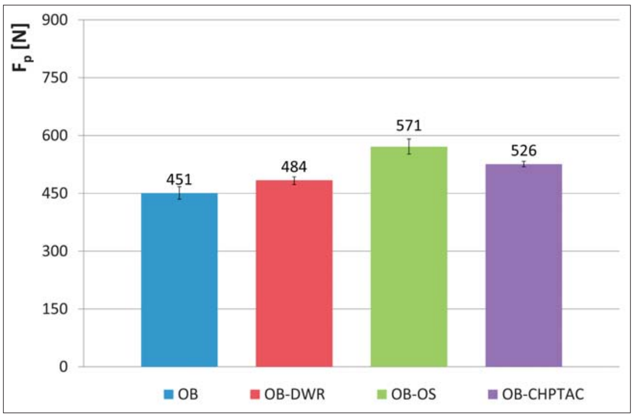
Sample	**m [g/m^2]**	**σ**	**CV [%]**	**Δm [%]**
OB	192.40	3.51	1.82	0.00
OB-DWR	213.80	4.09	1.91	10.01
OB-OS	225.80	2.28	1.01	14.79
OB-CHPTAC	235.20	2.17	0.92	18.20

*m - average mass per unit area [g/m^2]; σ - standard deviation; CV – variation coefficient

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-

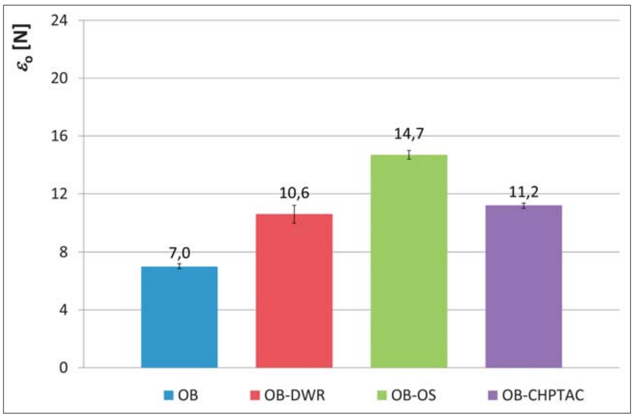


a)



b)

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



a)

b)

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

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

	Fabric density - warp				**Fabric density - weft**			
Sample	**No [cm^{-1}]**	**σ**	**CV [%]**	**ΔNo [%]**	**Np [cm^{-1}]**	**σ**	**CV [%]**	**ΔNp [%]**
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

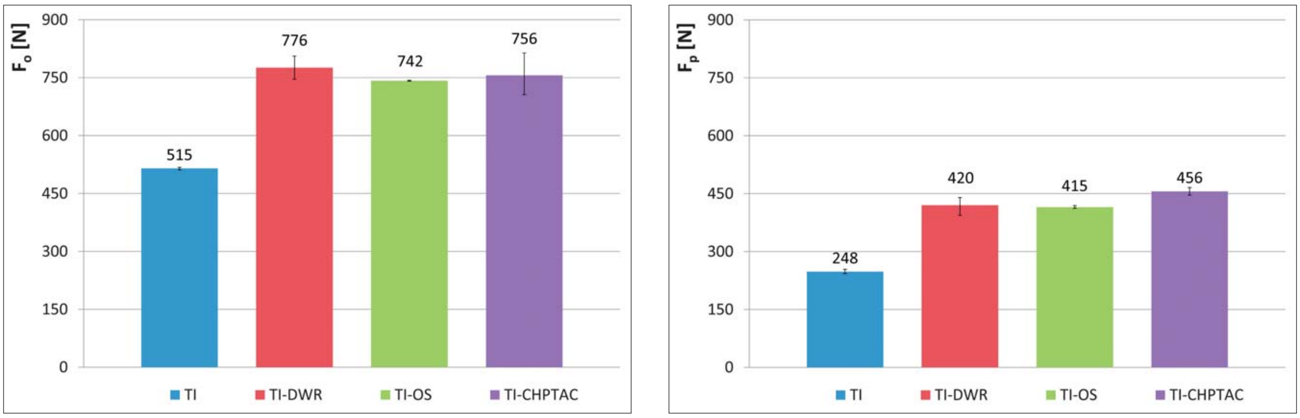
*No - average count per cm; σ - standard deviation; CV - variation coefficient

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 highes resulting in the greatest increase in yarn count and surface mass.

Tab.6 Mass per unit area m [g/m^2] of printed waste cotton fabric before and after cationization

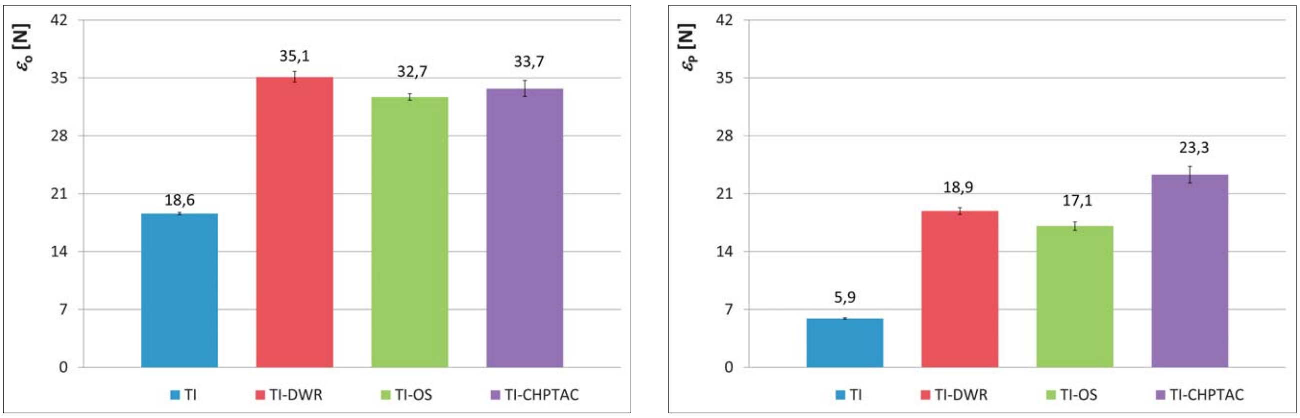
Uzorak	**m [g/m^2]**	**σ**	**CV [%]**	**Δm [%]**
TI	165.80	2.95	1.78	0.00
TI-DWR	225.00	3.81	1.69	26.31
TI-OS	283.80	1.30	0.46	41.58
TI-CHPTAC	293.00	4.69	1.6	43.41

*m - average mass per unit area [g/m^2]; σ - standard deviation; CV - variation coefficient



a) b)

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



a) b)

Fig.5 Breaking elongation of printed waste cotton fabric before and after cationization: a) warp direction (ε_o), 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/m^2.

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 increace 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 eleongation.

4. Conclusion

In this paper the possibility of modification – cationization of waste cotton 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 brigthened, 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 optica 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 optical brightened waste cotton fabric would be a good raw material for the production of waste.

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