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Implementation of Chitosan into Cotton Fabric
Implementacija hitozana na bombažni tkanini

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Abstract
Chitosan, produced through chitin hydrolysis, has been highly appreciated for medical purposes. For the last decade, its application in textiles and biomaterials has grown significantly. It has been well-implemented in man-made fibre, but achieved properties in natural fibres have not proven durable. Thus, in this study, two chitosans with differing degrees of deacetylation were implemented into cellulose material using a mercerisation process. The following methods of analysis were used for physical-chemical characterisation: Fourier-transform infrared spectrometry (FTIR), electrokinetic potential, scanning electron microscopy (SEM) and thermal gravimetric analysis. For the purpose of studying durability, characterisation was performed after one washing cycle. Performed analyses confirmed that both chitosans are well-implemented into cellulosic fabric. Fabric treated with chitosan with a higher degree of deacetylation has more positively charged amino groups and better thermal stability.
Keywords: chitosan, cotton fabric, FTIR, electrokinetic potential, FE-SEM, thermal gravimetric analysis

Izvleček
Hitozan, ki nastane s hidrolizo hitina, je zelo cenjen v medicini. V zadnjem desetletju se je njegova uporaba v tekstilstvu in biomaterialih znatno povečala. Uspešno je bil uporabljen v kemičnih vlaknih, na naravnih vlaknih pa dosežene lastnosti niso bile trajne. V tem članku je predstavljena uporaba dveh hitozanov različne stopnje deacitiliranja, ki sta bila na celulozni material nanešen z mercerizacijo. Za fizikalnokemijsko karakterizacijo so bile uporabljene analitične metode, kot so infrardeča spektrometrija s Fourierjevo transformacijo (FTIR), merjenje elektrokinetičnega potenciala, vrstična elektronska mikroskopija (SEM) in termična gravimetrija. Raziskave obstojnosti so bile ocenjene po enem ciklusu pranja. Analize so potrdile dobro obstojnost obeh vrst hitozana na celulozni tkanini. Tkanina, obdelana s hitozanom z višjo stopnjo deacetiliranja, je imela več pozitivno nabitih amino skupin in boljšo termično stabilnost kot tkanina, obdelana s hitozanom z nižjo stopnjo deacetiliranja.
Ključne besede: hitozan, bombažna tkanina, FTIR, elektrokinetični potencial, FE-SEM, termična gravimetrija

1 Introduction

Chitosan is the (β-1,4) linked D-glucosamine derivative of the polysaccharide chitin (poly N-acetyl-d-glucosamine) found in the outer shell of crustaceans (e.g. shrimp and crab). Chitosan is usually produced through the alkaline hydrolysis of chitin, a process that results in N-deacetylation and depolymerisation. Chitosan has been highly appreciated for medical purposes, such as antibacterial wound dressings and drug delivery systems, and for enhancing immune activities [1–15].

For the last decade, its application in textiles and biomaterials has grown significantly [2–13]. It has been well-implemented in man-made fibre, but achieved properties in natural fibre have not proven durable

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[3, 7, 9]. Because the antimicrobial property of chitosan is strongly affected by molecular weight, pH and degree of deacetylation (DDA) [12], two chitosans with differing degrees of deacetylation were implemented into cellulose material in this study, while characterisation was performed for the purpose of determining durability after one washing cycle.

2. Material and methods

2.1 Material

Peroxide bleached 100% cotton woven fabric (article: "Fedora") from Tekstilna tvornica Trgovišće, Croatia, of mass per unit area 150 gm^{-2}, yarn density and fineness: warp 55 cm^{-1}, 16 tex; weft 32 cm^{-1}, 20 tex was used.

Chitosans of different molecular weight (M_n) and degrees of deacetylation (DDA) were purchased from Mathani Chitosan Pvt. Ltd. The chitosans were milled in a Planetary Micro Mill PULVERISETTE 7 premium line. Ceramic balls with a diameter of 5 mm were used at a milling time of 30 minutes at 900 rpm. After milling, a chitosan powder suspension in water was formed, and a fraction with a diameter greater than 1 μm after 5 minutes was sedimented. A chitosan fraction of less than 1 μm was obtained by evaporating the slurry. Nanoadditives were characterised in terms of their size distribution profiles by means of dynamic light scattering (DLS) using a Zetasizer apparatus from Malvern Instruments. The DLS results indicated that the average particle diameter obtained was within the range of 1 to 0.5 μm. The characteristics of chitosans are given in Table 1. Sodium hydroxide p.a. (NaOH) was purchased from Grammol d.o.o., 99.7% acetic acid from VWR International Ltd. and Subitol MLF from CHT-Bezema.

Table 1: Characteristics of chitosan

Chitosan	DDA	M_n [kDa]	Average particle diameter [μm]
C-P2	80	60	1–0.5
C-TRI	90	80	1–0.5

2.2 Procedure

Chitosan was implemented into cotton fabric by using a mercerisation process [16]. Mercerisation was performed following the technological process (with 0% tension) in a bath containing 24% NaOH, 5 gl^{-1} anionic surfactant Subitol MLF (Bezema) as a wetting agent in a liquor ratio of 1:20, for 2 minutes at 17 °C. Before hot rinsing, the alkali cotton fabrics were treated with 5 gl^{-1} of chitosan in a water bath (pH 13), with the same liquor ratio of 1:20, for 2 minutes at 17 °C. The fabrics were then rinsed with hot water (T = 98 °C) for 40 seconds, followed by cold water, neutralised with 0.1 M acetic acid and rinsed until pH 7, and finally air-dried.

In order to determine treatment durability, fabrics were washed at 60 °C according to ISO Standard 6330:2012 with a phosphate-based standard ECE detergent without fluorescent whitening agents. The labels and treatments are listed in Table 2.

Table 2: Labels and treatments

Label	Treatment
B	Peroxide bleached 100% cotton woven fabric
P2	Chitosan C-P2 implemented in cotton fabric
TRI	Chitosan C-TRI implemented in cotton fabric
–WC	Washed for 1 washing cycle

2.3 Methods

The samples were analysed using a FTIR-ATR spectrometer (PerkinElmer, software Spectrum 100). Four scans at a resolution of 4 cm^{-1} were recorded for each sample between 4000 and 380 cm^{-1}.

Electrokinetic potential versus pH was measured through the streaming potential method using a Brookhaven-Paar electrokinetic analyser (EKA) with a stamp cell, and calculated according to the Helmholtz-Smoluchowsky equation [17]. The zeta potential and isoelectric point (IEP) of the textile fabrics were determined and analysed.

Scanning electron microscopy was done on cotton fabrics before and after one washing cycle using a MIRA\FE-SEM, Tescan, Czech Republic. The specimens were sputter-coated with a palladium-gold alloy and analysed using a SEM operating at an accelerating voltage of 5.00 kV and magnification of 2000 x.

Thermogravimetric (TG) analysis were carried out in atmospheric conditions using a Pyris 1 TGA thermogravimetric analyser from Perkin Elmer. All samples of 5 to 6 mg were heated in a temperature range

from 50 to 800 °C at a heating rate of 10 °C min^{-1} with continuous air flow at a rate of 30 ml min^{-1}.

3 Results and discussion

The results of FTIR analysis for chitosan (C-P2 and C-TRI), cotton fabric (B) and fabrics with implemented chitosan (P2 and TRI) are shown in Figures 1 and 2.

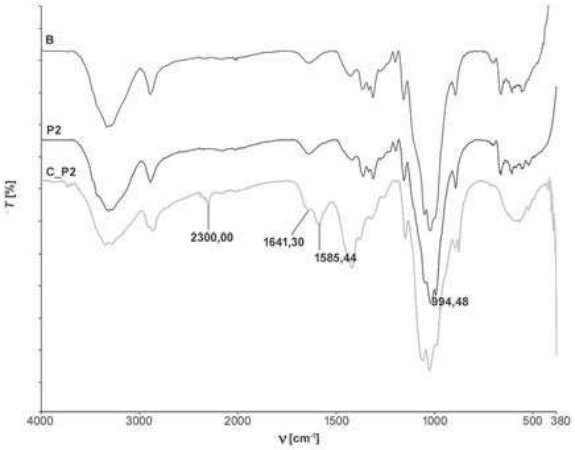

Figure 1: FTIR analysis of chitosan (C-P2), bleached cotton fabric (B), and chitosan C-P2 implemented fabric (P2)

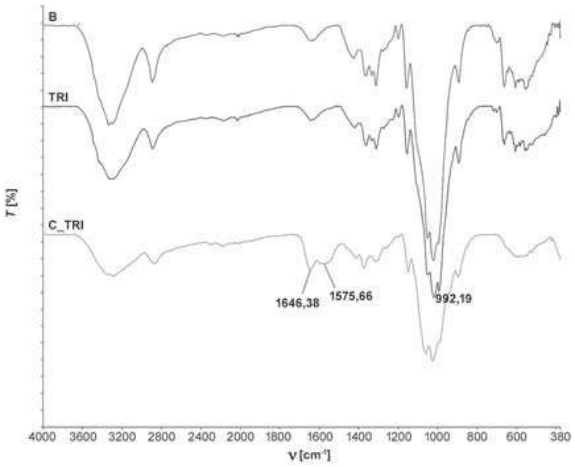

Figure 2: FTIR analysis of chitosan (C-TRI), bleached cotton fabric (B), and chitosan C-TRI implemented fabric (TRI)

Basic transmission bands for chitosan and cellulose can be seen from the results shown in Figures 1 and 2. A peak at 1640 cm^{-1} corresponds to the C=O stretching of the secondary amide band (amide I). For both chitosans (C-P2 and C-TRI), that figure is 1641 and 1646 cm^{-1}, respectively. The chitosan characteristic band at 1563 cm^{-1}, which is assigned to the stretching vibration of amino group of chitosan, N–H deformation (amide II), shifted for both chitosans applied C-TRI (1575 cm^{-1}) and C-P2 (1585 cm^{-1}) [14]. It is evident that the shape of bands between 1500–1750 cm^{-1} changed. The band at 2300 cm^{-1} can be attributed to NC=O group characteristic for the chitin, suggesting that the C-TRI chitosan sample is more acetylated than the C-P2 sample.
For chitosan-treated fabrics, the intensity of peaks is lower than in cotton cellulose. The reason may lie in the possible overlapping of cellulose with chitosan. An increased intensity at bands 994 and 992 cm^{-1} for P2 and TRI chitosan implemented fabrics was observed. This can be attributed to the possible positive interference of peaks of both cellulose and chitosan. No other changes relative to the cellulose were noted. Electrokinetic analysis was thus performed. The results are shown in Figures 3 and 4, and in Table 3.

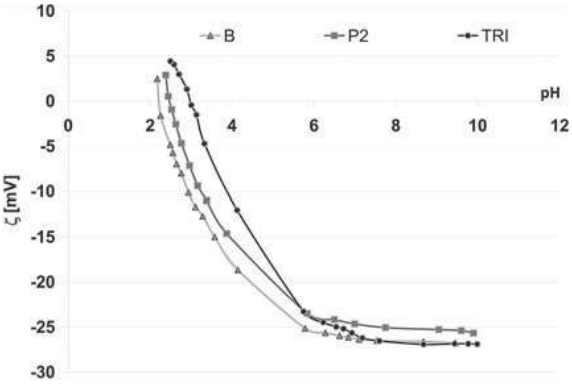

Figure 3: Electrokinetic potential (ζ) vs. pH of 0.001 M KCl of bleached cotton fabric (B) and chitosan P2 and TRI implemented fabrics

Table 3: Zeta potential (ζ) at pH 10, pH 7 and isoelectric point (IEP) of modified cotton fabrics before and after one washing cycle

Sample	ζ at pH 10 [mV]	ζ at pH 7 [mV]	IEP [pH]
B	–27.7	–26.4	2.2
B-WC	–19.0	–19.0	2.3
P2	–26.4	–24.6	2.5
P2-WC	–20.5	–20.1	2.5
TRI	–26.9	–26.2	3.0
TRI-WC	–20.4	–19.0	3.0

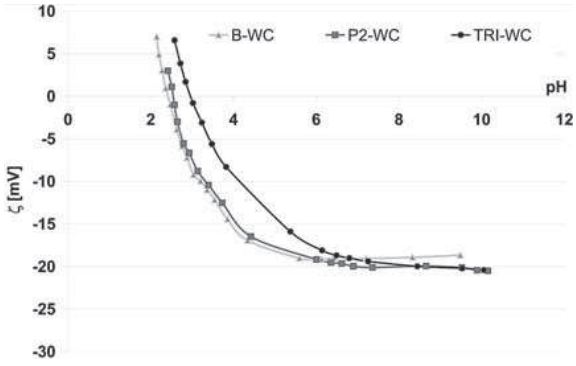

Figure 4: Electrokinetic potential (ζ) vs. pH of 0.001 M KCl of bleached cotton fabric (B) and chitosan P2 and TRI implemented fabrics after one washing cycle

The results of the electrokinetic analysis indicate that both implementations went well. The results of zeta potential in alkali and neutral electrolyte solutions show slightly higher potential as a consequence of the chitosan amino group, from –27.7 mV for B to –26.4 mV for P2, and –26.9 mV for TRI in an alkali medium (pH 10), as well as in a neutral medium at pH 7, from –26.4 mV for B to –24.6 mV for P2, and –26.2 mV for TRI, respectively. The isoelectric point (IEP) confirms that finding. It changes significantly from 2.2 for B to 2.5 for P2 and 3.0 for TRI chitosan-treated fabrics. Even the P2 has a higher zeta potential in a neutral medium, while the IEP indicates the higher implementation of C-TRI chitosan. This can be explained by the DDA, which represents the number of amine or acetyl amine groups on the glycoside unit of chitosan. Since the DDA of TRI is 90, a higher zeta potential and IEP were expected.

The results of electrokinetic potential after one washing cycle indicate that all fabrics have a higher zeta potential in alkali and neutral mediums, of about –20 mV. The reason for this lies in fabric shrinkage during the washing process. The zeta potential curves show similar behaviour as before washing, the difference being the plateau at higher values. It should be noted that the IEP is almost the same, suggesting the same presence of the chitosan in the fabrics after one washing cycle.

For the characterisation of the fibre surface, scanning electron microscopy was performed on cotton

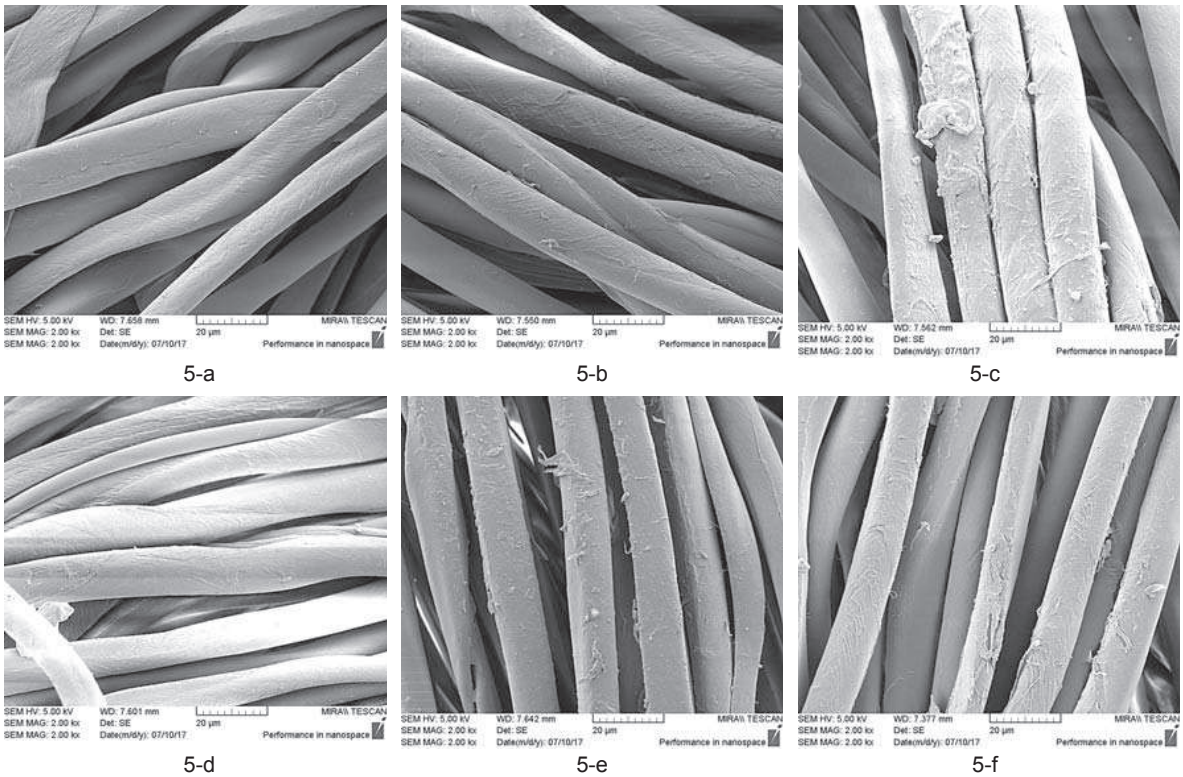

Figure 5: SEM micrographs of cotton fibres with a magnification of 2000x in (a) bleached cotton fabric (B), (d) bleached cotton fabric after one washing cycle (B-WC), (b) fabric with implemented chitosan C-P2 (P2), (e) fabric with implemented chitosan C-P2 after one washing cycle (P2-WC), (c) fabric with implemented chitosan C-TRI (TRI), (f) fabric with implemented chitosan TRI after one washing cycle (TRI-WC)

fabrics before and after one washing cycle. The SEM micrographs in Figure 5 show the surface of bleached cotton fabric (Figure 5a) and just cleaned after one washing cycle (Figure 5d). No fibrillation, which usually occurs when the washing process is repeated due to mechanics, was noticed. For the fabric with implemented chitosan, a higher amount of chitosan C-TRI (Figure 5c) can be found on the fibre surface than C-P2 (Figure 5b). After one washing cycle, some fibrillation as noted for both fabrics with implemented chitosan, as well as movement of chitosan particles to the surface. This observation suggests that some particles will be washed when the washing process is repeated.

The structural properties of the chitosan-treated cotton fabrics were studied using TG analysis. The results of TG analysis in a range from 50 °C to 800 °C with changes of 10° min^{-1} are shown in Figures 6 and 7, and in Table 4.

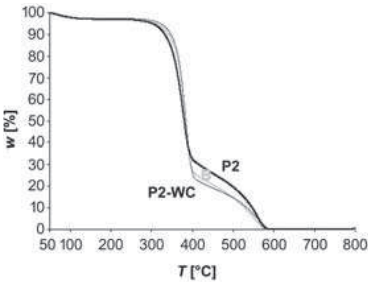

Figure 6: TG curves of bleached cotton fabric (B), and chitosan C-P2 implemented fabric (P2) and after one washing cycle (P2-WC)

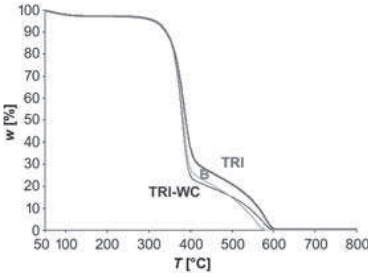

Figure: 7 TG curves of bleached cotton fabric (B), and chitosan C-TRI implemented fabric (TRI) and after one washing cycle (TRI-WC)

Table 4: Weight at 500 °C; temperature of complete degradation (T_d) and total residue of modified cotton fabrics before and after one washing cycle

Sample	Weight at 500 °C [%]	T_d [°C]	Residue [%]
B	14.954	582.14	0.144
P2	19.766	585.43	0.149
P2-WC	14.564	587.67	0.433
TRI	20.806	602.41	0.520
TRI-WC	15.215	594.83	0.650

It is evident from TG analysis that the chitosan is implemented into the fabric. The weight at 500 °C is significantly higher for fabric treated with chitosan. The amount for cotton fabric (B) is 14.9%, while the amount for chitosan implemented fabrics is 19.8% for P2 and 20.8% for TRI. The amount is slightly lower after one washing cycle, but still present. Taking into account the temperature of complete degradation, it is evident that chitosan-treated fabrics have better thermal stability, which is 20 °C for chitosan C-TRI, while T_d increased from 582 to 602 °C. In terms of total residue, it is evident that a higher amount is achieved through the implementation of C-TRI chitosan. It should be noted that the washing process led to an increase in residue. One possible reason for this may be the phosphate from the standard ECE detergent, which is well known for its flame retardant properties.

4 Conclusion

FTIR-ATR showed characteristic peaks for chitosan and cellulose, but not of implementation. Performed electrokinetic and thermogravimetric analyses, as well as FE-SEM microscopy confirmed that both chitosans were well-implemented into cellulosic fabric. Fabric treated with higher DDA chitosan (TRI) has more positively charged amino groups and better thermal stability. Fabric shrinkage occurred during the washing process, resulting in a higher zeta potential. However, the IEP remains the same, suggesting that achieved implementation is stable after one washing cycle.

Because the obtained results have shown that chitosan with higher DDA gives slightly better properties, its implementation into cellulose will be the subject of the further research.

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