THE INFLUENCE OF MALEIC ACID CONCENTRATION ON THE BINDING OF CHITOSAN WITH COTTON CELLULOSE

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Abstract: *Chitosan is an environmentally friendly agent used to achieve the antimicrobial properties of textiles. Due to the increasing demands on the stability of antimicrobial properties to multiple maintenance cycles, many authors are conducting research to permanently bind chitosan to the textile substrate. Aim of this study was to explore influence and persistence of the processing on cellulose textile substrates with an aqueous solution of chitosan using maleic acids in concentrations of 15 and 25 g/l with sodium hypophosphite monohydrate as catalyst. For the purpose of durability treated fabrics were washed according to ISO 6330:2012. The ability of maleic acid to crosslink chitosan with cellulose was tested before and after maintenance cycles using Fourier infrared spectrometry in the ATR technique (FTIR-ATR). The mechanical properties of the treated fabric were investigated before and after cycles of maintenance in accordance with ISO 13934-1. Maleic acid proved to be good crosslinking agent for chitosan and cellulose, regardless of applied concentration. The mechanical damage is higher in samples treated with a higher concentration of maleic acid due to the sensitivity of cotton to the action of acids.*
Keywords: *Cellulose, chitosan, maleic acid, FTIR-ATR, mechanical properties*

1. Introduction

Chitosan is biopolymer available in nature and is cheap to be produced. It is an environmentally friendly agent which shows good biocompatibility, bio-absorbability, wound-healing, haemostatic, anti-infection, anti-bacterial, non-toxicity and adsorption properties and usually used to achieve the antimicrobial properties of textiles which can be specifically used for medical purposes. It is knowing the major problems of chitosan as an antimicrobial agent are its poor durability on textile fabrics due to its lack of strong bonding with fabrics [1,2]. In last few years' different agents for crosslinking chitosan and cotton were used, eg. glutaraldehyde, some inorganic salts, phenols and thiophenoles, antibiotics, and formaldehyde derivatives. However, most of them are controversial for the environment and/or humans. Polycarboxylic acids (PCAs) for crosslinking with chitosan and cotton fabric are the best choice [1].

Therefore, in this paper, the effect of maleic acid concentration on the binding of chitosan to sodium hypophosphite monohydrate as a catalyst, as well as its durability, were investigated.

2. Materials and Methods

100% cotton standard fabric by WFK, marked as 10A, made in accordance with DIN 53919 / ISO2267 was used. Chitosan is obtained from Tricomed, Łódź, Poland. The samples were ground in a PULVERISETTE 7 micromill which has the ability to grind hard, medium hard and soft materials to a fineness of 100 nm. In the process of crushing, ceramic balls with a diameter of 20 mm and a crushing time of 48 minutes with a rotation speed of 900 rpm were used. Thus, crushed chitosan was used in the process of processing cellulosic material. For the purpose of crosslinking of chitosan and cellulose was used maleic acid types from Scharlau, and sodium hypophosphite monohydrate, Sigma Aldrich as a catalyst.

All samples were kept 20 h in the bath and after that treated in microwave oven for 5 min at 80 W. Finishing process of the samples provide from pad-dry-cure method, with wet pick-up 100%, conductive drying was carried out at 100 °C for 2 minutes and thermocondensation at 150 °C for three minutes.

Treated fabrics were washed according to ISO 6330:2012 *Textiles - Domestic washing and drying procedures for textile testing,* up to 10 washing cycles, in a Wascator FOM71 CLS device in accordance with ISO 6330, 6N in program 58 with the addition of 20 g of standard detergent. Properties were determined after 3rd and 10th washing cycle. In Table 1 list of samples with associated labels is shown.

Table 1: List of samples with associated labels

Sample	Treatment	pH of bath
CO	100% cotton standard fabric marked WFK 10A	
CO_K1	Cotton treated with a bath containing 15% MA and chitosan	4.27
CO_K1_3W	Cotton treated with a bath containing 15% MA and chitosan, after 3 maintenance cycles	
CO_K1_10W	Cotton treated with a bath containing 15% MA and chitosan, after 10 maintenance cycles	
CO_K2	Cotton treated with a bath containing 25% MA and chitosan	3.67
CO_K2_3W	Cotton treated with a bath containing 25% MA and chitosan, after 3 maintenance cycles	
CO_K2_10W	Cotton treated with a bath containing 25% MA and chitosan, after 10 maintenance cycles	

The ability to bind chitosan with cellulose by maleic acid before and after washing cycles was tested using Fourier infrared spectrometry (Perkin Elmer, software Spectrum 100) in the Attenuated total reflection (FTIR-ATR) technique. For each sample, 4 scans were recorded at a resolution of 4 cm^{-1} between 4000 and 380 cm^{-1}.

The mechanical properties (breaking force (F) and elongation(ε)) of the fabric were investigated before and after the treatment on a TensoLab Strength Tester (Mesdan S.p.A., Puegnago del Garda, Italy) in accordance with ISO 13934-1:2013 *Textiles — Tensile properties of fabrics — Part 1: Determination of maximum force and elongation at maximum force using the strip method*, with distance between clamps 100 mm, bursting speed 100 mm/min and pretension 2 N.

Mechanical damage was calculated according to ISO 4312:1989 *Surface active agents—Evaluation of laundering—Methods of analysis and tests for unsoiled cotton control cloth*:

$$U_m = \frac{F_0 - F}{F_0} \cdot 100 \quad (1)$$

where *Um* is mechanical damage (wear) [%], F_0 is breaking force of start fabric [N], and *F* is breaking force of treated and/or washed fabric [N].

The antimicrobial activity was determined according to AATCC TM 147-2016, *Antibacterial Activity Assessment of Textile Materials: Parallel Streak Method*. The activity was determined to Gram-positive bacteria Staphylococcus aureus ATCC 6538, Gram-negative bacteria Escherichia coli ATCC 8739 and microfungi–yeast Candida albicans ATCC 10231.

3. Results and Discussion

In this paper, the effect of maleic acid concentration on the binding of chitosan with cotton cellulose was investigated. Sodium hypophosphite monohydrate was used as a catalyst. For the purpose of durability testing, fabrics were washed up to 10 cycles. The ability of maleic acid to crosslink chitosan with cellulose was tested after treatment and after 3rd and 10th washing cycles using Fourier infrared spectrometry in the ATR technique (FTIR-ATR). The results of the spectral curves obtained by FTIR-ATR analysis of untreated 100% cotton material and the same after treatment are shown in Figures 1 and 2.

Spectral bands on treated and untreated samples at 3341 cm^{-1} indicate racking in –OH groups that was altered in the treated samples due to overlap within the stretching of N-H group present in the chitosan in the same region. The spectral bands of the sample CO_K1 and CO_K2 indicate the appearance of symmetrical and asymmetric vibrations within the C-H bonds characteristic of polysaccharides at wave numbers 2946 cm^{-1}, 2889 cm^{-1}, and a peak at 2821 cm^{-1} indicates a change in the methyl group. The peak at 2158 cm^{-1} is more visible in the CO_K1 sample than in the CO_K2 sample and indicates the presence of a Si-H group that may be present in the chitosan due to the method of preparation. The peak at 1640 cm^{-1} and 1644 cm^{-1}, respectively, in both treated samples has a lower intensity compared to untreated cotton, and occurs due to

the stretching of the C = O bond within the cellulose. It can be assumed that the change in intensity was due to the presence of residual N-acetyl groups present in chitosan.

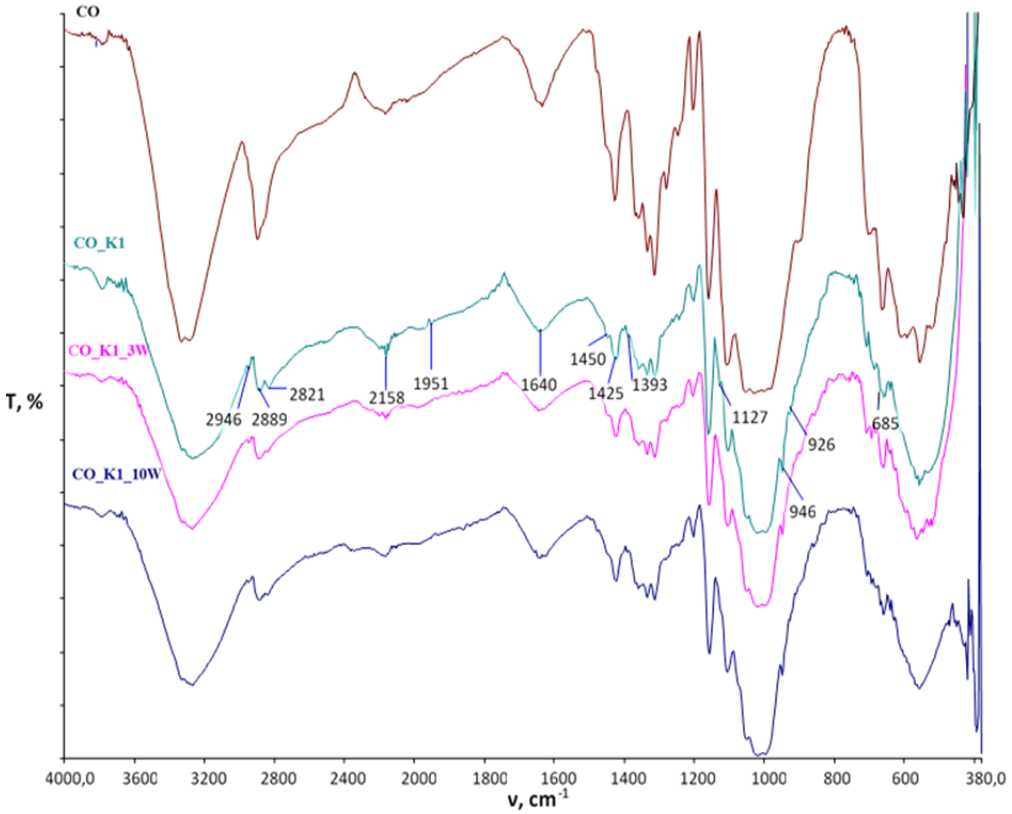

Figure 1: FTIR spectral bands of cotton treated with 15% MA with the addition of chitosan before and after maintenance cycles compared to untreated fabric

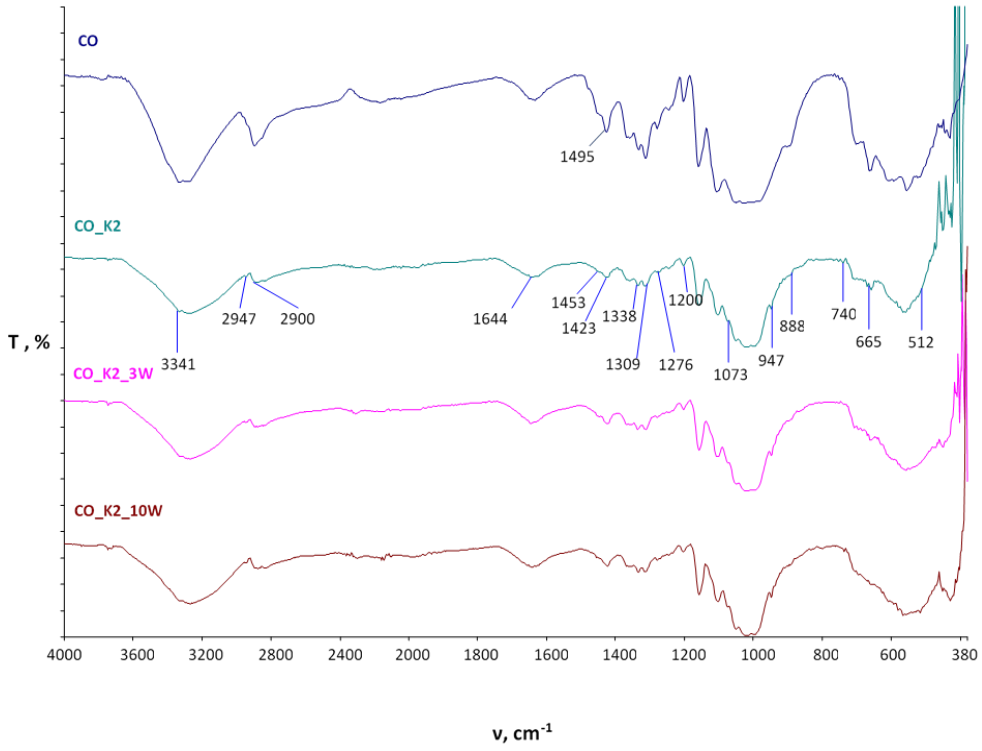

Figure 2: FTIR spectral bands of chitosan cotton treated sample with 25% MA before and after maintenance cycles compared to untreated fabric

At the wave number 1450 cm^{-1} and 1453 cm^{-1}, respectively, a peak was formed due to stretching within the CH_2 group, while at 1425 cm^{-1}, 1423 cm^{-1} and 1393 cm^{-1}, CH_3 groups were present along with CH_2. According to the literature, the peak in the 946 cm-1, 947 cm-1, and 926 cm-1 wavelengths represents the binding of the P-O group to the trimethyl group that may be present in the chitin structure. At the wave number 1495 cm^{-1} in the case of untreated cotton fabric, a sharp peak is visible, formed by bending in the -OH plane from the -C-O-H group, which is much lower in intensity on chitosan treated cotton fabrics [3-7]. All shown physicochemical changes on the spectral bands of the treated samples after 3 and 10 washing cycles are clearly visible with a possible change in intensity and indicate a constant modification of the physicochemical properties of the treated samples.

The mechanical properties (breaking force and elongation) of the treated fabric were investigated before and after 3rd and 10th washing cycle in accordance with ISO 13934-1. The results are presented in Table 2. From the results of breaking force, mechanical damage was calculated according to ISO 4312. Results are presented in Table 3.

Table 2. Mechanical properties (breaking force (F) and elongation (**ε)**) of cotton samples before and after treatment and multiple maintenance cycles

Samples	F warp [N]	ε warp [%]	F weft [N]	ε weft [%]
CO	726	8.400	803	21.800
CO_K1	471	10.900	472	23.400
CO_K1_3W	480	13.587	424	23.210
CO_K1_10W	436	12.800	471	21.500
CO_K2	400	10.379	376	25.900
CO_K2_3W	453	12.100	358	23.900
CO_K2_10W	364	12.000	367	20.300

F – breaking force, ε - elongation

Table 3: Mechanical damage to cotton samples before and after treatmend and multiple maintenance cycles

Samples	Mechanical damage of warp [%]	Mechanical damage of weft [%]
CO_K1	35.12	41.22
CO_K1_3W	33.88	47.20
CO_K1_10W	39.94	41.34
CO_K2	44.90	53.18
CO_K2_3W	37.60	55.42
CO_K2_10W	49.86	54.30

From the results in tab. 2-3 it can be seen that some mechanical damage has occurred since the values are 35-45% less depending of MA concentration. The damage was caused by finishing cotton fabric samples in an acidic medium. The acid damage to cellulose was greater in samples treated in a bath with a higher concentration of maleic acid.

In washing process, with heat and rinsing in water, the bonding between the MA and the two polymers is interrupted, and it is breaking. During the process of thermocondensation due to the heating of the MA, the anhydride is initially formed which is the reactive intermediate responsible for the networking of the MA with the cellulose, and analogue with chitosan. Addition of SHP as a catalyst promote an effective cross-linking between cellulose and chitosan by ester formation [1]. The results of antimicrobial efficacy of the samples before and after the treatments and multiple wash cycles shown in Table 4.

Table 4: Antimicrobial efficacy of samples

Samples	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
CO	-	-	-
CO_K1	-	-	+/-
CO_K1_3W	-	-	+/-
CO_K1_10W	-	-	+/-
CO_K2	-	-	+/-
CO_K2_3W	-	-	+/-
CO_K2_10W	-	-	+/-

From the results of antimicrobial efficacy presented in Table 4 is visible that the *Staphylococcus aureus* and *Escherichia coli* were present on all samples. The presence of *Candida albicans* on the surface of the treated samples was absent, but still the zone of inhibition was not achieved. However, since the *Candida albicans* was not present on or beneath the sample, it can be pointed out that this treatment gives only antimicrobial activity to micro fungi. This clearly indicates the need to modify the concentration ratios of chitosan in the bath, with the possibility for achieving better antimicrobial activity.

4. Conclusion

Chitosan is eco-friendly and safety substance which usually used for the medical applications like promoting tissue growth, accelerating wound-healing, bone regeneration, antimicrobial treatment etc. The binding stability of chitosan to cellulosic material by maleic acid was confirmed by FTIR-ATR analysis of samples CO_K1 and CO_K2 whose spectral bands indicate the resulting changes after processing and multiple maintenance cycles. Maleic acid proved to be good crosslinking agent for chitosan and cellulose, regardless of applied concentration. For a detailed interpretation of the mechanism of binding of chitosan to cellulose with maleic acid as a crosslinker in further research, samples will be analyzed for X-ray diffraction (XRD), Differential scanning calorimetry (DSC), Field Emission Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy analysis (FE_SEM-EDS) and others.
The mechanical damage occurred in all treated samples before and after maintenance damage is higher in samples treated with a higher concentration of maleic acid due to the sensitivity of cotton to the action of acids. However, this paper provides good indicators for achieving stronger binding of chitosan to cellulose, and further research will seek to modify the treatment process in order to reduce mechanical damage and obtain better antimicrobial efficacy.

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