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## The Stability of the Chitosan Coating on Polyester Fabric in the Washing Process

### *Stabilnost hitozanskega nanosa na poliestrski tkanini pri pranju*

Original scientific article/Izvorni znanstveni članek

Received/Prispelo 1-2023 • Accepted/Sprejeto 5-2023

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### Abstract

The sensitivity of chitosan to environmental conditions and processing conditions can stress its structure and cause degradation of this polymer on various application carriers. The stability of chitosan in a designed textile structure of standard polyester fabric with chitosan was analysed in a multiple washing process with a standard detergent by studying the properties before and after 10 washing cycles. The chitosan was coated on standard and alkali treated polyester fabrics. Washing was performed with an ECE A reference detergent at 60 °C according to the Standard protocol HRN EN ISO 6330 in 10 cycles. The washing stability of chitosan onto polyester fabrics was monitored by a staining test, zeta potential, breaking force, breaking elongation, pilling propensity, touch, whiteness, moisture transport, antimicrobial activity and morphological features. The staining test confirmed the wash stability of chitosan coated on alkali hydrolysed polyester fabrics, while the chitosan coated on standard polyester fabric disappeared. Zeta potential proved to be the significant parameter for determining chitosan stability. The tensile properties of fabric samples were harmonised with other characterisation parameters. Coating of polyester fabric with chitosan increased the elasticity of all samples. The antimicrobial activity of polyester fabrics coated with chitosan against *Staphylococcus aureus* was reduced by 20% after 10 washing cycles. All the characterisation parameters proved that polyester fabric as a chitosan carrier should be surface modified for designing a stable bioactive textile structure of chitosan and polyester.

Keywords: polyester fabric, chitosan, washing, stability

### Izvleček

Hitozanski nanosi na različnih nosilcih so izpostavljeni tako okoljskim kot tudi procesnim pogojem. Le-ti vplivajo na strukturo hitozana in lahko povzročijo njegovo degradacijo. Proučevali smo stabilnost hitozanskega nanosa na poliestrski tkanini pri večkratnem pranju s standardnim detergentom, pri čemer smo analizirali lastnosti obdelane



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tkanine pred pranjem in po desetih ciklih. Hitozan smo nanegli na standardne poliestrske tkanine in poliestrske tkanine po alkalni obdelavi. Prali smo z referenčnim detergentom ECE A pri 60 °C po standardnem protokolu HRN EN ISO 6330 v desetih ciklih. Stabilnost hitozanskega nanosa na poliestrskih tkaninah smo spremljali s testom obarvanja, zeta potencialom, določitvijo pretržne sile in pretržnega raztezka, nagnjenostjo k luščenju, dotikom, belino, transportom vlage, protimikrobno aktivnostjo in morfološki značilnostmi. Preskus obarvanja je potrdil stabilnost hitozanskega nanosa na poliestrski tkanini, predhodno obdelani z alkalno hidrolizo po pranju, medtem ko hitozanskega nanosa na standardni poliestrski tkanini po pranju nismo zaznali. Zeta potencial se je izkazal kot pomemben parameter za določanje stabilnosti hitozanskega nanosa. Natezne lastnosti vzorcev tkanine so bile usklajene z drugimi karakterizacijskimi parametri. Vsem poliestrskim tkaninam s hitozanskim nanosom se je povečala elastičnost. Antimikrobna aktivnost poliestrskih tkanin s hitozanskim nanosom proti *Staphylococcus aureus* se je po desetih ciklih pranja zmanjšala za 20 %. Vsi karakterizacijski parametri so pokazali, da je treba poliestrski nosilec predhodno površinsko modificirati, da je dosežena stabilna bioaktivna tekstilna struktura hitozana in poliestra.

*Ključne besede: poliestrska tkanina, hitozan, pranje, stabilnost*

## 1 Introduction

Chitosan is a natural, multifunctional polysaccharide, which, due to its exceptional biological and physicochemical properties, is used in various fields of application, such as the medicine, biomedicine, pharmacy, cosmetics, textile, chemical and paper industries, as well as in agriculture [1–3].

Chitosan, along with some other polymers, has been shown to be a useful dye transfer inhibitor in the wash bath. Its hydrogelling property provides a suitable physical form for the adsorption of dyes, which makes it a suitable material for the treatment of wastewater contaminated with dyes [4,5]. Such a wide range of applications demands the development of effective bioactive chitosan products. Numerous studies and results show the activity and added value of using chitosan in textiles, where it is used for its non-toxicity, biocompatibility, biodegradability, microbicidal activity, antistatic activity, complexing (chelating) properties, deodorising properties, film-forming ability, chemical reactivity, ability to improve the dyeing process, thickening properties, accelerated wound healing, etc. [6].

This cationic polymer consists of (1-4)-2-amino-2-deoxy- $\beta$ -D-glucan, which is, as a derivative, more important than the chitin, the main component of the cell wall of fungi, skeletal shells of crustaceans and insects and fish scales [7].

The chitin source, as well as preparation methods, make chitosan available in a range of deacetylation grades and molecular weights, which are important factors in the type and quality of the polymer. One of the main disadvantages of chitosan is its low solubility in water [8]. It is soluble in dilute inorganic

and organic acids with a lower pH than chitosan ( $pK_a \approx 6.3$ ), and forms a non-Newtonian liquid [9].

Free amino groups are protonated at low pH, which leads to electrostatic repulsion between the polymer chains, and, consequently, to dissolution.

The sensitivity of chitosan to environmental conditions and processing conditions (e.g., heating or freezing) can stress its structure and cause degradation of this polymer. Factors affecting the stability of chitosan can be internal (purity, molecular weight, polydispersity index, degree and method of deacetylation, moisture content) and external (environment – temperature and humidity and process – dissolution in acid, sterilisation, thermal treatments, physical methods) [10].

Its stability in formulations can be achieved by controlling environmental factors and process conditions (e.g., temperature), introducing stabilising compounds, combining with other polymers, and modifying chitosan with chemical or ionic compounds. Molecular weight, polydispersity, degree of deacetylation, purity and moisture content play an important role in determining the mechanism and rate of polymer degradation [10]. A decrease in average molecular weight and an increase in the degree of deacetylation were observed as a result. Simultaneously with the breaking of the chitosan chain, there is a degradation and/or destruction of the functional groups (amino, carbonyl, amido and hydroxyl groups), and, in addition, the depolymerisation of chitosan can lead to the formation of free radicals. Strong intermolecular interactions between the formed chitosan fragments (interchain cross-linking) change the structure of the polymer, leading to irreversible loss of its physicochemical properties. Therefore, the problem of low stability of

systems developed with chitosan can be a limiting factor for their application.

In this research, the stability of chitosan in a differently designed textile structure with chitosan in a multiple washing process with a standard detergent was analysed by studying the properties before and after 10 washing cycles.

Considering the partial compatibility of the biopolymer chitosan with the synthetic polymer polyester, the modification of the polyester fabric by alkaline hydrolysis, which can be considered as a preparatory phase for the adhesion of various substances, was also included in the research [11–14].

## 2 Materials and methods

### 2.1 Materials

A standard white polyester fabric (PN-01) from the supplier Centre for Testmaterials (CFT) B.V., The Netherlands, and Chitosane (low molecular weight-LMW with an 85% degree of deacetylation), from Aldrich® was used for the design of the polyester and chitosan biopolymer textile structure. Chitosan of LMW was selected as suitable for textiles, food, photography, medical and environmental applications [15].

The polyester fabric (PES) used, with a unit per surface area of 156 g/m<sup>2</sup>, was woven in plain weave with a density of 27.7 threads/cm in the warp direction and 20 threads in the weft direction, using a warp yarn fineness of 30.4 tex and a weft yarn fineness of 31.9 tex.

#### Design of chitosan-PES textile structure

Prior to coating with chitosan, the standard polyester fabric was modified by alkaline hydrolysis with

a sodium hydroxide solution, 2% NaOH (aq.), purchased from Ivero d.o.o., Croatia, and by alkaline hydrolysis with the addition of a cationic promoter, benzalkonium chloride, contained in the product Barquat™50 from the supplier QuatChem, England, at a concentration of 3 g/L. Both modifications were carried out under the same process conditions, bath ratio (BR) 1:5, 98 °C for 30 min in a W. Mathis apparatus. After alkaline hydrolysis, the fabrics were washed twice with hot water at 98 °C, and rinsed twice with cold water at 20 °C and air dried. Untreated and alkaline hydrolysed polyester fabrics and chitosan at a concentration of 0.5%, prepared with 0.1 mol/L hydrochloric acid (HCl), whose pH was adjusted to 3.6, were used for the design of the chitosan-PES textile structure. These fabrics were impregnated with a chitosan solution in a Benz stenter with a pressure of 12.5 kg/cm, and then dried at 90 °C for 40 s and cured at 130 °C for 20 s in the same apparatus to achieve a better fixation of the chitosan on the textile material in the impregnation process

#### Washing process

The washing process was performed using a standard ECE A detergent with a concentration of 1.25 g/L in a Rotawash laboratory washing machine, SDL Atlas at 60 °C with BR 1:8 according to the Standard protocol HRN EN ISO 6330 in 10 cycles, except for the samples after 5 cycles to monitor the degree of changes and the stability of chitosan on the designed chitosan - PES structures. The identifications of all the analysed samples are described in Table 1.

Table 1: Description of polyester fabrics and chitosan-PES fabrics

Description	PES fabric	Chitosan-PES fabric
Untreated	U	Ch-U
Untreated washed 5 times	U-5	Ch-U-5
Untreated washed 10 times	U-10	Ch-U-10
Alkali hydrolysed	AH	Ch-AH
Alkali hydrolysed washed 5 times	AH-5	Ch-AH-5
Alkali hydrolysed washed 10 times	AH-10	Ch-AH-10
Alkali hydrolysed with promoter	AH_C	Ch-AH_C
Alkali hydrolysed with promoter washed 5 times	AH_C-5	Ch-AH_C-5
Alkali hydrolysed with promoter washed 10 times	AH_C-10	Ch-AH_C-10

## 2.2 Methods

### Staining test

Identification of chitosan in the designed chitosan-polyester textile structure before, after 5 and 10 washing cycles was performed qualitatively and quantitatively. The samples were subjected to the dyeing process with the reactive dye Remazol Red RB (C.I. Reactive Red 198) at the concentration 1% (o.w.f.) from the manufacturer DyStar in a W. Mathis laboratory apparatus with BR 1:50 at 60 °C for 30 min. After dyeing, the fabrics were washed with cold water, followed by post-treatment with Kemopon 50 supplied by Kemo, Croatia, in the same apparatus, at a concentration of 2 g/L at 90 °C for 10 min. The composition of this washing agent is a mixture of anionic and nonionic surfactants suitable for removing of dye non-fixed to the fabric. After washing the samples were air dried, and then analysed microscopically and spectrophotometrically.

### Microscopic examination

A DinoLite digital microscope, Premier IDCP B.V., Almere, The Netherlands, was used to analyse the surface of the dyed samples at 50× and 230× magnification.

The fabric surface before and after the design of the chitosan-polyester structure and 10 washing cycles was observed with a Scanning Electron Microscope, Tescan, MIRA /LMU, Czech Republic, under a magnification of 1,500x. Prior to observation, the samples were sputtered with gold and palladium for 90 s (Quorum Technologies, Q150T ES Plus, UK).

### Spectrophotometric measurements

Quantitative evaluation of the hue of the chitosan-polyester textile structure before, after 5 and after 10 washing cycles was performed spectrophotometrically by determining the colour strength (K/S value) measured according to the Kubelka-Munk equation using the DataColor 850, a Swiss instrument with a constant instrument aperture, standard illumination D65 and d/8° geometry.

The whiteness degree according to Ganz Griesser ( $W_{GG}$ ), tint deviation (TD) and tint value (TV) of all the fabrics were determined using the DataColor 850, with the aperture size of 20 mm, under the standard illumination D65. The whiteness degree (W) was calculated automatically according to ISO 105-J02:1997 Textiles—Tests for colour fastness—Part J02: Instrumental assessment of relative

whiteness and expressed as medium values of four individual measurements [16].

### Streaming potential method

The zeta potential, determined by the streaming potential method, was chosen as a parameter to characterise the fabric before, after 5, and after 10 washing cycles, to monitor the stability of chitosan during cyclic washing. The analysed samples placed in the Adjustable Gap Cell were subjected to the measurement of the streaming potential in 1 mmol/L KCl by a titration procedure, starting from alkaline (adjusted with 1 mol/L NaOH) to acidic (adjusted with 1 mol/L HCl) in the SurPASS electrokinetic analyzer, A. Paar GmbH, Austria. During the measurement, in addition to the streaming potential in mV, the parameters are also recorded from which the zeta potential was calculated as a function of pH according to the Helmholtz-Smoluchovsky equation [17, 18].

In addition, the control samples and the samples washed 10 cycles were analysed by other applied methods.

### Breaking force and breaking elongation

The breaking force and breaking elongation of the unwashed and 10-cycle washed samples were selected, to evaluate the tensile properties and elasticity, considering that the properties change with the modification of polyester fabric by alkaline hydrolysis, the treatment with chitosan and the washing process. The tensile properties were determined in accordance with the Standard HRN EN ISO 13934-1:2013: Textiles -- Tensile properties of fabrics -- Part 1: Determination of maximum force and elongation at maximum force by the strip method using a Tensolab 3000 dynamometer, Mesdan s.p.A., Italy.

### Tendency to pilling generation

The surface propensity of the samples before and after 10 washing cycles to produce pilling was analysed after 125, 500, 1000, 2000, 5000 and 7000 cycles according to HRN EN ISO 12945-2:2003: Textiles – Determination of the tendency of textiles to surface fuzzing and pilling – Part 2: Modified Martindale method.

### Moisture management

The dynamic transfer of moisture through the samples from the front and back surfaces was measured using the MMT 290 Moisture Management Tester from SDL Atlas.

By choosing the wetting time (WT), the similarities and differences between each sample, before and after the design of the chitosan- PES structure and after 10 washing cycles, were determined by HCA-Hierarchical Cluster Analysis using Minitab software and Ward's dendrograms [19]. HCA is an advanced mathematical and statistical method used to classify samples in groups by similarity and dissimilarity. In this research, it was used as an additional method for mathematical confirmation of the obtained differences of the samples before and after the washing process.

### Tactile properties

The alkali modified and chitosan-polyester fabrics, before and after washing, were characterised by a Fabric Touch Tester, FTT M293 from SDL Atlas, USA. The properties are specified by smoothness, softness, warmth, total hand and total touch [20].

### The antimicrobial activity

The antimicrobial activity (AMA) of chitosan was analysed before and after 10 wash cycles according to the ASTM E 2149-01 method: Standard Test Method for Determining the Antimicrobial Activity of Immobilised Antimicrobial Agents Under Dynamic Contact Conditions. The bacterial species defined in the Standard is *Klebsiella pneumoniae*, American Type Culture Collection (ATCC) No. 4352, and one gram-positive bacteria, found commonly on skin, *Staphylococcus aureus* ATCC 29213, was used as well, in order to broaden the spectrum of antimicrobial activity of the examined chitosan-polyester fabrics.

The 2 g test samples were cut into 1 × 1 cm pieces, divided in two and autoclaved, and then placed in suspensions. A suspension with a volume of 25 mL and a density according to the Standard used of  $2.0 \times 10^5$  of one culture and the other was transferred to Falcon tubes and then incubated for 1 h under rotational mixing. Then, 0.01 mL from each vial was diluted serially 10x into microtiter plates, these dilutions were applied to nutrient agar, and the plates were incubated for 24 h at 35 °C. The results are expressed as the percentage of reduction of microorganisms in contact with the sample according to Equation 1:

$$\text{Reduction} = \frac{(B - A)}{B} \times 100 (\%) \quad (1)$$

where:

A is CFU per mL of treated sample after contact in a certain time,

B is "0" time of contact CFU per mL before placement of the sample.

## 3 Results and discussion

Chitosan is positively charged in the neutral conditions, and can be used for adsorption of anionic substances due to electrostatic interactions [4]. Accordingly, the identification of chitosan on the designed chitosan - PES textile structure (untreated, alkaline hydrolysed and alkaline hydrolysed with a cationic promoter) was performed before, and after 5 and 10 wash cycles, after dyeing with Remazol Red RB reactive dye. According to the literature, this is a dye with excellent light, perspiration and soaping fastness [21]. The single azo reactive bifunctional dye Remazol Red RB (C.I. Reactive Red 198) [22] (Figure 1) contains two different reactive systems in the same molecule. The first reactive centre (RC. 1) is a 2-sulphatoethyl sulphone precursor of the vinylsulphone reactive system, and the second (RC. 2) is based on nitrogen-containing heterocyclic ring, bearing a halogeno substituent undergoing nucleophilic substitution [21, 23].

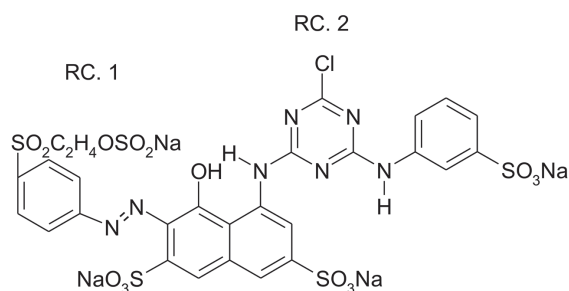


Figure 1: Chemical constitution of the reactive dye Remazol Red RB (C.I. Reactive Red 198) [21, 23]

The vinylsulphone reactive system (RC. 1) reacts via a nucleophilic addition mechanism. In this system the carbon-carbon double bond is polarised by the powerfully electron-attracting sulphone group. This polarisation imparts a positive character on the terminal carbon atom, and favours the nucleophilic addition of the chitosan anion.

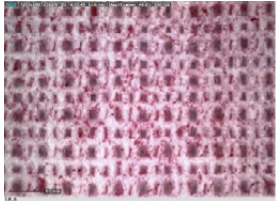
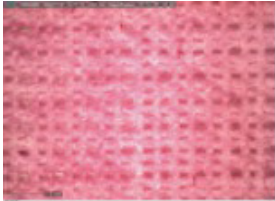

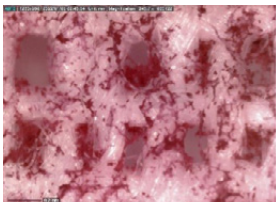
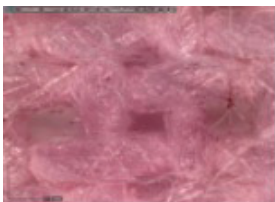
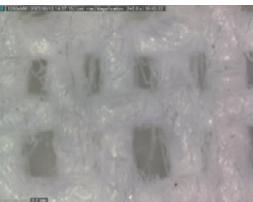
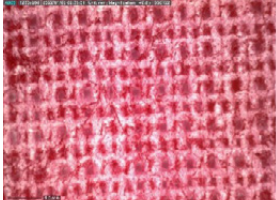



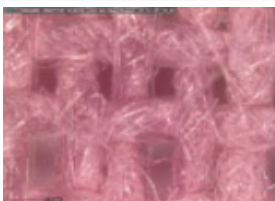
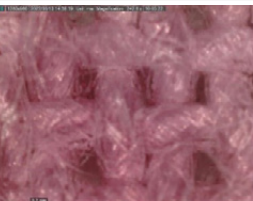
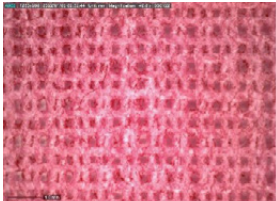
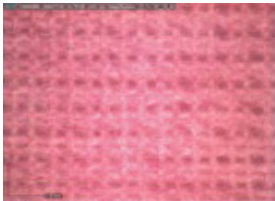
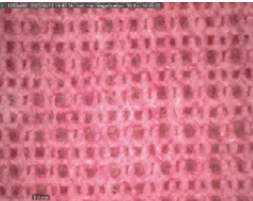
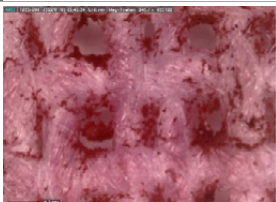
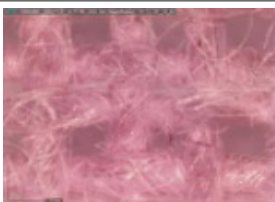
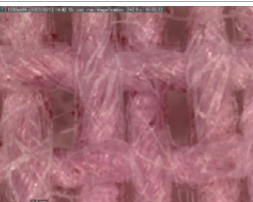
The reactive centre, based on a nitrogen-containing heterocyclic ring (RC. 2) bearing a halogen substituent, undergoes nucleophilic substitution. The heteroatoms (-Cl) in the aryl ring activate the sys-



tem for nucleophilic attack of a chitosan anion due to their electronegativity [24]. The red shade of the colour proves the presence of the biopolymer chitosan. The intensity of the staining shows the degree

of saturation of the polyester fabric with this biopolymer [25–28]. A digital image of the surface of the examined samples with a magnification of 50 and 230 times is shown in Table 2.

Table 2: Digital micrographs of the chitosan-PES fabrics before and after washing cycles dyed with Remazol Red RB under magnification of 50x and 230x

Magnification	Ch-U	Ch-U-5	Ch-U-10
50x			
230x			
Magnification	Ch-AH	Ch-AH-5	Ch-AH-10
50x			
230x			
Magnification	Ch-AH_C	Ch-AH_C-5	Ch-AH_C-10
50x			
230x			

An image of the red-stained surface of the control sample before (Ch-U) and after 5 wash cycles (Ch-U-5) confirms the stability of the chitosan during the wash cycles. However, the 230x magnification shows clearly that this stability is not permanent, as the chitosan particles visible on the control samples (Ch-U) have disappeared on sample ChU5. A snapshot of the sample (Ch-U-10) shows an unstained surface, confirming that no chitosan was present on the sample after 10 wash cycles, indicating the instability of the adhered chitosan on this sample. This is due to the weaker compatibility and interactivity of the natural and synthetic polymer on the studied structure. The intensity and uniformity of staining of each sample differed before and after 5 and 10 cycles.

The multifunctional properties of polyester, identified as compatibility with chitosan, increase in reactivity and enhanced hydrophilic character, were the result of modification by alkaline hydrolysis [29]. Visual inspection confirmed that the best effect was obtained with the biopolymer textile structure chitosan-alkaline hydrolysed PES fabric (Ch-AH). However, the red colouration of the samples chitosan-alkaline hydrolysed PES fabric after 10 washing cycles (Ch-AH-10 and Ch-AH\_C-10) confirms the good stability of chitosan. This proves that it is necessary to modify the surface of polyester fabric to develop a stable bioactive textile structure of chitosan and polyester. The stability results obtained are consistent with previous studies, even though these were carried out under different processing conditions [30].

The dyed textile structures with chitosan were evaluated spectrophotometrically, and the results of the colour strength (K/S) of the samples are shown in Table 3.

*Table 3: Colour strength (K/S) of the control and washed chitosan-PES fabrics dyed with Remazol Red*

Fabric	K/S
Ch-U	1.5056
Ch-U-5	1.6378
Ch-U-10	1.1517
Ch-AH	2.9824
Ch-AH-5	1.6101
Ch-AH-10	1.5208
Ch-AH_C	3.2686
Ch-AH_C-5	1.5913
Ch-AH_C-10	1.4995

The colour strength shows the stability of coated chitosan on PES fabric before and after modification numerically. It can be seen that alkaline hydrolysis affects the coating potential of chitosan favourably. The analysis shows that the unmodified chitosan coated fabric had the best stability after 5 wash cycles (Ch-U-5), while, after 10 wash cycles (Ch-U-10), the chitosan was lost, due to poor compatibility between the two polymers, polyester and chitosan. This proves the need for an increase in the compatibility of chitosan with polyester, e.g. by alkaline hydrolysis, or some other chemical or physical methods. The colour strength of the alkaline hydrolysed samples was almost twice that of the unmodified samples. However, the results show that chitosan is not completely stable, but some of it is lost under the alkaline conditions of the washing process. The values shown indicate the highest loss over 5 cycles. Further wash cycles up to the analysed 10 did not result in significant changes in colour strength, indicating that the chitosan had stabilised through 5 washing cycles.

Benzalkonium chloride as a cationic compound promoted alkali hydrolysis of polyester fabric and improved compatibility between chitosan and polyester. The presence of free quaternary ammonium groups of the cationic promoter and protonated amino groups of chitosan on the surface of the sample Ch- AH \_C improved its colour strength. This effect of quaternisation of polyester fabric modified with chitosan did not improve wash fastness, as the K/S values of the alkaline hydrolysed samples (Ch-AH and Ch- AH \_C) were comparable after 5 and 10 washes. Considering the fact that surface properties change with the modification and functionalisation of textiles, the surfaces of all the studied samples were analysed before and after 5 and 10 washing cycles. The characterising parameter is the zeta potential, which is determined as a function of the pH of the 1 mmol/L KCl solution, Figures 2–7. It is well known that the most hydrophobic synthetic fibres, including polyester, have a highly negative value of zeta potential. Esterified carboxylic groups of polyester result in negative zeta potential values from -40 mV to -80 mV, depending on the structural parameters and modification/functionalisation process [31]. The zeta potential values of the standard polyester fabric (U) are due to preparations [11] lower throughout the pH range than the values shown in other research findings [31,32]. After 5 and 10 washing cycles, the zeta potential of the washed

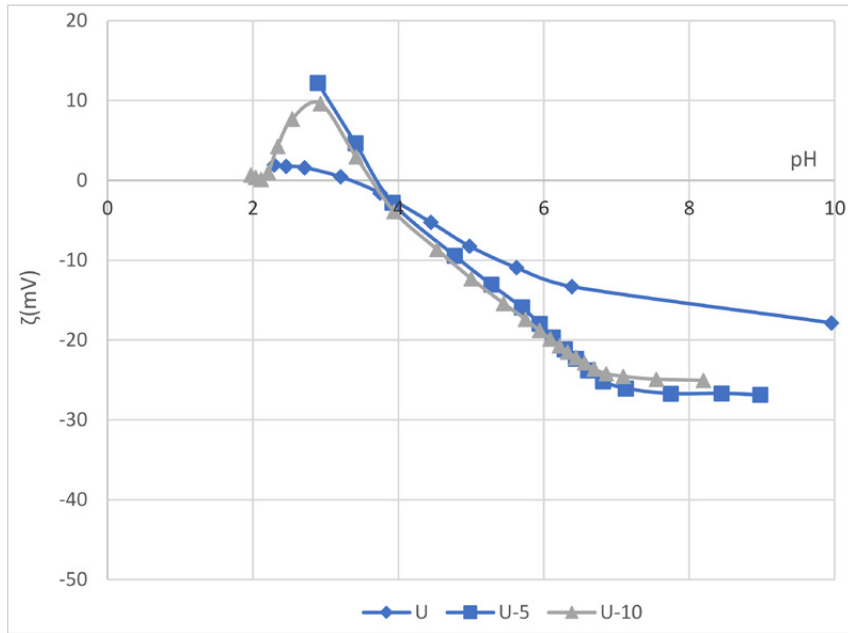


Figure 2: Zeta potential of untreated fabrics before and after washing cycles in variations of pH 1 mmol/L KCl

standard polyester fabric (U-5 and U-10) was more negative compared to the control sample (U). This relationship shows that the washing process had a purifying effect, although the values obtained were still lower compared to those characterising polyester textiles.

Figure 3 shows that the designed chitosan-polyester structure (Ch-U) has positive values of zeta potential throughout the studied pH range, which is in agreement with the results of zeta potential of chitosan, which is 12 mV at pH 7 [4, 33]. The zeta potential curves of the washed chitosan-polyester fabric are negative in the whole pH range. The shape of

the titration curves depends on the surface changes caused by the number of washing cycles. The curve of the 10-cycle washed sample (Ch-U-10) is flatter than the curve describing the electrokinetic behaviour of the Ch-U-5 sample, which means that the 5-cycle washed sample has a more negative zeta potential than the 10-cycle washed sample. A possible reason for the less negative surface of the 10 times washed fabric (Ch-U-10) than the 5 times washed (Ch-U-5) can be accumulation of detergent ingredients, e.g. insoluble zeolites, or inorganic substances from hard water.

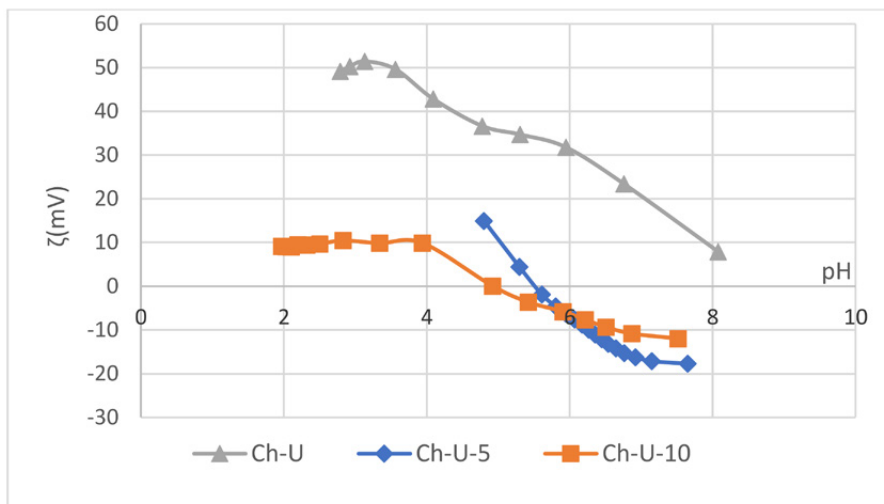


Figure 3: Zeta potential of chitosan-PES fabrics before and after washing cycles in variations of pH 1 mmol/L KCl



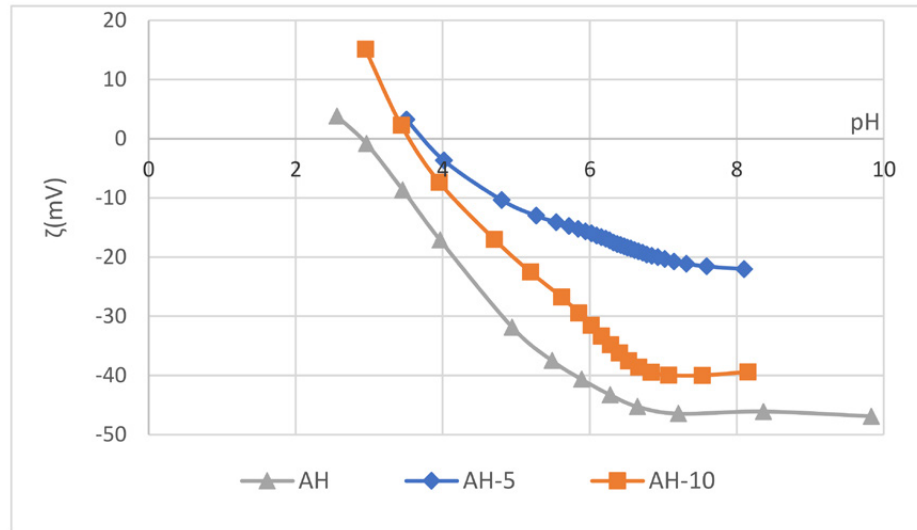


Figure 4: Zeta potential of alkali hydrolysed PES fabrics before and after washing cycles in variations of pH 1 mmol/L KCl

Modification of the polyester fabric by alkaline hydrolysis (AH) resulted in a decrease in zeta potential compared to the control sample (U), Figure 4. The modification of polyester in alkali hydrolysis should be observed as a preparation process, where a surface was purified and peeled to a certain degree. The zeta potential curves show that the zeta potential of the washed fabrics continued to decrease, with the decreasing trend following the patterns described previously, where 5 cycles (AH-5) resulted in more negative zeta potential values compared to 10 cycles (AH-10). The Isoelectric points (IEPs) of the 5 and 10 times washed alkali hydrolysed samples are very

close, despite a difference in the negative zeta potential values. The influence of the number of washing cycles on the state of the modified surface cannot be compared with untreated polyester fabric (U), which is covered with impurities (Figure 2).

The zeta potential curve of the alkaline hydrolysed polyester fabric treated with chitosan (Ch-AH) as a function of pH is completely in the positive range, Figure 5. The size and stability of the titration curve indicates the presence of chitosan on the surface. After 5 and 10 wash cycles, it can be seen that the curves of the washed samples (Ch-AH-5 and Ch-AH-10) go completely into the negative range, with

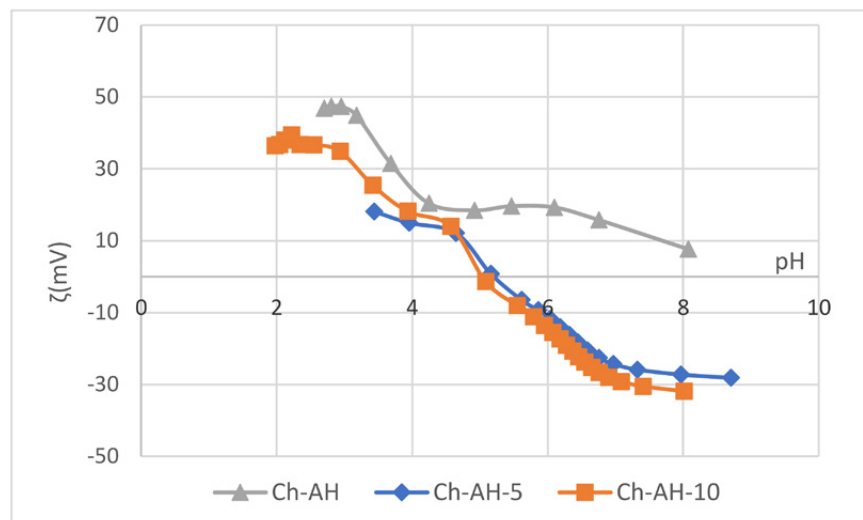


Figure 5: Zeta potential of chitosan-alkali hydrolysed PES fabrics before and after washing cycles in variations of pH 1 mmol/L KCl

the values of the 10 wash cycles being slightly more negative than those of the 5 wash cycles. The comparison of the alkaline hydrolysed sample treated with chitosan after 10 washing cycles (Ch-AH-10) with the alkaline hydrolysed sample after 10 cycles (AH-10) shows that the values were less negative. This confirms that chitosan is still present on the surface of the polyester fabrics after 10 washing cycles. The results are in agreement with the identification by the staining results and the colour strength values.

The zeta potential curves of the alkaline hydrolysed samples with the addition of a cationic surfactant, before and after 5 and 10 wash cycles, overlap, Figure 6. The alkaline hydrolysed control fabric with cationic surfactant (AH\_C) shows a typical curve of polyester textiles [31,32]. This process of alkaline hydrolysis with the addition of a promoter caused the removal of the existing preparations and the pilling of the surface, which changed the surface properties completely compared to the control fabric (U).

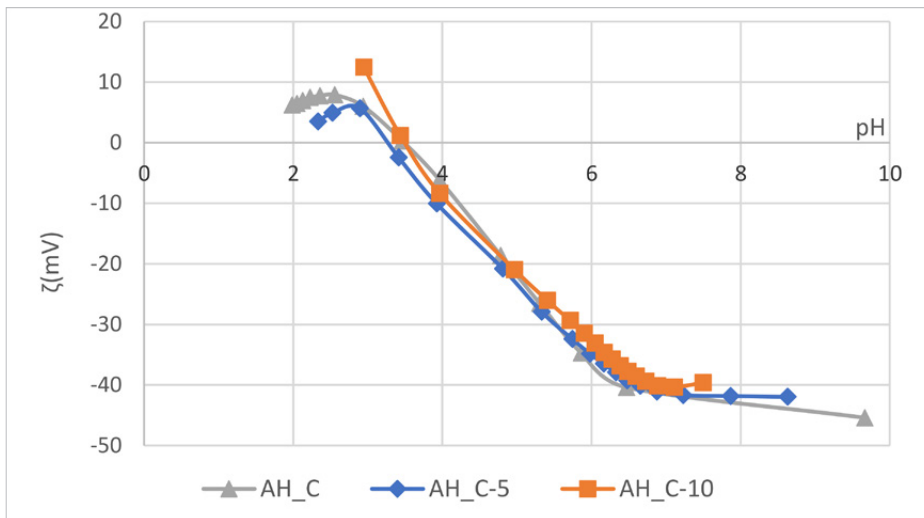


Figure 6: Zeta potential of alkali treated with promoter fabrics before and after washing cycles in variations of pH 1 mmol/L KCl

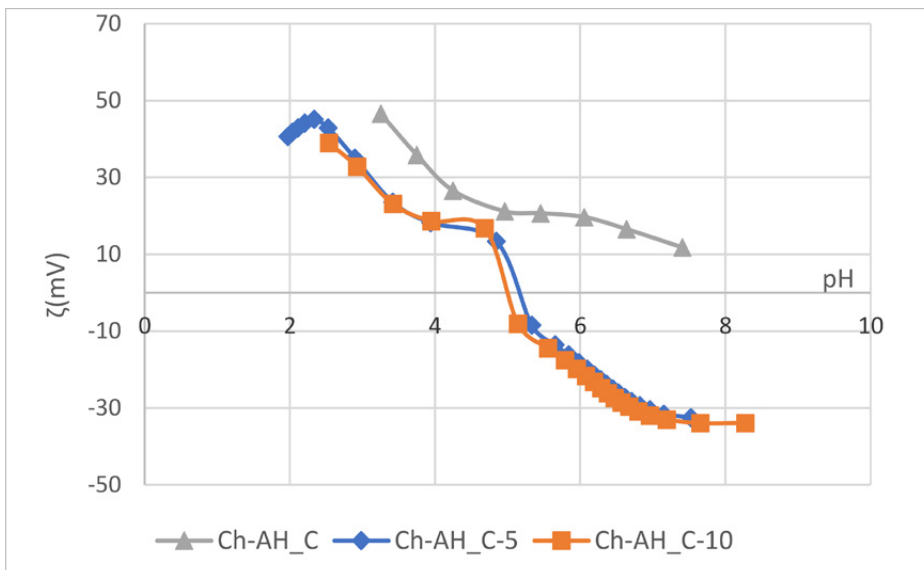


Figure 7: Zeta potential of chitosan-alkali hydrolysed with promoter PES fabrics, before and after washing cycles in variations of pH 1 mmol/L KCl

The zeta potential of the chitosan-polyester sample alkaline hydrolysed with the promoter is positive throughout the pH range, confirming a complete coating that is stable over the entire studied range, Figure 7. Washing this fabric changes the surface, the zeta potential values are negative, and their size shows that some chitosan remains on the surface. The differences between 5 and 10 cycles of the washed samples (Ch-AH\_C-5 and Ch-AH\_C-10) are insignificant.

The tensile properties of textile materials are an important structural characteristic, and it is important to monitor them and evaluate the appropriateness of the modification and functionalisation process based on the values obtained. In this research, the tensile properties of all control samples of a standard polyester fabric and the same after 10 washing cycles, were analysed by measuring the breaking force and the breaking elongation, Figure 8 and Table 4.

Figure 8 shows data of the breaking force of the analysed samples before and after 10 washing cycles.

The breaking forces ( $F_p$ ) of the washed samples after 10 cycles compared to certain control groups of samples before washing show a decrease and an increase in tensile properties, depending on the degree of modification and functionalisation of each fabric sample.

According to these data, the influence of 10 washing cycles is shown by a decrease in tensile properties of fabric samples (AH, Ch-U, Ch-AH), while the tensile properties of fabric samples (U, AH\_C, Ch-AH\_C) improved. The indexes of increase and decrease indicate the structural characteristics of the studied structures. The approximate value of increase (about

25%) is characteristic for alkaline hydrolysed PES fabrics with the addition of a cationic surfactant before (AH\_C) and after chitosan coating (Ch-AH\_C). This increase can be attributed to the compactness of the polyester fabric, weakened by alkaline hydrolysis due to the chitosan coating and washing process. This increase in the breaking force of the sample during washing (Ch-AH\_C-10) can be attributed partially to the more uniform surface coverage of the chitosan-coated fabric, as confirmed by the uniform colouring of this sample, Table 2 and Table 3.

The elasticity of the analysed samples was compared by breaking elongation and statistical indicators, Table 4.

Table 4: Elongation ( $\epsilon$ ) and statistical indicators of the tested fabrics

Fabric	$\epsilon$ (%)	$\sigma$ (%)	CV (%)
U	18.66	0.457	2.451
U-10	21.35	1.4569	6.82
AH	18.24	0.567	3.110
AH-10	20.35	0.4822	2.37
AH_C	11.37	0.707	6.216
AH_C-10	13.30	1.8755	14.10
Ch-U	19.32	0.652	3.38
Ch-U-10	20.75	0.6245	3.010
Ch-AH	19.53	2.149	11.002
Ch-AH-10	19.35	0.7500	3.88
Ch-AH_C	11.88	1.389	11.689
Ch-AH_C-10	13.34	1.2388	9.28

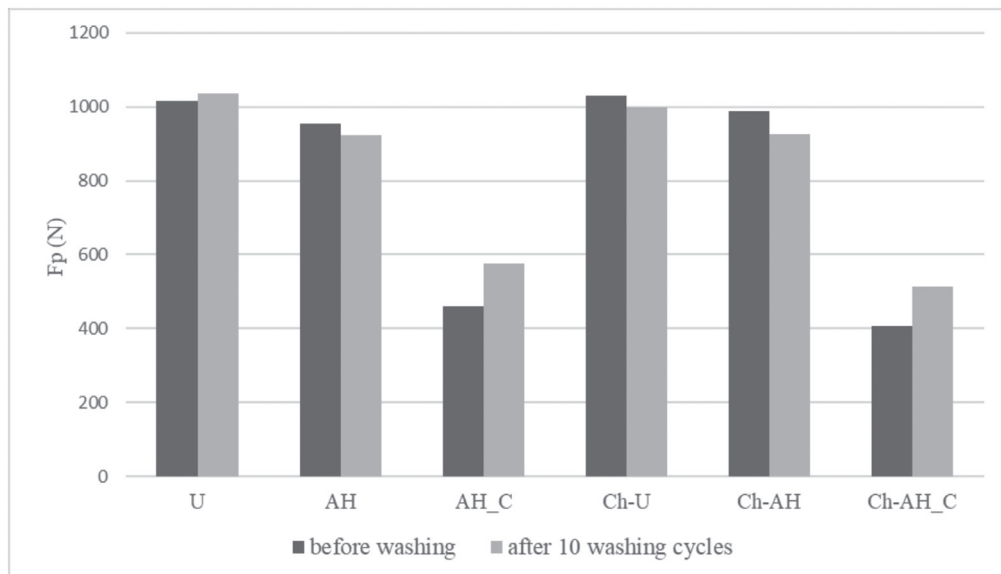


Figure 8: Breaking force of the tested fabrics before and after washing

The results in Table 4 show a significant decrease in the elastic properties of polyester fabrics when modified by alkaline hydrolysis with the addition of a cationic surfactant. The decrease in the tensile and elastic properties of AH\_C are the result of modification of the polyester fabric by alkaline hydrolysis with a promoter, leading to a polyester fabric of different structural features. Coating polyester fabrics with chitosan increases the elasticity of all samples by about 1 unit.

The tendency of the textile surface to pilling is a property that must be monitored for synthetic textiles that exhibit this tendency. Accordingly, the surface of PES fabric samples was evaluated before and after 10 washing cycles with a different number of rubs (125 - 7000 cycles), Table 5.

Table 5: Pilling grades

Fabric	Cyclic rubs					
	125	500	1000	2000	5000	7000
U	5	5	5	5	4-5	3-4
U-10	5	4	3-4	3	3	3
AH	5	5	5	5	4	3
AH-10	5	4	3-4	3-4	3-4	3
AH_C	5	5	5	5	4	3-4
AH_C-10	5	5	5	4-5	4	3-4
Ch-U	5	5	5	5	4-5	3-4
Ch-U-10	5	5	4-5	4-5	4	3-4
Ch-AH	5	5	5	5	4-5	3-4
Ch-AH-10	5	4-5	4-5	4-5	3-4	3-4
Ch-AH_C	5	5	5	5	4	4
Ch-AH_C-10	5	5	5	5	4-5	4-5

Grade 1 - very heavy pilling; grade 5 - no pilling

From the evaluations of the appearance of the surface after cyclic abrasion of PES fabric samples before and after 10 washing cycles, it is clear that the washing process affects the tendency of samples to form pilling, which is evident at 125 cycles, 500 cycles, 1000 cycles, 2000 cycles, and 5000 cycles. However, at 7000 cycles, almost no significant differences were observed between the unwashed and washed fabrics.

Since the standard polyester fabric is white, the effect of modification and functionalisation on whiteness was investigated in the research, Table 6. From the values listed in the Table, the whiteness ( $W_{GG}$ ) of the original control fabric (U) increased

Table 6: Whiteness degree ( $W_{GG}$ ), tint deviation (TD) and tint value (TV) of PES and Chitosan-PES fabrics before and after 10 washing cycles

Sample	$W_{GG}$	TD	TV
U	58.36	G2	1.96
U-10	71.78	G2	1.83
AH	58.98	G2	1.83
AH-10	78.76	G2	1.98
AH_C	58.35	G2	1.63
AH_C-10	75.52	G1	1.46
Ch-U	55.98	G1	1.33
Ch-U-10	61.47	G2	1.90
Ch-AH	52.25	G2	1.75
Ch-AH-10	58.48	G2	1.75
Ch-AH_C	52.92	G2	1.57
Ch-AH_C-10	58.93	G2	1.66

through 10 washing cycles. The standard detergent does not contain optical brightener, so the whiteness increases in proportion to the effect of the other detergent ingredients. Alkali modifications and chitosan treatment reduced the whiteness of all samples by several units. The slightly yellowish hue of the chitosan solution and the thermal processes of drying and cure affected the slight yellowing of all chitosan-treated fabrics. On washing, the whiteness of chitosan treated fabrics increased somewhat, but did not reach the values of modification after 10 wash cycles. The whiteness decrease is not valorised by tint deviation (TD) and tint value (TV).

The surface of the polyester fabric samples before and after modification and functionalisation with chitosan was analysed structurally by Scanning Electron Microscopy at a magnification of 1,500x, Figures 9–10.

The micrographs show clearly the roughness upon the influence of sodium hydroxide as an alkali in both variants (AH, AH\_C) on the surface appearance of the polyester fabric. The formation of micro sized craters is caused by the action of hydroxyl ion to the ester bonds of polyester, that is in line with previous findings [34]. The addition of the promoter, together with sodium hydroxide during alkaline hydrolysis, caused a change in the surface, which detached partially and no longer showed irregularities. After 10 washing cycles with standard detergent, the surface of all samples was loaded with solids, due to zeolite and other silicate formations.

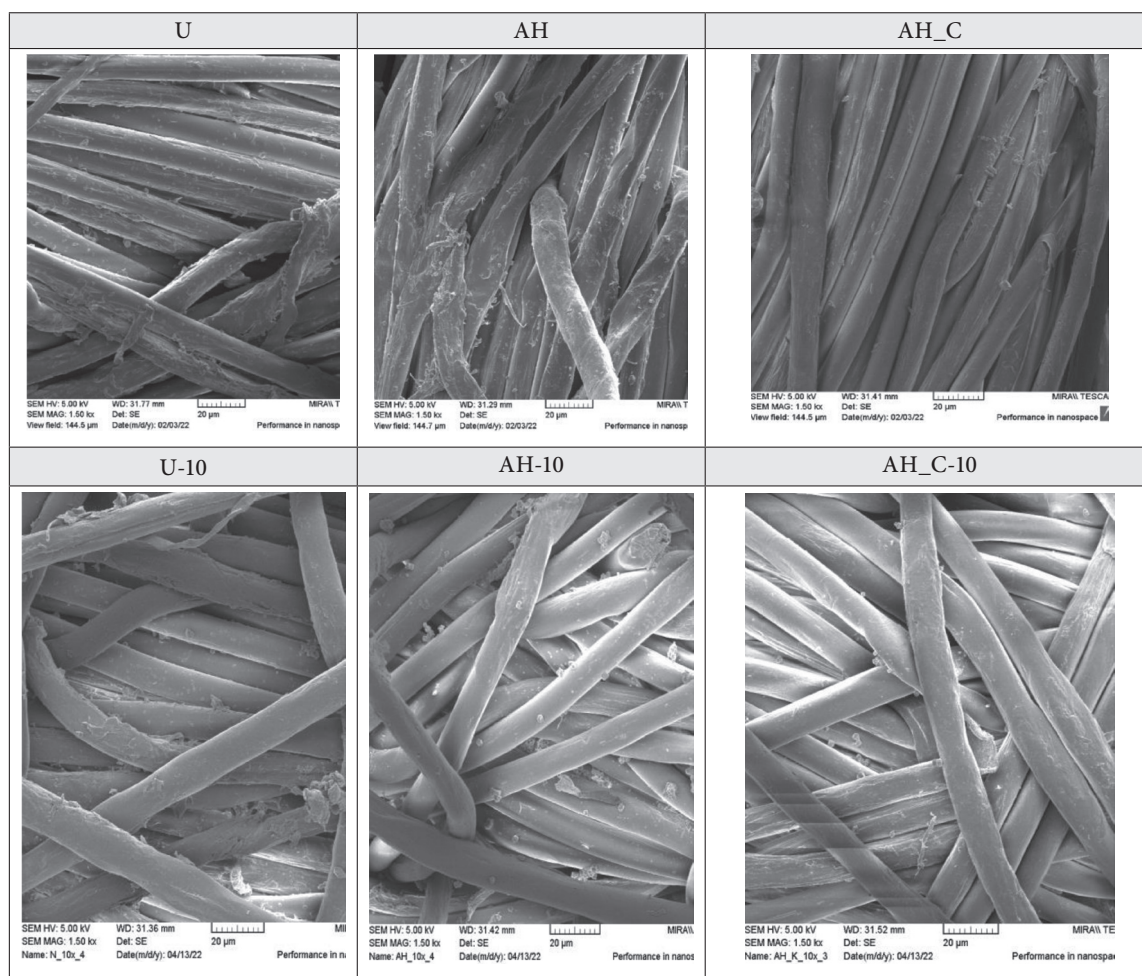


Figure 9: Micrographs of control (U) and modified polyester fabrics (AH, AH\_C) before and after washing (U-10, AH-10, AH\_C-10) magnified 1,500- $\times$

The microscopic images of the chitosan-polyester fabric show changes in the morphological properties of the polyester structure due to the coating of the individual fibres by the chitosan [29], although no significant differences are visible between the individual samples, Figure 10. However, after 10 washing cycles, differences became visible between the individual samples. The surface of the sample (Ch-U-10) was loaded with agglomerates, which is due to the complete loss of the chitosan, as confirmed by the digital images of the stained samples. The distribution and proportion of similar agglomerates on the surface of the samples (Ch-AH-10 and Ch-AH\_C-10) was significantly lower than for the Ch-U sample. The reason for this is the remaining protective layer of chitosan on the surface, which prevents the deposition of substances from the washing baths on the surface of the fabrics.

MMT wetting time is considered as a time when top surface and bottom surface of textile sample begins to wet accordingly [35]. The wetting time (top surface and bottom surface) of untreated and modified polyester fabrics was analysed by HCA analysis, Figure 11.

The values of MMT wetting time of polyester fabrics are slightly lower on the bottom side than on the top surface. Results of determining the MMT wetting time of polyester fabrics top surface before and after modification is in the range of 3.5 s to 2.2 s respectively. Modification of the fabric by alkaline hydrolysis and alkaline hydrolysis with promotor increases the hydrophilicity, which is reflected in a decrease of the wetting time. Washing process of polyester fabrics with alkaline detergent medium affects the mild hydrolysis of the surface and the further reduction of the wetting time between 1.2 and 2.0 s.



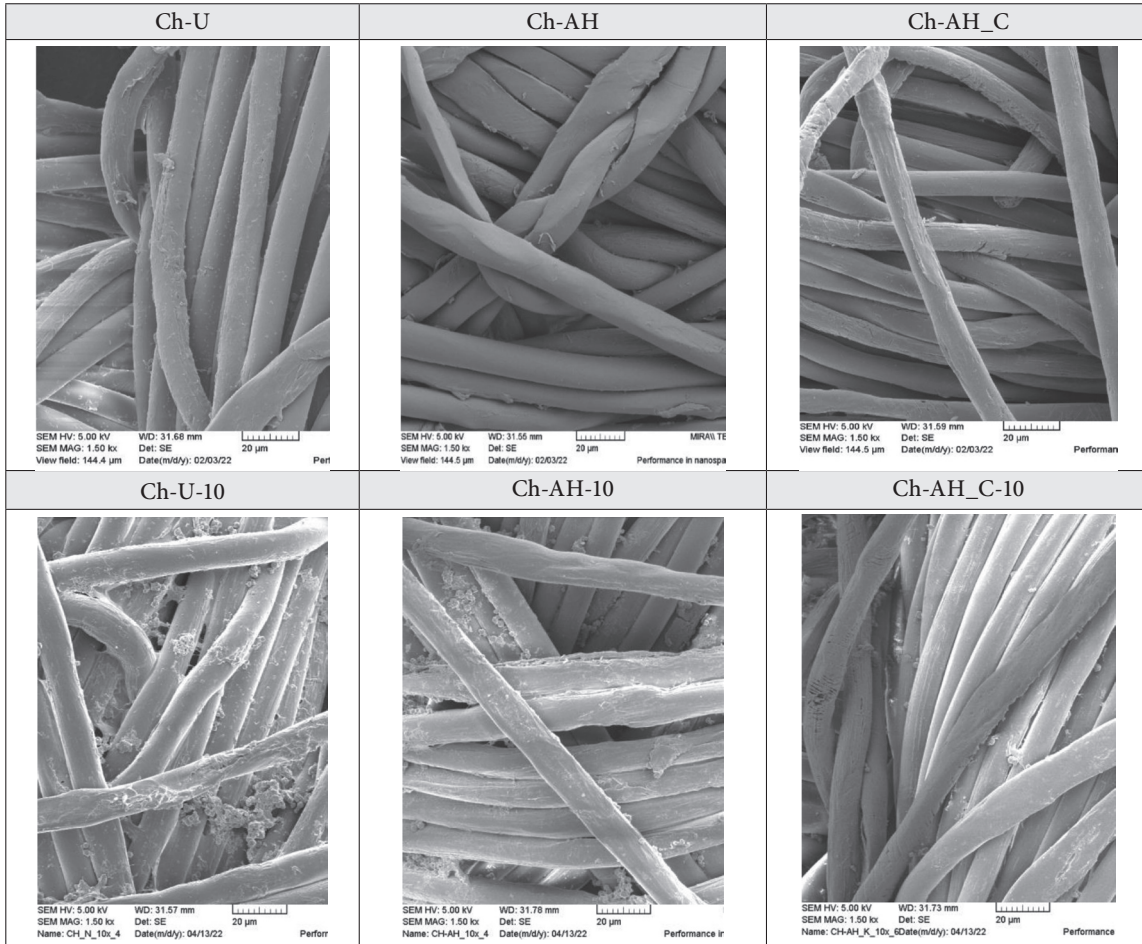


Figure 10: Micrographs of polyester fabrics coated with chitosan (Ch) before and after washing (Ch-U-10, Ch-AH-10, Ch-AH\_C-10) magnified 1,500- $\times$

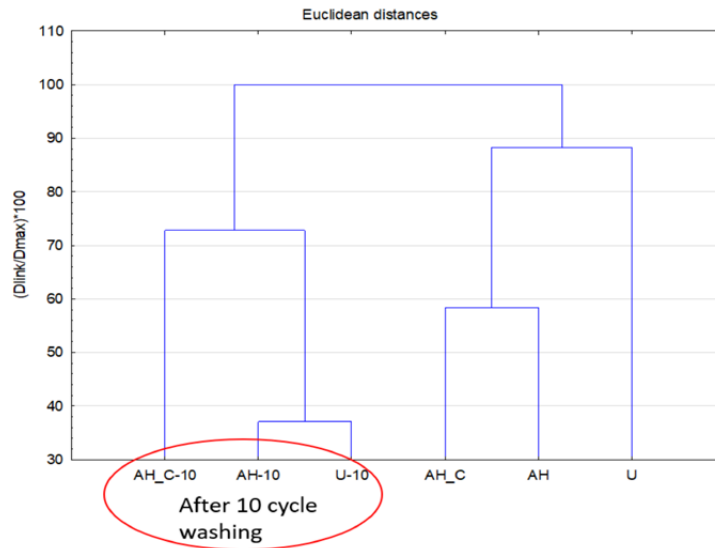


Figure 11: Dendrogram of the Euclidean distance for 6 variables (control standard fabric before and after 10 washing cycles, alkali hydrolysed and alkali hydrolysed with a promotor before and after 10 cycles) according to the MMT wetting time data (top surface and bottom surface)

Hydrophobic surfaces require a longer time for wetting than hydrophilic ones. MMT wetting time proves that modified surfaces before and after washing are hydrophilic, considering that it is less than 3 s. In Figure 11 is visible a distribution by groups obtained by applying HCA analysis, where one group includes samples that have been washed 10 times, while modified samples before washing form another group. The level of grouping in the samples washed 10 times shows the similarity of U-10 and AH -10 and the difference with AH\_C-10, but still belonging to the same group. On the other hand, in the group of samples before washing, the similarity of the treated samples AH\_C and AH is visible, while a significant difference is visible with respect to the untreated sample, but also belonging to the same group.

The moisture transport of the chitosan-polyester structures (top surface and bottom surface) before and after 10 washing cycles was also analysed by HCA analysis, Figure 12.

Treating the polyester samples with chitosan shortens the wetting time, and the differences between the top and bottom surfaces are smaller. The untreated chitosan sample has a shorter wetting time compared to the samples of chitosan alkaline hydrolysed polyester, while the sample alkaline hydrolysed with a promotor has a longer wetting time than the alkaline hydrolysed one. Washing these chitosan-treated samples results in minor differences in wetting time within this group of samples. Figure 12 shows a

distribution by group for the washed and unwashed samples of chitosan-polyester fabrics. Group formation of the 10 cycles washed chitosan polyester samples is visible. The level of grouping shows small differences in the samples of washed chitosan polyester structure treated with AH and AH\_C belonging to the same group. The next level belongs to an untreated chitosan structure, but with great similarity of samples, so they can be grouped together, and this is marked on the graphical representation. The unwashed samples are placed on the following levels, where the difference is between untreated and samples treated with AH and AH\_C, while untreated Ch-U is placed on the highest level, which is an indicator of a big difference compared to the other samples.

The surface of the standard polyester fabric was modified by alkaline hydrolysis and the process of coating with the biopolymer chitosan, which is expected to change the tactile properties. Accordingly, the characterisation of the fabric samples was performed before and after 10 washing cycles with the device FTT, Fabric Touch Tester, Table 7.

From the results in Table 7 it can be seen that the standard control fabric (U) had the highest smoothness, which may be related to the preparations, especially the silicone product [11]. It can be seen that the smoothness is disturbed by the surface treatments with alkaline hydrolysis, and additionally by the treatment of all samples with chitosan.

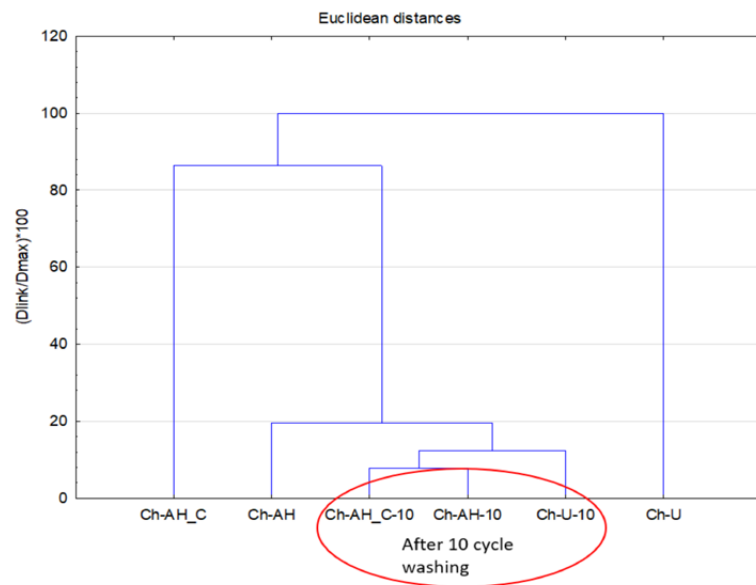


Figure 12: Dendrogram of the Euclidean distance for 6 variables (chitosan - polyester structures before and after 10 washing cycles) according to the MMT wetting time (top surface and bottom surface)

Table 7: FTT evaluation parameters of the tested fabrics

Fabric	Smoothness	Softness	Warmness	Total touch
U	4.0	2.0	2.0	3.0
U-10	3.0	3.0	3.0	3.0
AH	3.0	3.0	4.0	3.0
AH-10	3.0	3.0	4.0	3.0
AH_C	3.0	4.0	4.0	3.0
AH_C-10	3.0	4.0	3.0	3.0
Ch-U	2.0	1.0	3.0	1.0
Ch-U-10	3.0	3.0	4.0	3.0
Ch-AH	1.0	1.0	4.0	1.0
Ch-AH-10	3.0	2.0	4.0	3.0
Ch-AH_C	2.0	1.0	4.0	1.0
Ch-AH_C-10	3.0	3.0	4.0	3.0

The softness of the fabric changes with the degree of treatment, and it is obvious that the alkaline hydrolysed samples with the addition of a cationic surfactant have better softness compared to the other samples. The samples treated with chitosan have worse tactile properties (total touch) compared to the control samples, and the values obtained are the same (value 1) in Table 7.

The total touch of the modified fabrics before and after 10 washing cycles was the same (total touch = 3), which was not expected given the fact that the samples were not soiled. It is known that detergent components can settle on the surface of textiles if they are not used to remove stains [36], which is not the case in this study. This may be explained in part by the fact that the washing process was performed in hard water, and that certain components of the detergent, particularly zeolite, were focused on the process of water softening rather than on loading the fabric surface.

Chitosan applied to the surface of the polyester fabric stiffened it partially and reduced the total touch (grade 1). In the chitosan-polyester samples, an increase in total touch (grade 3) was observed after 10 wash cycles compared to the total touch of chitosan-polyester (grade 1). This increase can be attributed to the loss of chitosan through 10 wash cycles due to its instability. The released chitosan has a tendency to combine with the zeolite from the detergent, and the improvement in touch can be attributed to the prevention of scaling (chitosan/zeolite). This synergistic effect of chitosan and zeolite from different sources is consistent with the

literature [37]. The added value of the chitosan/zeolite composite is evident in the reduction of the chemical oxygen demand (COD) value from the water, since the absorption capacity of the composite is greater compared to the individual structural elements, zeolite and chitosan [38].

As chitosan is recognised and used as an antifungal and antibacterial agent [39–45], the antimicrobial activity (AMA) of chitosan- polyester fabric samples before and after 10 washing cycles against selected gram-positive (*Staphylococcus aureus* ATCC 29213, SA) and gram-negative (*Kebsiella pneumoniae* ATCC, KP) bacteria was analysed, and the effect was expressed through CFU and % in reduction, Tables 8–9. As the experiments were performed in triplicate, the statistical parameters were integrated in both Tables. All chitosan-polyester fabrics before and after 10 washing cycles possess antimicrobial activity against gram-positive bacteria *Staphylococcus aureus* ATCC 29213 (SA). The antimicrobial efficiency of chitosan-polyester fabrics after 10 washing cycles (Ch-U-10, Ch-AH-10, Ch-AH\_C-10) in comparison to samples before washing (Ch-U, Ch-AH, Ch-AH\_C) was preserved partly. The reduction in AMA depends on the pretreatment phase, so the chitosan-polyester fabric showed 17.5%, chitosan-alkali hydrolysed polyester 25.7% and chitosan-alkali hydrolysed polyester with promoter 15.7%.

The obtained results indicate leaching of the chitosan during 10 washing cycles and a certain instability. The best effect was achieved by the alkaline hydrolysed sample with the addition of the promoter, benzalkonium chloride – a known quarternary

Table 8: Antimicrobial activity (AMA) of chitosan in polyester fabric before and after 10 washing cycles against *Staphylococcus aureus* ATCC 29213

Sample	Staphylococcus aureus ATCC 29213			
	Reduction (%)	CFU	$\sigma$	CV (%)
Ch-U	80.00	$6.00 \times 10^3$	$5.66 \times 10^3$	94.3
Ch-U-10	66.60	$6.66 \times 10^4$	$4.71 \times 10^4$	70.7
Ch-AH	90.00	$1.10 \times 10^4$	$1.27 \times 10^4$	116.0
Ch-AH-10	66.80	$6.63 \times 10^4$	$4.70 \times 10^4$	71.0
Ch-AH_C	100.00	0.00	0.00	0.00
Ch-AH_C-10	84.34	$1.85 \times 10^5$	$1.91 \times 10^5$	103.0

Table 9: Antimicrobial activity (AMA) of chitosan in polyester fabrics before and after 10 washing cycles against *Klebsiella pneumoniae* ATCC 4352

Sample	Klebsiella pneumoniae ATCC 4352			
	Reduction (%)	CFU	$\sigma$	CV (%)
Ch-U	No	$3.30 \times 10^6$	$2.40 \times 10^6$	72.9
Ch-U-10	No	$9.99 \times 10^6$	$7.06 \times 10^6$	70.7
Ch-AH	55.5	$65.0 \times 10^6$	$35.4 \times 10^6$	54.4
Ch-AH-10	98.0	$5.10 \times 10^6$	$6.93 \times 10^6$	136.0
Ch-AH_C	No	55	63.6	116.0
Ch-AH_C-10	96.6	$3.10 \times 10^5$	$4.10 \times 10^5$	132.0

ammonium compound with antimicrobial properties against bacteria, fungi, and viruses [45].

The results of the antimicrobial activity of chitosan-polyester fabrics (Ch-U, Ch-AH\_C) against gram-negative *Klebsiella pneumoniae* ATCC 4352 (KP) were absent, while the fabric (Ch-AH\_C-10) showed a high reduction level. The absence of antimicrobial activity of the samples treated with chitosan before washing was not to be expected. The results of AMA against gram-negative *Klebsiella pneumoniae* ATCC 4352 were not consistent and require further experiments and tests with other methods.

## 4 Conclusion

The stability of the differently designed textile structures with chitosan in the multiple washing process with a standard detergent was analysed based on the modification protocol and the number of washing cycles. Modification of the standard polyester fabric was performed with sodium hydroxide and sodium hydroxide and a cationic surfactant. The absence of chitosan on the standard polyester fabric-chitosan after 10 washing cycles proved the

weak stability of the biopolymeric chitosan-PES textile structure during washing and the need to implement a chitosan on modified polyester fabric. The Remazol Red staining test is a suitable qualitative method for the identification of chitosan. The staining and uniformity of the red colouration of the chitosan - treated alkaline hydrolysed PES fabric after 5 and 10 washing cycles confirmed the presence of chitosan on the surface, i.e. the washing stability of these structures during washing. The zeta potential has been useful to monitor the stability of chitosan as a function of pH and other environmental impacts. Other methods, Scanning Electron Microscopy, pilling propensity, touch, whiteness, breaking force and breaking elongation and MMT wetting time, are also suitable for monitoring the washing stability in a designed chitosan-polyester structure. Hierarchical cluster analysis confirmed the differences in the MMT wetting time of the chitosan-polyester structure with chitosan designed by different methods and washing. All the chitosan-polyester fabrics, before and after 10 washing cycles, possessed antimicrobial activity against the gram-positive bacteria *Staphylococcus aureus*. The obtained results indicate the leaching of chitosan during multiple washing cycles.

### Funding – Acknowledgment

This work was supported in part by the Croatian Science Foundation under project no. HRZZ-IP-2020-02-7575.

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