sustainability

Article

Sustainability-Oriented Surface Modification of Polyester Knitted Fabrics with Chitosan

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Abstract: The existing research deals with the process of modifying polyester knitted fabrics and polyester/cotton knitted fabrics with chitosan and the stability of functionalized surface with chitosan in the washing process according to a standard and an innovative washing procedure. The current research concept aims to evaluate the degree of progressivity and progressiveness: the modification of polyester knitted fabrics with chitosan and an innovative washing process. The polyester and polyester/cotton fabrics modified with chitosan were characterized by a staining test, microscopic analysis, zeta potential measurement, and pilling tendency of the knitted fabrics before and after five and ten washing cycles with reference detergent ECE A. The results of the zeta potential measurement of knitted fabrics functionalized with chitosan confirmed cationization of the polyester and polyester/cotton fabric with chitosan. The presence of chitosan on the washed knitted fabrics in reduced quantities is demonstrated by the staining test, the colour strength (K/S), and the zeta potential values. The staining test and surface charge of the tested knitted fabrics confirmed the research hypothesis regarding the degree of progressivity of the modification of polyester and polyester/cotton knitted fabrics with chitosan and the sustainability of the innovative washing process. The streaming potential proved to be a favorable method for monitoring the stability of chitosan in the washing process in combination with a staining test with the selected dye Remazol Red RB.

Keywords: knitted fabrics; polyester; polyester/cotton; chitosan; washing; surface

Citation: Pušić, T.; Bušac, T.; Šimić, K.; Čurlin, M.; Šaravanja, A.; Grgić, K.; Volmajer Valh, J. Sustainability-Oriented Surface Modification of Polyester Knitted Fabrics with Chitosan. *Sustainability* **2024**, *16*, 1121. https://doi.org/10.3390/su16031121

Academic Editor: Hailong Yu

Received: 7 December 2023
Revised: 5 January 2024
Accepted: 22 January 2024
Published: 29 January 2024

1. Introduction

Chitosan is an essential biopolymer in fundamental science, applied research, and industrial biotechnology because of its superior macromolecular structure, physical and chemical characteristics, bioactivity, and adaptability compared to synthetic polymers [1,2]. It is a powerful cationic adsorbent for removing dyes, specific organic contaminants, pharmaceutical residues, and heavy metal ions [3–5]. Chitosan's hydroxyl and amino groups serve as points of coordination for heavy metal ion bonding, and their bonding capacity can be increased by grafting with inorganic adsorbents [6,7].

The biopolymer chitosan may be used to enhance the qualities of textile fabrics in a variety of ways. The tensile strength and resistance to deformation, wetting, hydrophilicity, antimicrobial resistance, decreased charging owing to static electricity, reduced felting, and dyeing capabilities of the substrate for ionic dyes can all be enhanced depending on the raw material composition [8–12]. Chitosan has recently been examined as a functional biopolymer in the context of minimizing the release of microplastics (MP) from polyester fabrics during the washing process [13–16], with the main concern being the durability of chitosan coatings to the washing process conditions [6].

The instability of chitosan-treated materials and their degradation [17,18] in a variety of applications, e.g., biocompatible/haemocompatible materials, antimicrobial surfaces, textiles, tissue engineering, drug delivery, etc. [19–21], it is necessary to address the need for a more effective and efficient use and stability of chitosan.

Since most synthetic polymers are inert, their compatibility with chitosan as a bioactive compound needs to be improved by surface modification of the polymers. The next step is to optimize the surface functionalization techniques to incorporate the desired type and amount of the reactive functional group [19,21–23]. Considering the importance of polyester as a synthetic polymer in this research, before treatment with chitosan, polyester materials can be modified by UV irradiation [23], plasma pretreatment [24,25], enzymatic treatments [26], or alkaline hydrolysis prior to treatment with chitosan to activate the surface and increase the hydrophilicity of the polymer structure [27–30].

Alkaline hydrolysis of polyester fibers in the alkali is a traditional high-efficiency pretreatment process that takes place on the surface [10,26–28]. Some studies have shown that alkaline hydrolysis can improve the coating of functional polymers to form fine roughness of polyester [12,30].

It is essential to optimize the coating's capacity to attach to polyester fabrics to boost its durability. Improving the stability of chitosan coated on the surface of textile fabrics and reducing polymer chain degradation may be accomplished in numerous ways: (i) surface treatment of textile materials for better interaction with chitosan; (ii) chitosan type and concentration selection; (iii) use of crosslinkers for better interaction of chitosan with textile materials [22]; (iv) use of thermal treatments for fixation of chitosan; and (v) optimizing washing process conditions [6].

The concentration of chitosan influences the release of fiber fragments; for example, untreated polyester fabric released 3047 fiber fragments per gram of fabric; however, the number reduces with concentration change. Fabric treated with 3% chitosan produced 27% fewer fragments than untreated fabric [31]. Modified polyester fabric with 1, 2, and 3% chitosan released 1726, 2497, and 2237 fibre fragments per gram of modified fabric, respectively.

The goal of this research is to implement the idea of sustainability to reduce the release of fibril fragments from polyester knitted fabrics during the washing process by a surface modification of polyester knitted fabrics with 0.5% chitosan in three separate processes. The first involves pretreatment of polyester knitted fabrics with alkaline hydrolysis, the second involves chitosan adhesion to polyester knitted fabrics without crosslinker, and the third involves a washing process according to standard and innovative procedures, both with reference ECE A detergent at 60 °C.

By characterizing the staining and surface of the investigated knitted fabrics, the research concept aims to evaluate the degree of progressiveness of the modification of polyester and polyester/cotton knitted fabrics with chitosan and sustainability of chitosan-modified knitted fabrics in the innovative washing process.

2. Materials and Methods

2.1. Materials

Two textile materials were selected for the research: double-faced interlock standard polyester weft knit, MRF-0008, Wfk, Krefeld, Germany, with a mass per unit area of 139.0 g/m^2, horizontal density (Dh = 16 stitches/cm), and vertical density (Dv = 21 stitches/cm) and polyester/cotton (50/50) jersey fabric, MRF-0012, with a mass per unit area of 139.5 g/m^2, Dh = 14 stiches/cm, and Dv = 18 stiches/cm.

Both knitted fabrics were treated with chitosan (Aldrich® (St. Louis, MO, USA) provided low molecular weight (LMW) chitosan with an 85% deacetylation).

The polyester knitted fabric was processed in an alkali hydrolysis procedure using a sodium hydroxide solution, 2% NaOH (aq.), acquired from the Ivero d.o.o. (Zagreb, Croatia) before being modified with chitosan. Starting at 20 °C, the procedure was carried out in a W. Mathis laboratory apparatus at a bath ratio (BR) of 1:5, with the bath being heated to a temperature of 98 °C for 15 min before the material was processed for another 30 min. After completion of the process, the polyester knitted fabric samples were washed twice with hot water at 98 °C and twice with cold water at 20 °C and air-dried. Polyester/cotton knitted fabrics were not subjected to alkali hydrolysis due to the cotton content in the blend.

Chitosan solution (0.5%) was prepared with hydrochloric acid (0.1 mol/L) and stirred overnight. At low pH, the free amino groups are protonated causing electrostatic repulsion between the polymer's chains, thus, enabling polymer solvation [18]. The final pH was then measured and adjusted to pH 3.6 with the same acid. Polyester and polyester/cotton knitted fabrics were modified with chitosan by impregnating the samples in the produced solution at 12.5 kg/cm pressure in a Benz stenter (Zürich, Switzerland). Thermal fixing of chitosan-coated polyester knitted fabrics was accomplished by drying at 90 °C for 40 s and curing at 130 °C for 20 s.

2.2. Washing Process

The washing of modified polyester and polyester/cotton knitted fabrics with chitosan was carried out in the SDL Atlas Rotawash device (Rock Hill, SC, USA) according to standard protocol EN ISO 6330 [32], and bath ratio of 1:7, following 2A procedure at 60 °C using the composition of a ECE A phosphate-free reference detergent in a concentration of 1.25 g/L. After washing, the samples were rinsed four times in water (BR of 1:8) according to two procedures. The first standard protocol was carried out in cold water (20 °C), while the innovative protocol with gradual cooling, the first cycle at 50 °C, the second at 40 °C, the third at 30 °C, and the fourth at 20 °C.

During drying under ambient settings, the samples of polyester and polyester/cotton knitted fabrics were protected from possible contamination from the laboratory environment. Table 1 lists samples of investigated polyester and polyester/cotton knitted fabrics.

Table 1. Description of polyester and polyester/cotton knitted fabrics.

Description of Samples	Polyester (P)	Polyester/Cotton (P/CO)
Untreated knitted fabric	P	P/CO
Alkali treated knitted fabric	A-P	-
Untreated knitted fabric modified with chitosan	CH-P	CH-P/CO
Knitted fabric alkali treated and modified with chitosan	CH-A-P	-
Untreated knitted fabric modified with chitosan and washed by standard procedure 5 times 10 times	 CH-P-St-5 CH-P-St-10	 CH-P/CO-St-5 CH-P/CO-St-10
Untreated knitted fabric modified with chitosan and washed by innovative procedure 5 times 10 times	 CH-P-Inn-5 CH-P-Inn-10	 CH-P/CO-Inn-5 CH-P/CO-Inn-10

2.3. Methods

By analyzing the dyeability and the surface of polyester and polyester/cotton knitted fabrics, the sustainability of the process of modifying polyester knitted fabrics with chitosan and the verification of the innovative process compared to the standard washing process were monitored.

2.3.1. Identification of Chitosan

The staining test was used for the preliminary identification of chitosan on the modified polyester and polyester/cotton knitted fabrics. After confirming that chitosan was present on the tested knitted fabrics, the same method was applied to the washed knitted fabrics, which were run through 5 and 10 cycles with both procedures.

Modified samples of polyester and polyester/cotton with chitosan before and after 5 and 10 washing cycles were subjected to the dyeing process with the Remazol Red RB (C.I. Reactive Red 198) at a concentration of 1% (o.w.f.) acquired from the manufacturer DyStar (Frankfurt, Germany), in a W. Mathis laboratory apparatus, with BR 1:50 at 60 °C during 30 min. After dyeing, the fabrics were washed with cold water and post-treated with 2 g/L Kemopon 50 (mixture of anionic and nonionic surfactants) from Kemo, Zagreb, Croatia, in the same apparatus, with BR 1:50, at 90 °C for 10 min to remove the dye not bound to the knitted fabric. After washing, the samples were air-dried under ambient conditions.

The surface of the dyed samples was observed microscopically using a DinoLite digital microscope, Premier IDCP B.V., Almere, The Netherlands, at 50× and 230× magnification. The quantitative evaluation of the dyed fabric samples before and after 5 and 10 washes was carried out using the DataColor 850 spectrophotometer, Basel, Switzerland. The colour strength (K/S value) according to the Kubelka–Munk equation with constant device aperture, standard illumination D65, and d/8° geometry was selected as the spectral value for the quantification of chitosan presence.

Since chitosan is coated on the surface of the investigated knitted fabrics, the zeta potential was chosen as a parameter to characterize the surface of the untreated, modified with chitosan and both knitted fabrics after 5 and 10 washing cycles.

2.3.2. Streaming Potential Method

The zeta potential of samples was determined by streaming potential method in the SurPASS electrokinetic analyser equipped with a titration unit and an adjustable gap cell (AGC) controlled with Attract software 2.0 (all from Anton Paar GmbH, Graz, Austria). After stabilization of the measurement parameters in the electrokinetic analyser, the streaming potential of knitted fabrics in electrolyte solution (1 mM/L KCl) was measured as a function of pH, starting from alkaline (adjusted with 1 mol/L NaOH) to acidic (adjusted with 1 mol/L HCl). During the titration procedure, the streaming potential in mV and other parameters were recorded from which the zeta potential was calculated as a function of pH according to the Helmholtz–Smoluchovsky equation [33,34].

The protective potential of chitosan coated on the surface of polyester and polyester/cotton knitted fabrics was determined through the resistance to the formation of pills and other surface distortions such as fuzzing.

2.3.3. Assessment of Pilling Generation

The surface resistance of the polyester and polyester/cotton knitted fabrics before and after 10 washing cycles to produce pilling and surface distortions was analysed after 125, 500, 1000, 2000, 5000, and 7000 rub cycles according to the modified Martindale method [35]. Pilling and other changes in appearance were evaluated on a grading scale from 1 to 5.

3. Results

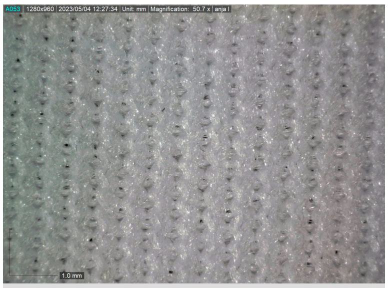
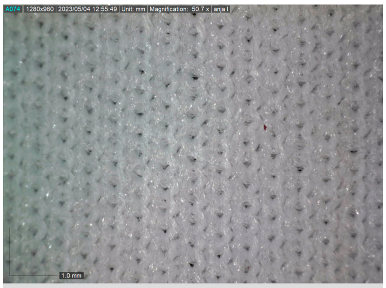
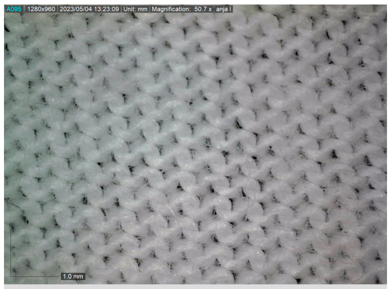
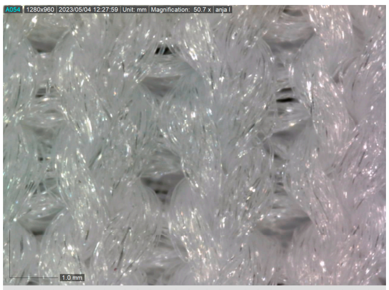
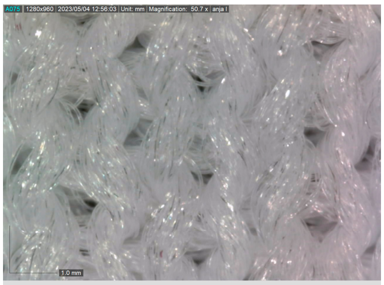
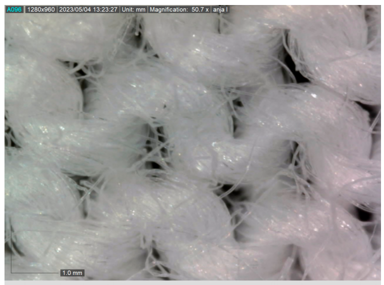
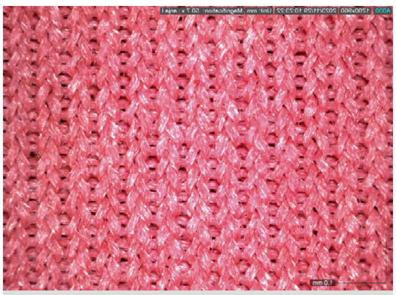
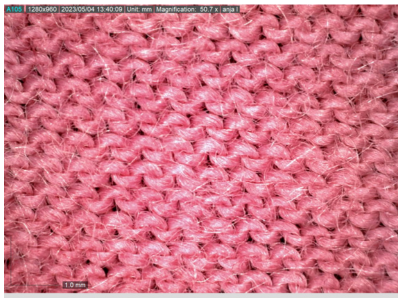
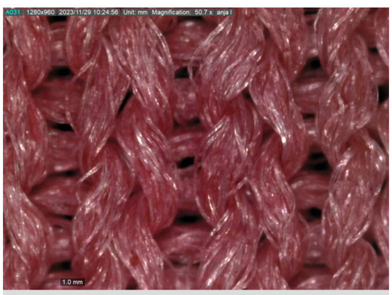
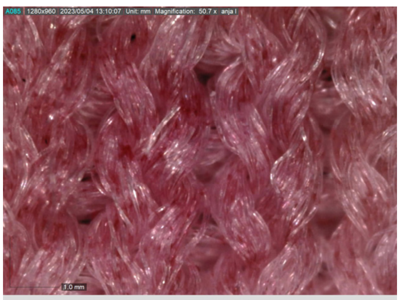
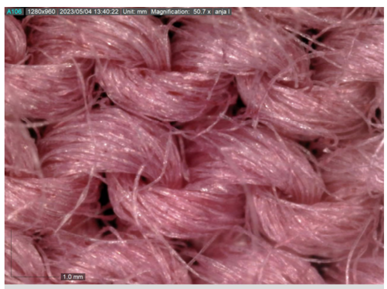
Various dyes are used to identify chitosan on polyester textiles functionalized with chitosan, the spectral values of which indicate the presence of chitosan on the surface, e.g., acid dye [22], disperse dye [36], curcumin natural dye [37], and reactive dye [38], whereby different interactions between the amino or hydroxyl groups of chitosan with the active groups of certain dyes occur.

The sensitivity of chitosan to environmental conditions and processing conditions 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, and moisture content) and external (environment–temperature and humidity and process–dissolution in acid, sterilisation, thermal treatments, and physical methods) [10].

Preliminary staining tests were carried out on untreated (P, A-P, and P/CO) and chitosan-treated knitted fabric samples: polyester (CH-P), alkali-treated polyester knitted fabric (CH-A-P), and polyester/cotton knitted fabric (CH-P/CO); these served as the basis for the presence of chitosan and continuing investigations of the stability of chitosan in the washing process using standard and innovative procedures.

The presence of chitosan on the samples was detected by red coloration and metrically objectified by colour strength (K/S). The results of the staining test are shown by a digital image of the surface of the samples examined at 50× and 230× magnification (Table 2).

Table 2. Digital micrographs of the chitosan-treated knitted fabrics dyed with Remazol Red RB at 50× and 230× magnification.

	Untreated Knitted Fabric Samples		
	P	**A-P**	**P/CO**
50×			
230×			
	Chitosan-Modified Knitted Fabric Samples		
	CH-P	**CH-A-P**	**CH-P/CO**
50×			
230×			
K/S	4.1132	4.3144	4.7068

Untreated polyester (P), alkali treated (A-P), and polyester/cotton (P/CO) knitted fabric samples are not red stained. This was expected because the dyestuff Remazol Red RB is selected for identification of the presence of chitosan on functionalized polyester textiles [29,38].

All chitosan-treated samples (CH-P, CH-A-P, and CH-P/CO) showed a red color. The intensity and uniformity of the coloration as well as the spectral value K/S provided information about the functionalization of knitted samples with chitosan as well as the effectiveness and homogeneity of the coating. The results demonstrated the correlation between the raw material compositions of the tested knitted fabrics and color strength (K/S). The polyester knitted fabric was red dyed, confirmed by K/S value (4.1132). The uniformity of red coloration indicated the homogeneity of the functionalization and modification with chitosan. The 230× magnification showed chitosan dotted in some areas of the dark-colored pattern of this knitted fabric. The color strength (4.3144) of alkaline hydrolyzed fabric (CH-A-P) was higher than chitosan-untreated sample with K/S of 4.1132. At 230× magnification, the digital image showed uneven coloration and varied distribution of the chitosan in the alkali hydrolised knitted fabric sample modified with chitosan. The polyester/cotton knitted fabric had the highest color strength (4.7068), which was due to the proportion of cotton component in the blend. Both magnifications confirmed the high degree of coating effectiveness of this sample (CH-P/CO) and its uniformity on the surface. The presence of chitosan on the polyester fabric detected with Remazol Red dye was consistent with previous results where the cationic nature of the polyester fabric functionalized with chitosan was stained red due to the sulfonated groups that can bind the OH groups of chitosan [38]. In the case where the disperse dye Bemacron Blue SE RDL was used as a dye for the detection of chitosan on polyester fabric, it stained both the blank polyester sample and the chitosan-treated polyester sample. Both samples were coloured blue, with the blank sample having a light shade and the treated sample a dark shade [36].

The surface charge is a key parameter at the interface between a textile material and an aqueous solution generated by two mechanisms: acid-base reactions of surface functional groups and ions adsorption [39]. The streaming potential approach was used to identify chitosan on the surface of polyester and polyester/cotton knitted fabrics, as well as to characterize chitosan durability and stability in the washing process using standard and innovative procedures. The surface charge of untreated textiles depends on the construction properties and the degree of hydrophilicity; textiles with high hydrophilicity have a lower surface charge than hydrophobic textiles.

The results of zeta potential of the polyester (P) and polyester/cotton (P/CO) knitted fabrics depending on pH value of the electrolyte solution are shown in Figure 1.

Due to its hydrophobic properties and the esterified carboxyl groups, the sample of the untreated polyester fabric (P) had a negative zeta potential value at pH 8 (approx. −60 mV). The presence of the hydrophilic cotton component in a blend with polyester contributed to lower negative values of zeta potential across the pH range compared to polyester fabrics, which was consistent with results from other publications [12].

The value of the zeta potential depends on the structural parameters and the modification/functionalization process of knitted fabrics with chitosan. In accordance with this and the results of the staining test, it was to be expected that the coated chitosan would influence the surface charge of the modified knitted fabrics. The results of the zeta potential of the analysed chitosan-modified knitted fabric as a function of the pH value of the electrolyte solution are shown in Figure 2.

Chemical and physical interventions are performed on the surface to improve the interaction between polyester, a synthetic polymer, and chitosan, a natural biopolymer. Alkaline hydrolysis of polyester textiles is a conventional chemical surface intervention targeted at optimizing its interaction with chitosan. This topochemical reaction in sodium hydroxide solution is saponification, which occurs through the hydrolysis of ions attached to the carbonyl group in the polyester chain [27]. Figure 3 demonstrates that alkaline hydrolysis (A-P) pre-treatment influenced the surface change of the polyester knitted fabric in relation to the polyester knitted fabric (P). When compared to the polyester knitted fabric, the increase in hydrophilicity of the alkaline hydrolysed polyester knitted fabric influenced the decrease in zeta potential. This relationship is not consistent with previous results obtained with polyester fabrics. The differences can be explained by the structural elements and the surface condition caused by the preparations applied [40].

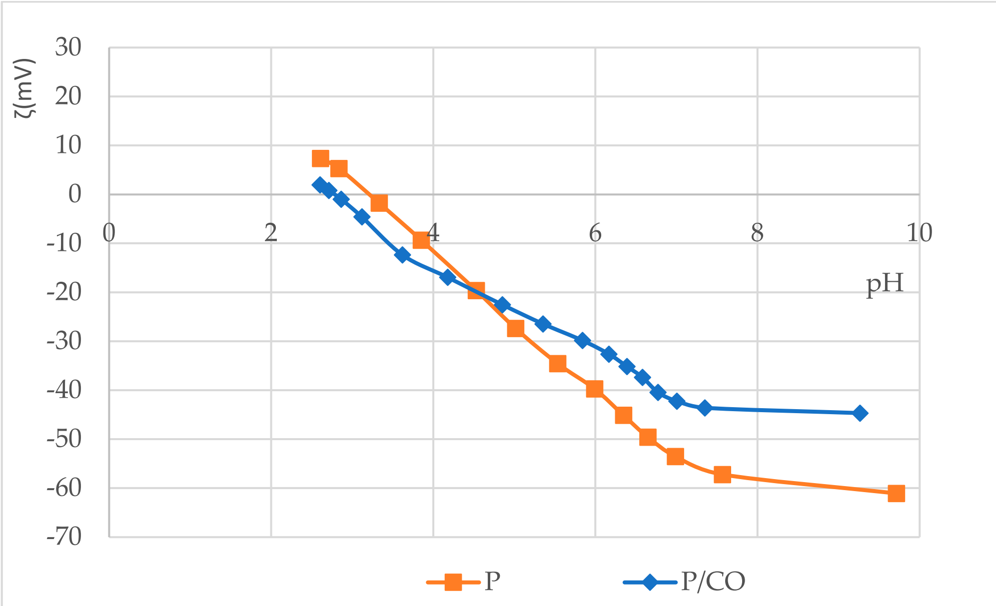


Figure 1. Zeta potential of polyester knitted fabric (P) and polyester/cotton knitted fabric (P/CO) in variation of pH of 1 mmol//L KCl.

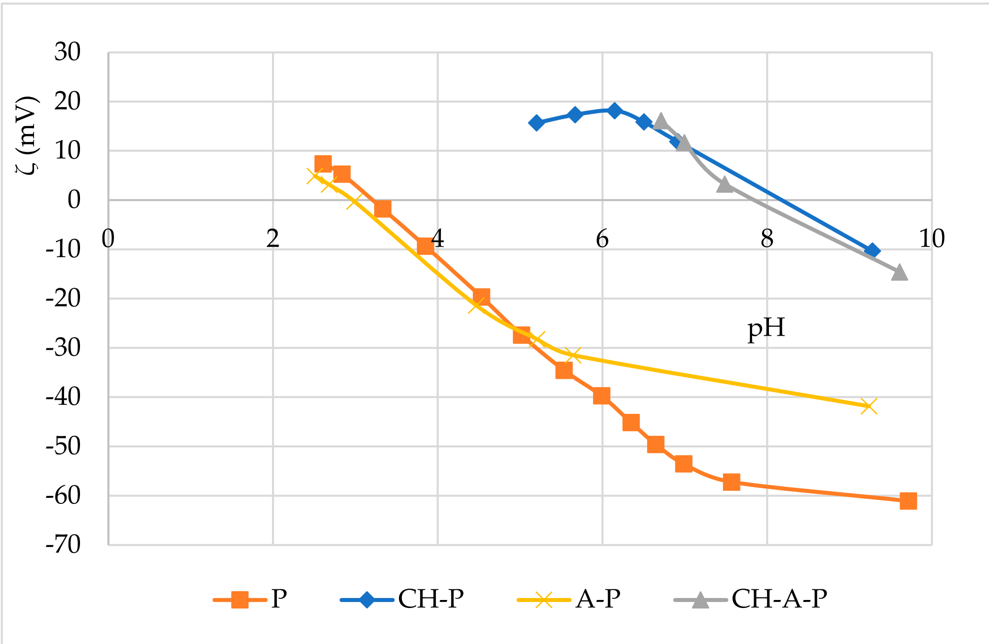


Figure 2. Zeta potential of polyester knitted fabric (P) and alkali hydrolysed polyester knitted fabric (A-P) before and after modification with chitosan (CH) in variation of pH 1 mmol/L KCl.

The effect of surface modification of polyester knitted fabric with chitosan (CH-P) and alkaline hydrolysed polyester knitted fabric with chitosan (CH-A-P) on zeta potential in the complete pH range was almost identical. The zeta potential values were positive in the pH range less than 8. The presence of chitosan was demonstrated by the positive zeta potential values of both polyester fabrics, which were the consequence of the material surface with basic behavior. Since the isoelectric point (IEP) is a strong indicator for the chemistry of functional groups on the surface of materials [39], the obtained IEPs (pH~8) prove the cationization of a surface of both chitosan-treated knitted fabrics (CH-P and CH-A-P). The obtained result did not agree entirely with the staining test results or the K/S values. The differences between two selected methods for identification of chitosan can be explained by the characteristics and principles of the analyses performed, how they were carried out, and the peculiarities of chitosan interaction with the surface of polyester substrates.

The almost similar amount of the zeta potential of chitosan-modified untreated and alkaline hydrolysed knitted fabric implied that alkaline hydrolysis was not required before the chitosan modification process. The absence of sodium hydroxide and the alkaline hydrolysis as a pre-treatment stage contributed to the sustainability of this chitosan modification process. This finding contradicted prior research, which demonstrated that alkaline hydrolysis was required for chitosan coating on the surface of polyester materials [12,40]. It proved the complexity of the textile structures requires the optimization of the processing according to the properties of the textile material, taking into account the sustainability, stability, and acceptable use cycle of the modified textiles.

The sustainability approach necessitates an examination of the stability and durability of modified and functionalized fabrics in wet and dry circumstances. The low stability of chitosan-based textile constructions can be an obstacle to their use. Following washing with a reference ECE detergent, knitted fabrics treated with chitosan showed a reduced colour strength, suggesting a partial release of chitosan, which acts as a surface protector and functional natural polymer.

As results showed that the chitosan was cationised on the surface of the polyester knitted fabric samples, the effect of the alkali and surfactants in the reference ECE detergent was tested in a washing process according standard and innovative procedures.

Tables 3 and 4 display digital micrographs of polyester fabrics treated with chitosan following 5 and 10 cycles of washing in accordance with the standard and innovative procedures, at magnifications of 50× and 230×.

Table 3. Digital micrographs of the chitosan-treated polyester knitted fabrics dyed with Remazol Red RB under magnification of 50× and 230× before and after 5 and 10 washing cycles according standard procedure.

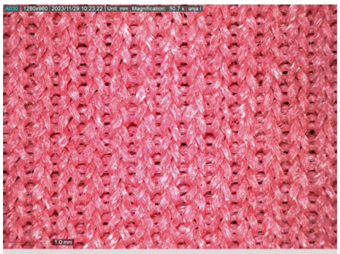
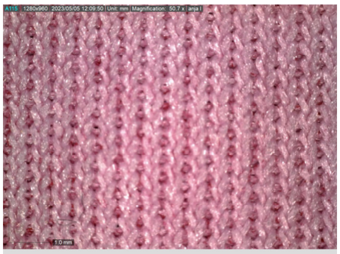
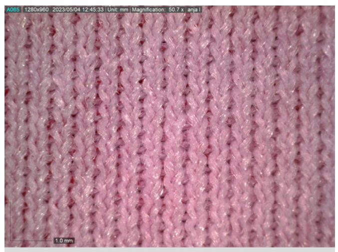
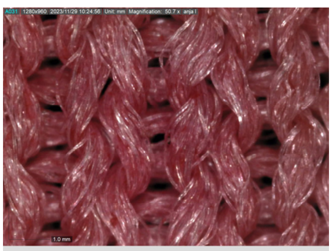
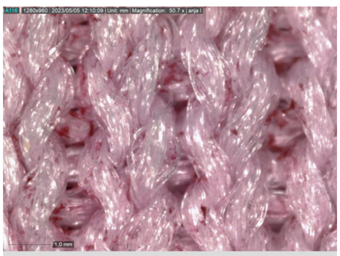
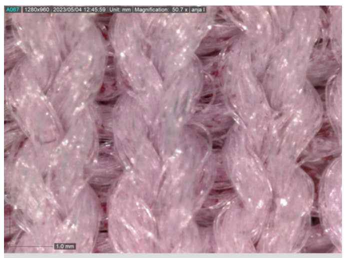
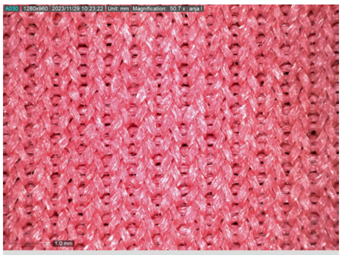
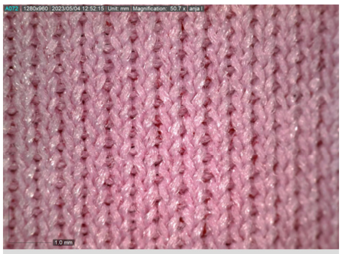
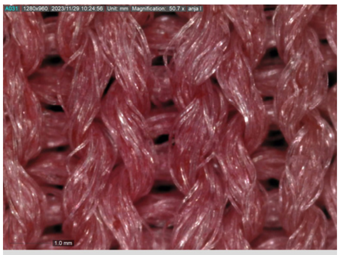
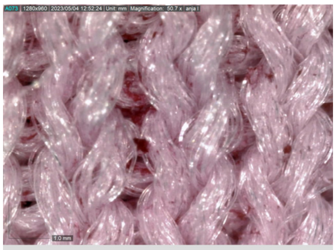
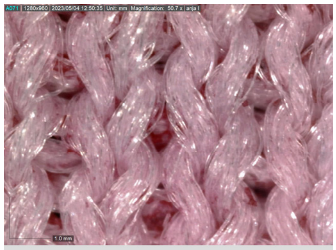
	Chitosan-Modified Knitted Fabric Samples		
	CH-P	**CH-P-St-5**	**CH-P-St-10**
50×			
230×			
K/S	4.1132	1.0898	0.728

Table 4. Digital micrographs, magnified at 50 and 230 times, showing the polyester knitted textiles treated with chitosan and dyed with Remazol Red RB before and after 5 and 10 washing cycles, following an innovative procedure.

	Chitosan-Modified Knitted Fabric Samples		
	CH-P	**CH-P-Inn-5**	**CH-P-Inn-10**
50×			
230×			
K/S	4.1132	1.1866	1.0948

Digital pictures of the surface of polyester knitted fabrics treated with chitosan (CH-P) demonstrate a higher intensity of coloration and uniformity (K/S 4.1132). A strong decrease in K/S (1.0898) is a consequence of the first wash cycles (5 washes). The influence of further wash cycles (10 washes) is significantly lower compared to the first cycles. Reduction in color strength values (K/S) proved a certain instability of chitosan through standard washing cycles.

Digital micrographs of the surface of polyester knitted fabrics reveal greater colour intensity and uniformity after 10 cycles of washing using the innovative procedure compared to the standard procedure. Furthermore, the variations in K/S values after 5 and 10 cycles are less, supporting the increased stability of chitosan in the washing process following the innovative procedure and the contribution of the innovative procedure to better stability and sustainability.

The same analysis was carried out for chitosan-modified polyester/cotton knitted fabrics (Tables 5 and 6).

The colour strength (K/S) of polyester/cotton knitted fabric modified with chitosan (CH-P/CO) is greater for app 0.6 units than that of polyester knitted fabric (CH-P), as predicted, given the cotton component's percentage and compatibility with the biopolymer chitosan. The loss of chitosan was influenced by washing through 5 and 10 cycles according to the standard procedure, with the variations between 5 and 10 cycles being insignificant. At 230× magnification, micrographs of washed polyester/cotton knitted fabric samples reveal a significant degree of fibrillation, particularly after 10 cycles of standard washing. The cotton component in the blend may be responsible for the appearance of protruding fibrils on the surface [41].

Washing polyester/cotton fabrics in 5 and 10 cycles using the innovative procedure affected the loss of chitosan, and the differences between 5 and 10 cycles were greater than with the standard procedure. These results indicate that the innovative procedure of washing knitted polyester/cotton fabrics is not any more effective than this standard procedure. Furthermore, micrographs of washed samples of polyester/cotton knitted fabrics at 230× magnification indicate a higher degree of fibrillation and the presence of fibrils after 5 and 10 washing cycles according to the innovative procedure is similar.

Table 5. Digital micrographs of the chitosan-treated polyester/cotton knitted fabrics dyed with Remazol Red RB at magnifications of 50× and 230× before and after 5 and 10 standard washing cycles.

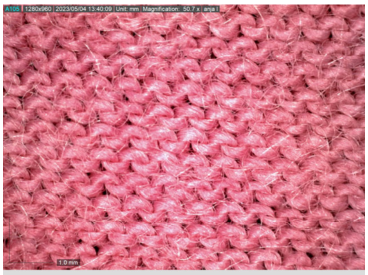
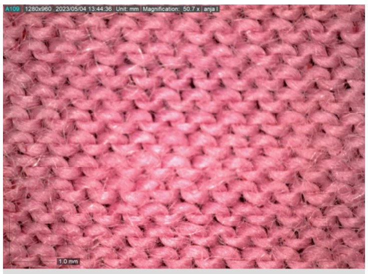
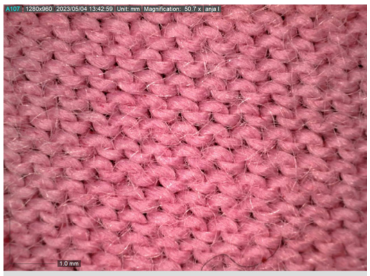
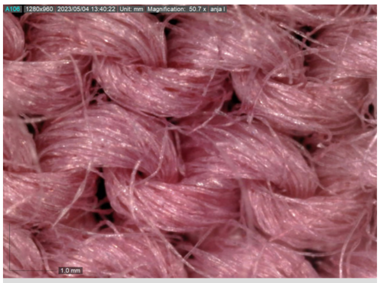
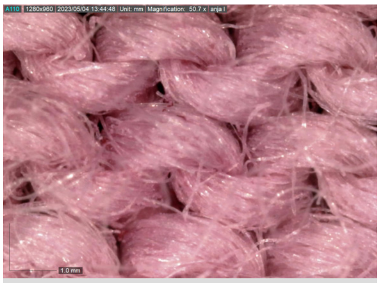
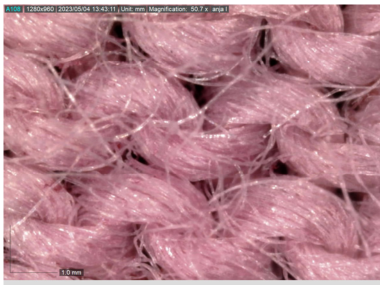
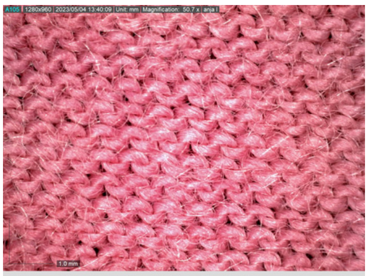
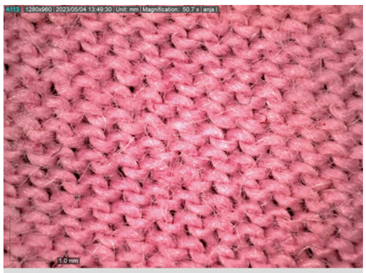
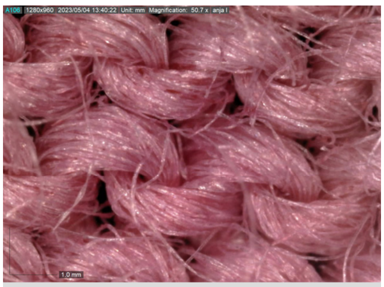
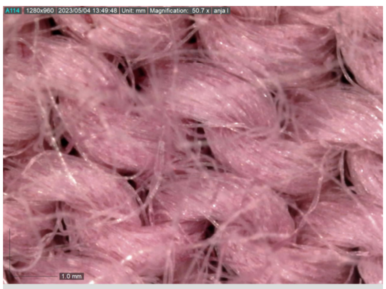
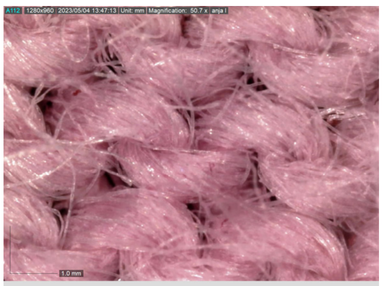
	Chitosan-Modified Knitted Fabric Samples		
	CH-P/CO	**CH-P/CO-St-5**	**CH-P/CO-St-10**
50×			
230×			
K/S	4.7068	1.998	1.9537

Table 6. Digital micrographs of the chitosan-treated polyester/cotton knitted fabrics dyed with Remazol Red RB at magnifications of 50× and 230× before and after 5 and 10 washing cycles, respectively, using the innovative procedure.

	Chitosan-Modified Knitted Fabric Samples		
	CH-P/CO	**CH-P/CO-Inn-5**	**CH-P/CO-Inn-10**
50×			
230×			
K/S	4.7068	1.9834	1.7002

The findings of the zeta potential dependency of chitosan-modified polyester knitted fabrics and polyester/cotton knitted fabrics before and after 5 and 10 wash cycles using standard and innovative procedures are presented in Figure 3. The extent to which the reference ECE detergent affects the loss of chitosan from the modified surfaces is examined in these figures (Figures 3 and 4).

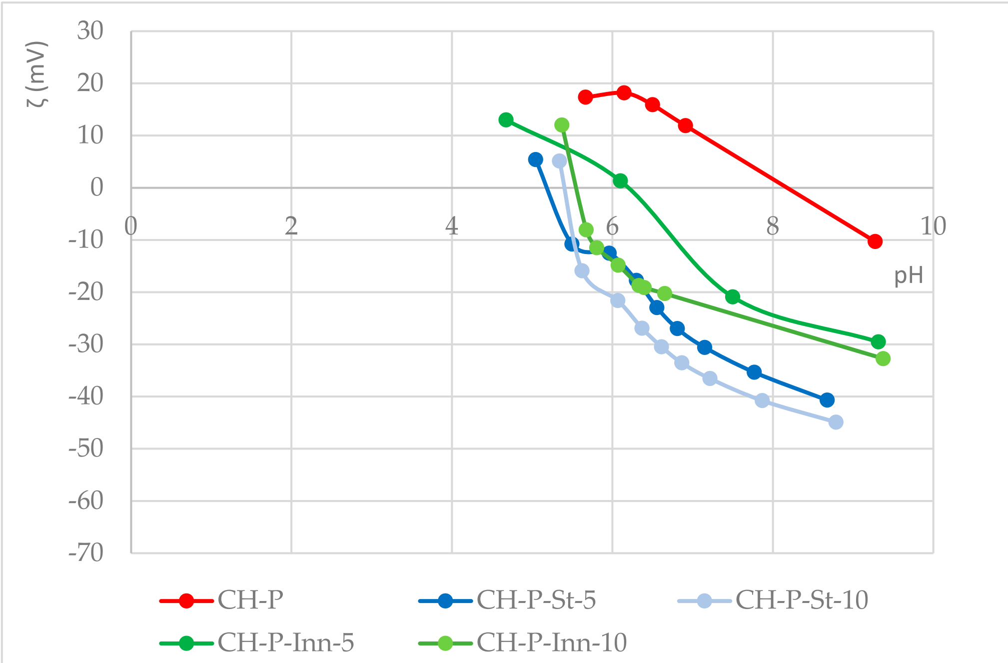


Figure 3. Zeta potential of chitosan-modified polyester (CH-P) knitted fabric before and after 5 and 10 cycles of washing according to standard and innovative procedures in variation of pH.

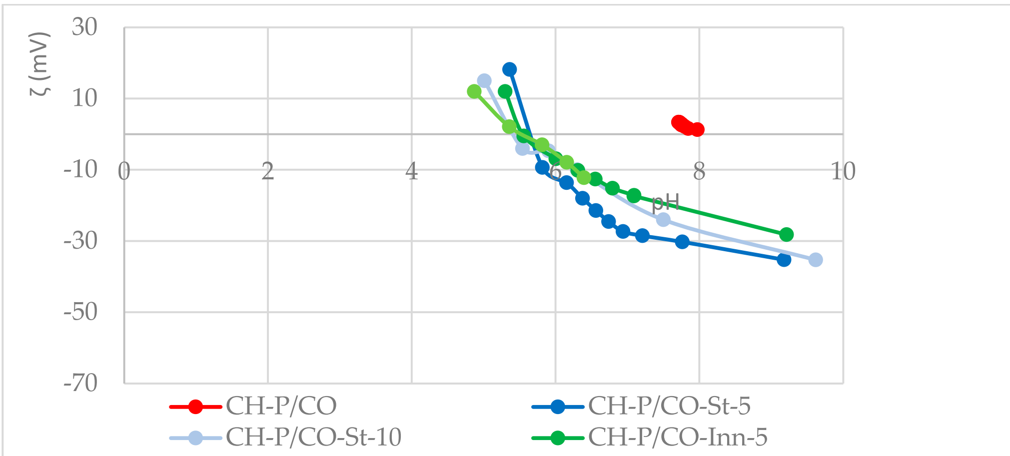


Figure 4. Zeta potential of chitosan-modified polyester/cotton knitted fabric (CH-P/CO) before and after 5 and 10 washing cycles according to standard and innovative procedures in pH variation.

The results of the zeta potential of polyester knitted fabric modified with chitosan before and after 5 and 10 washing cycles according to standard and innovative procedures show their different influences on the surface charge and, indirectly, on the stability of chitosan. According to the relationships obtained, the standard procedure had a stronger effect on chitosan loss compared to the innovative procedure. The influence of the number of wash cycles on the reduction in the zeta potential is different for these two processes. The mutual changes between 5 and 10 washing cycles using the standard procedure are insignificant when compared to the innovative procedure, which demonstrates the gradual release of chitosan coated on the surface of the knitted fabric under consideration. The titration pH curves of the washed chitosan-modified samples were shifted towards lower values, indicating differences in electrokinetic behavior. The smallest IEP shift was observed in the sample washed in 5 cycles according to the innovative washing procedure, while the samples washed in 10 cycles according to the innovative procedure and in 5 and 10 cycles according to the standard procedure were similar.

The results of the zeta potential confirm that the polyester-cotton fabric (CH-P/C) is cationised. The amount of zeta potential of the chitosan-modified polyester/cotton fabric after 5 and 10 wash cycles using standard and innovative procedures is less negative than that of the chitosan-modified polyester. These ratios indicate a better durability and stability of chitosan. According to the relationships, the knitted fabric sample is more negative after 5 wash cycles using the standard method than after 10 cycles. These deviations may be due to the shrinkage of the cotton component in the standard wash and stabilization through 10 cycles. In the whole pH range, the zeta potential values of polyester/cotton knitted fabrics washed using the innovative method are equal for 5 and 10 cycles. According to the values of the zeta potential, the stability of chitosan is better in the washing process according to the innovative procedure. Despite the differences of pH titration curves, the IEPs of all washed samples are close, confirming their similarity in electrokinetic behavior and surface charge.

The basic requirement for pilling to occur at all is the existence of a fibre layer on the surface that has a specific length and density. Table 7 indicates the propensity of the face of the untreated polyester knitted fabric and chitosan-modified polyester knitted fabric before and after 10 washing cycles in accordance with standard and innovative procedures to produce pilling following cyclic rubbing.

Table 7. Pilling grades of polyester knitted fabrics.

Sample	Rub Cycles					
	125	500	1000	2000	5000	7000
	Grade					
P	5	5	5	5	5	5
CH-P	5	5	5	5	5	5
CH-P-St-10	5	5	5	5	5	5
CH-P-Inn-10	5	5	5	5	5	5

5—no pilling.

The appearance of the top surface of all knitted fabrics after 125, 500, 1000, 2000, 5000, and 7000 rub cycles listed in Table 7 showed no pilling, indicating excellent resistance to surface fuzzing and pilling.

Table 8 indicates the propensity of the face of the untreated polyester/cotton knitted fabric and chitosan-modified polyester/cotton knitted fabric before and after 10 washing cycles in accordance with standard and innovative procedures to produce pilling following cyclic rubbing.

Digital micrographs of stained polyester/cotton knitted fabrics with chitosan washed with 5 and 10 cycles using standard and innovative procedures showed fibrils on the surface. Table 8 presents the results that demonstrate that, even after 125 cycles (3–4), the grades of the surface of knitted polyester/cotton fabrics are deteriorated. The chitosan-modified polyester/cotton knitted fabric has an even lower grade (3), which means that chitosan did not cover the surface in such a way as to reduce the number of fibrils on the surface. The chitosan-modified polyester/cotton knitted fabric was washed 10 times using both standard and innovative procedures and this did not stop the surface grades from further deteriorating. The stability of chitosan-coated on polyester/cotton knitted fabric in the washing process according to standard and innovative procedures is equivalent, according to this method of analysis. The grades of the untreated chitosan-coated polyester/cotton knitted fabric before and after 10 cycles of washing demonstrate outstanding resistance to the washing process by both processes.

Table 8. Pilling grades of polyester/cotton knitted fabrics.

Sample	Rub Cycles					
	125	500	1000	2000	5000	7000
	Grade					
P/CO	3–4	3	2–3	2–3	2	1–2
CH-P/CO	3	2–3	2–3	2	1–2	1–2
CH-P/CO-St-10	3	2–3	2–3	2	1–2	1–2
CH-P/CO-Inn-10	3	2–3	2–3	2	1–2	1–2

4—slight pilling; 3—moderate pilling; 2—severe pilling; and 1—very severe pilling.

4. Conclusions

The results of colour strength (K/S) measurement, red staining test, zeta potential calculation, and pilling grades measurement showed different relationships between the stability of chitosan on polyester and polyester/cotton knitted fabrics when washed with standard detergents using standard and innovative procedures. The streaming potential proved to be a favorable method for monitoring the stability of chitosan in the washing process in combination with a staining test with the selected dye Remazol Red RB. The results show that alkaline hydrolysis is not necessary as a preparatory phase for improved interaction of chitosan with polyester knitted fabric.

The protective potential of chitosan applied to polyester and polyester/cotton is better preserved when washed using the innovative procedure than using the standard procedure, confirming the sustainable benefits of washing using the innovative procedure.

The pH titration curves of polyester and polyester/cotton knitted fabrics treated with chitosan proved the presence of chitosan on the surface. Chitosan from cationized polyester and polyester/cotton knitted fabrics is probably partially removed from the surface due to the interaction with the ECE reference detergent; the polar head of the anionic surfactant in the detergent interacts with the chitosan.

Thus, further research will focus on the selection of detergents based on non-ionic and amphoteric surfactants for washing of chitosan-modified polyester and polyester/cotton knitted fabrics and will be another step towards sustainability.

Author Contributions: Conceptualization, T.P.; methodology, T.B., A.Š., K.Š. and K.G.; formal analysis, T.B., A.Š., K.Š. and K.G.; investigation, T.B., A.Š., K.Š. and K.G.; writing—original draft preparation, T.P., J.V.V. and M.Č. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Croatian Science Foundation, grant number HRZZ-IP-2020-02-7575.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

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