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HT process for treatment of PET fabrics with chitosan-containing recipes

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ABSTRACT

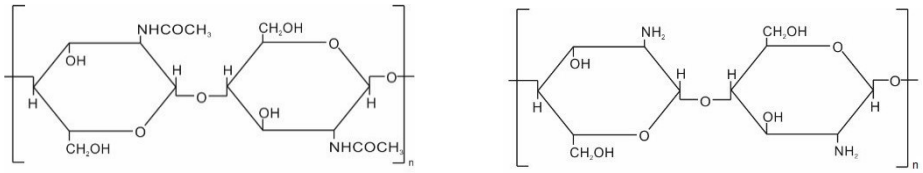
Polyester is the leading man-made fiber in the field of textiles and clothing. Polyester is usually dyed and finished using a process temperature in the range of 120 to 135 °C. Such a process is known as a high-temperature (HT) process. The application of chitosan on cellulosic materials is an interesting approach to textile functionalization. In contrast, the application of chitosan by the HT process for the functional treatment of polyester is less investigated. With this background, the present study is related to the surface characteristics of different polyester fabrics with implemented chitosan after performing the HT process.

1 Introduction

Polyester is the most important and widely used textile fiber in different fields of application. Often mentioned advantageous properties of polyester fibers are strength, dimensional stability after heat-setting, good elastic recovery, and low cost [1]. Polyethylene terephthalate (PET) is the most important among other types of polyesters [2]. The polyester used for textiles usually consists of smooth and rod-like fibers with round or trilobal cross-sections [3]. Polyester fibers contain a moderate resistance against both organic and mineral acids, bases, oxidizing, and reducing agents. However, hot and concentrated acids and alkalis attack PET fibers quickly. Further, polyester fibers in textiles exhibit also several drawbacks, because polyester is hydrophobic, and there are no hydrophilic or chemically reactive groups on the polyester fiber surface [4]. Polyester fibers are mainly dyed with disperse dyes, so the finishing process illustrated in this study is related to this dyeing method but is performed with bio-based polymer chitosan instead of disperse dyes [5].

Traditionally, high-temperature (HT) processes are used to modify polyester yarn or fiber. In this case, process temperatures higher than 100 ºC are applied, and often temperatures in the range of 120 to 135 ºC are used [5-8]. At such elevated temperatures disperse dyes can diffuse inside the amorphous areas of polyester fibers, as the process temperatures are above the glass transition temperature (T_g) of the polyester (T_g(PET) = 80 °C … 85 ºC) [9]. Fixation of the dyes or finishing agents leads to good wash fastness and strong up-take and fixation into the fabric are reached if fibers open up at elevated process temperature [10,11].

Chitosan is one of the most important derivatives gained from the natural biopolymer chitin [12], which is a biodegradable, biocompatible, and non-toxic biopolymer. Additionally, antimicrobial, antistatic, and anti-odor properties are reported for chitosan [12-17]. It is reported that the antimicrobial activity of chitosan is influenced by the molecular weight of this polymer and its degree of deacetylation. Further, the pH value of the surrounding medium is reported to have a certain influence [14,15,18,19]. Hu et al. presented chitosan grafting on glutaraldehyde-treated PET through esterification or imine formation [20]. As glutaraldehyde and formaldehyde derivatives as cross-linking agents are not eco-friendly, Grgac et al. used polycarboxylic acids in the after-treatment [21]. Their work explained a pretreatment method with 20% NaOH followed by finishing in the gelatin chitosan bath. For comparison, Figure 1 shows the general structure of chitin and chitosan.



(a) (b)

Fig. 1 Chemical structure of (a) chitin, (b) chitosan.

In this research work, chitosan was dissolved in a citric/acetic acid solution to apply to different polyester samples for the functional treatment of PET fiber samples using an HT process. High-temperature dyeing is an extensively applied process for dyeing polyester fabrics, but for this research, chitosan was applied as a natural biopolymer finishing agent instead of dyes. The purpose of this research work was to develop a textile finish based on chitosan to confer new properties on polyester. Moreover, the presence of chitosan is identified through the drop test and ninhydrin test. These investigations should be the starting point for further functional finishing and the development of chitosan on synthetic fibers like PET. In addition, they can support in general the application of biopolymers to synthetic fibers, by showing the principal relation between parameters used in the HT process.

2 Materials and Methods

2.1 Materials

In this research, different woven polyester fabrics were used. Table 1 shows the description of the polyester fabrics used with different properties. Chitosan was purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany) and citric acid from Bernd Kraft GmbH (Duisburg, Germany).

Table 1. Fabric description for woven polyester used in the experiments.

Fabric	No. of warp threads/cm	No. of weft threads/cm	Mass per unit area (g/m²)
1	17.5	15.5	220
2	16.5	14.5	150
3	17.5	20.0	340
4	17.0	15.0	240

2.2 Treatment procedure

Chitosan solutions in different concentrations were prepared using 197 mL of deionized water with 2 mL (w/v) of citric acid (20 %) and 1 mL (w/v) of acetic acid (6 %). The pH value of the acidic solution without

chitosan was 2.89. Chitosan powder was carefully added into the citric/acetic acid solution successively in 0.5%, 1%, and 2% concentrations. To dissolve the chitosan powder into an acidic solution completely, a magnetic stirrer was used. Before implementing the chitosan solution (w/v) into the pots for finishing treatment, the pH value was determined again (Figure 2). After adding and solving chitosan completely, the pH of the solutions increases, because of the alkaline property of the amino groups in chitosan.

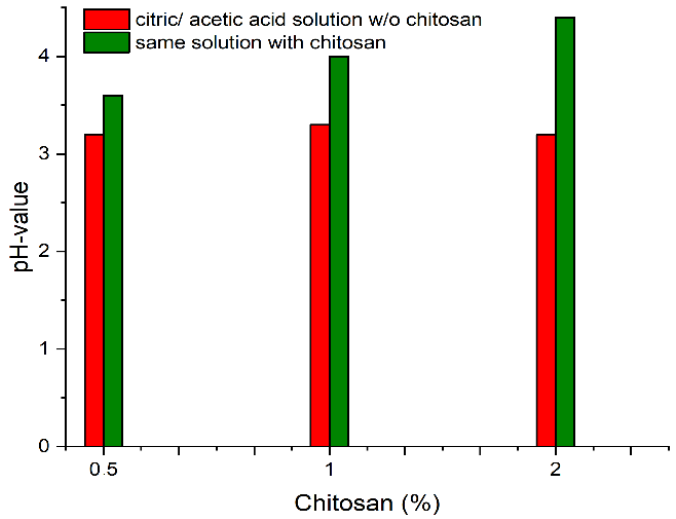


Fig. 2 Effect of chitosan (%) on pH value of citric/acetic acid solution.

Four different polyester fabrics were cut in sizes 7 cm × 15 cm and weighed for the mass gain assessment before and after the HT process. The temperature profile of the used HT process for the polyester fabrics with implemented chitosan (0.5%, 1%, and 2%) is presented in Figure 3.

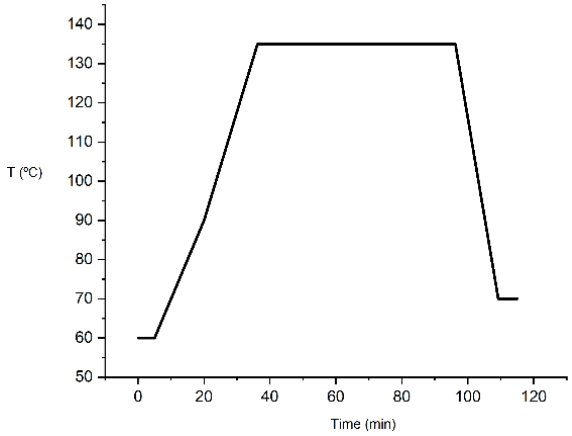


Fig. 3 Temperature profile of used HT process.

The high-temperature finishing process was carried out in a Zeltex Polycolor exhaust dyeing machine (Werner Mathis AG, Switzerland). The maximum process temperature was set to 135 ºC. The pots carrying the polyester fabrics in chitosan solutions were inserted into the machine at the temperature of 60 ºC. The high temperatures of 90 ºC to 135 ºC were reached by a heating rate of 2 K/min. The process temperature was maintained for 60 minutes (Figure 3). The cooling temperature was set to 70 ºC at 5 K/min. No wash cycle was performed afterward. The treated samples were kept for line drying at room temperature overnight.

2.3 Analytical methods

The morphology of fabric surfaces was observed using a scanning electron microscope (SEM) (Tabletop Microscope TM3000, Hitachi, Japan). SEM was used to demonstrate the surface morphology of different polyester fabrics untreated (reference) and treated with chitosan. The used SEM is equipped with an EDS unit (energy dispersive spectroscopy; Quantax 70 supplied by Bruker). This EDS unit enables to

detect chemical elements on the sample surface and determine their surface concentration. The chemical element hydrogen cannot be detected by this EDS method. For the element nitrogen, the sensitivity of the EDS method is quite low, so nitrogen can be only detected if it occurs in significant amounts on the sample surface. Further characterization of different polyester samples was performed by Fourier transform infrared (FT-IR) spectroscopy (IR Tracer-100, SHIMADZU Deutschland GmbH). For recording the IR spectra, 40 scans were done for each sample. The recorded spectral range was set between 3500 cm^{-1} and 750 cm^{-1}. The hydrophilic properties of treated and untreated polyester fabrics were determined by using the TEGEWA drop test. For the detection of amino groups on chitosan-treated polyester fabrics, a 0.35% ninhydrin solution is used. After spraying this ninhydrin solution on the polyester samples, the samples were dried at 100 °C for 4 minutes. The reflectance of the ninhydrin-treated samples was measured using a Datacolor 400 spectrophotometer from Datacolor Europe GmbH.

3 Results and Discussion

In this study, chitosan in different concentrations was implemented in polyester fabrics by high-temperature finishing using a Polycolor dyeing machine. The presented results were obtained after chitosan treatment and drying at room temperature overnight without any further washing procedure. In other research investigations, primarily a pretreatment procedure is followed by chitosan finishing, especially opening up the structure using a catalyst. There was no pretreatment used during this research. For cotton or cotton blends, there is a pretreatment process similar to mercerization [21], depending on the fabric type chemical additives can be selected. However, the extra process costs extra time and in this study, the additional pretreatment and usual washing were not performed to figure out if chitosan shows any kind of effect on 100% polyester fabrics. For future experiments, the wash procedure will be vital and separate works will be published regarding bacterial and odor resistance of chitosan on 100% polyester fabric.

3.1 Wet pick-up evaluation

The wet pick-up is determined to support information about the wetting properties of the polyester fabrics with implemented chitosan (0.5%, 1%, and 2%) and was calculated as:

$$\text{Wet pick-up (\%)} = \frac{w - w_0}{w_0} \times 100\ \% \quad \text{..... (i)}$$

From equation (i), w is the weight of wet samples and w_0 is the weight of the original (dry) sample.

Table 2 shows the wet pick-up (%) for different concentrations of chitosan on different polyester fabrics after high-temperature treatment. It is obvious to have more weight of the samples after-wet treatment with chitosan solution and the wet pick-up rate is quite different as the samples themselves contain different properties.

Table 2. Wet pick-up in the percentage of different polyester fabrics.

Polyester	Chitosan conc. (%)	Mass before treatment (g)	Mass after treatment (g)	Wet pick-up (%)
Fabric 1	0.5	5.0	13.0	**159**
	1.0	5.0	13.7	**176**
	2.0	5.0	12.6	**152**
Fabric 2	0.5	3.6	10.2	**182**
	1.0	3.5	10.0	**186**
	2.0	3.6	10.0	**178**
Fabric 3	0.5	8.5	19.2	**126**
	1.0	8.5	19.2	**127**
	2.0	8.5	19.9	**135**
Fabric 4	0.5	5.1	16.6	**228**
	1.0	5.2	14.8	**187**
	2.0	5.1	13.0	**154**

3.2 Surface Analysis

The surface morphology of the treated and untreated polyester fabrics was evaluated by SEM. Figure 4 shows microscopic images of different polyester fabrics untreated and treated with 2% chitosan recorded with a magnification of 300x. The SEM images of polyester fibers/filaments (Figures 4a-d) in untreated reference polyester fabrics show flat, shiny, and foreign particles depending on handling. Contrastingly, the SEM images of polyester samples with implemented chitosan (2%) show (Figures 4e-h) few cracks (especially fabric 2) perhaps due to the deposition of chitosan particles as a consequence of the applied process. However, it can be stated that mostly the sample topography is not influenced by the chitosan application if the images are recorded with the used magnification. For this, clear detection of chitosan on used polyester fabrics is not possible by SEM. Also, by the EDS method, the detection of nitrogen is not possible on the chitosan-treated samples. The content of applied amino groups is probably too low to reach a nitrogen content that can be detected by EDS.

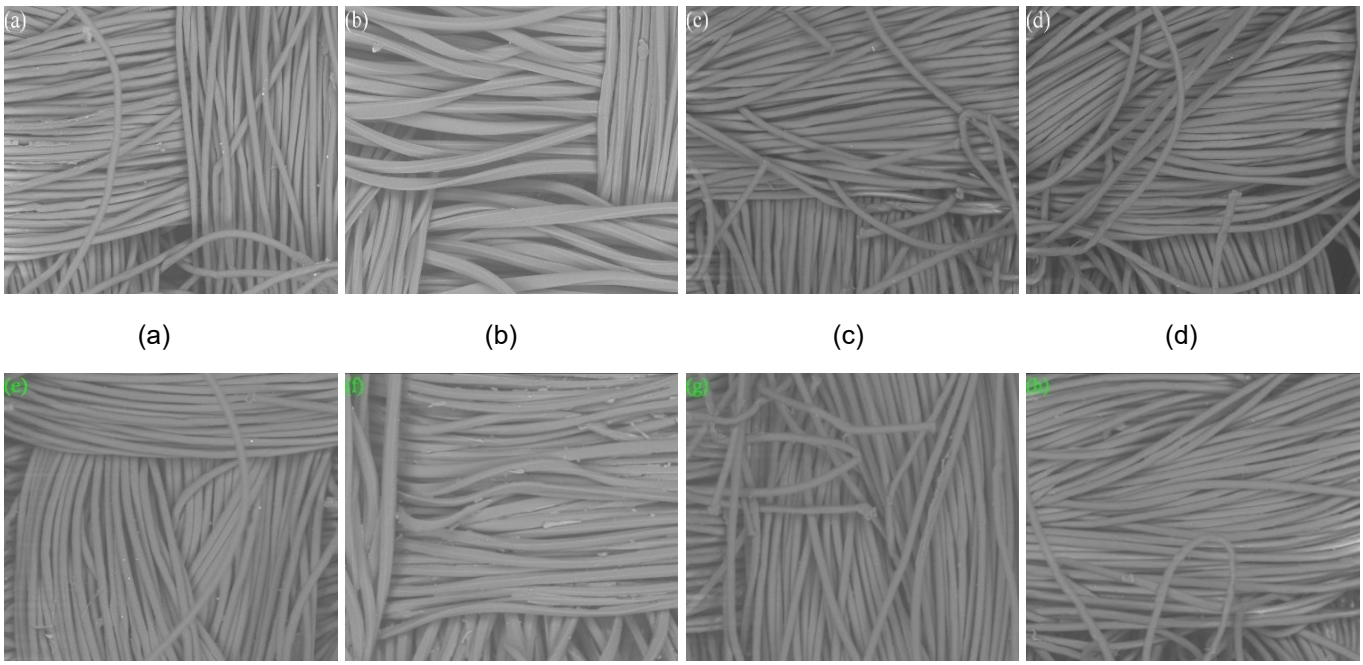


Fig. 4 SEM images of different polyester fabrics as reference (a-d) and finished with 2% chitosan (e-h).

3.3 Infrared Spectroscopy Investigations

IR spectra are recorded on PET fabrics before and after the application of the chitosan-containing recipes. As a reference, the IR spectrum of the used chitosan powder is recorded (Figure 5). The IR spectrum of the chitosan powder exhibits two broad signals at 3246 cm^{-1} and 2886 cm^{-1} (Figure 5a). These signals are assigned to O-H and C-H stretching vibrations. The signal at 1614 cm^{-1} can be assigned to C=O stretching vibration of the amide groups.

The strongest peak at 1024 cm^{-1} is related to C-O stretching vibrations. In contrast, the spectra of the PET fabrics are mainly determined by a strong peak at 1713 cm^{-1} assigned to the C=O stretching vibration of the ester group (Figures 5b-e). Further weak signals around 2900 cm^{-1} are related to C-H stretching vibration. Altogether, the spectra of the four different PET fabrics are nearly similar, and the chitosan application does not change the IR spectra. This spectroscopic method is probably unsuitable for detecting the applied chitosan on the treated PET fabrics.

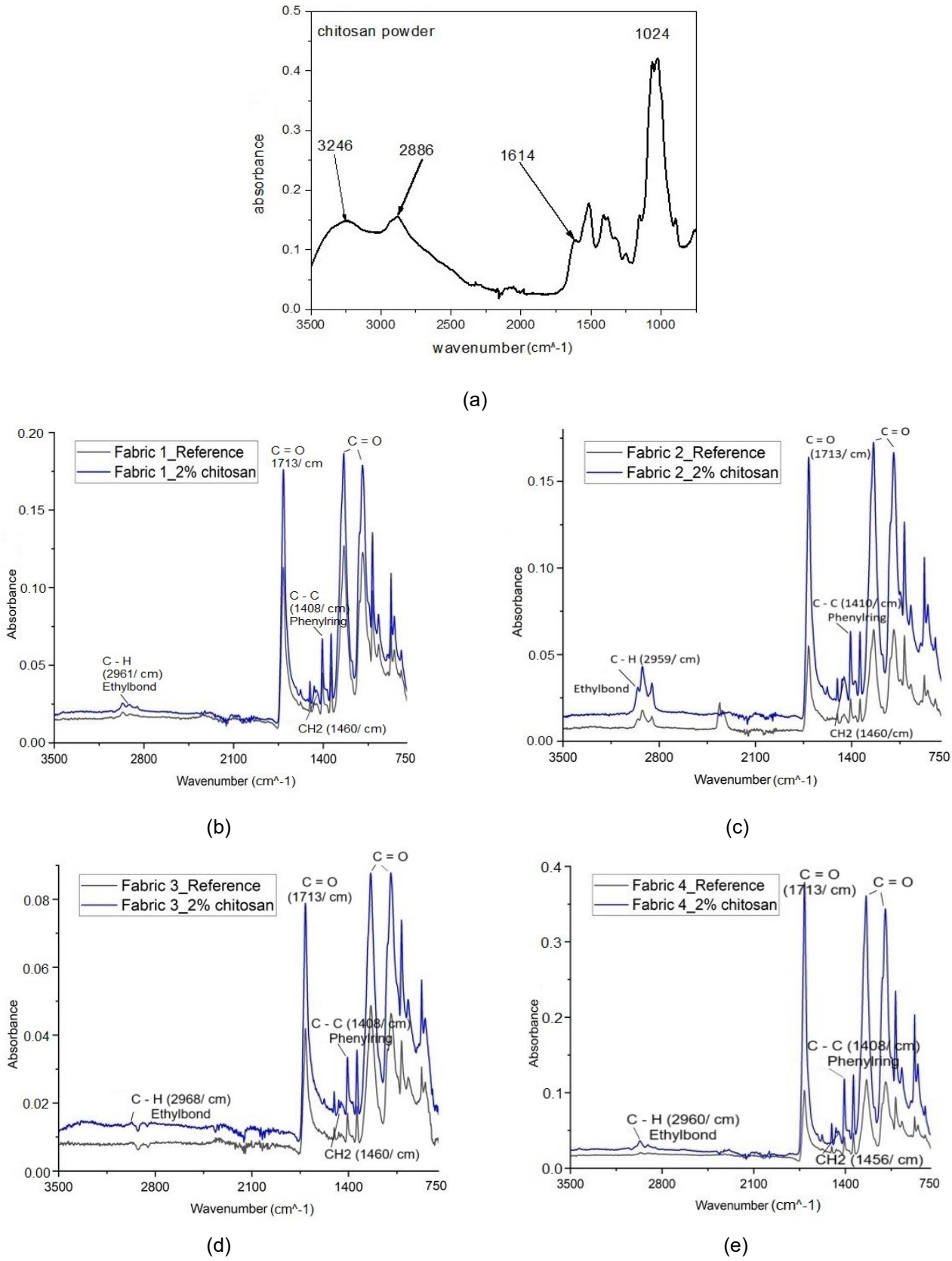


Fig. 5 FT-IR spectra: (a) Chitosan powder and different polyester fabrics (original) without chitosan and with 2% implemented chitosan, (b) fabric 1, (c) fabric 2, (d) fabric 3, (e) fabric 4.

3.4 Drop-test

The drop-test was performed with the dye Tegewa Patentblau V (2% solution) on different polyester fabrics to determine changes in the water up-take performance. Three measurements were taken from each fabric and the mean value is shown in Table 3 for fabrics 1, 2, and 3. The test specimens were

mounted onto a circular area and adjusted properly to apply drops of Patentblau V using a dripper. Hence, the absorption time of the droplets was recorded as shown in Table 3. Figure 6 shows the samples after the drop-test performed on fabrics 1, 2, and 3 without chitosan (a, c, e) and with chitosan (b, d, f). The spreading of the droplets on functionalized samples was relatively smaller than for the references. It is obvious that the chitosan application on the surface delayed the water penetration and Table 3 addresses the droplet sizes were influenced due to the presence of chitosan in both vertical and horizontal directions. By using this drop test method, the applied chitosan can be determined indirectly. Remarkable is the short sink-in time of the untreated PET fabrics of less than one second, because PET is itself of hydrophobic nature. In contrast, the application of chitosan is more hydrophilic in nature leading to a larger sink-in time for the applied water drops. This effect could be explained by the closure of open structures on the PET fabric structure by an applied chitosan layer.

Table 3. Results of drop-test.

	Fabric 1		**Fabric 2**		**Fabric 3**	
	Ref.	**2% chitosan**	**Ref.**	**2% chitosan**	**Ref.**	**2% chitosan**
Vertical drop Size (cm)	4.3	2.9	7.6	4.2	4.5	3.2
Horizontal drop Size (cm)	3.5	2.8	4.5	3.2	3.4	1.5
Sink-in time (sec)	0.9	33.8	0.5	3.2	0.4	16.2

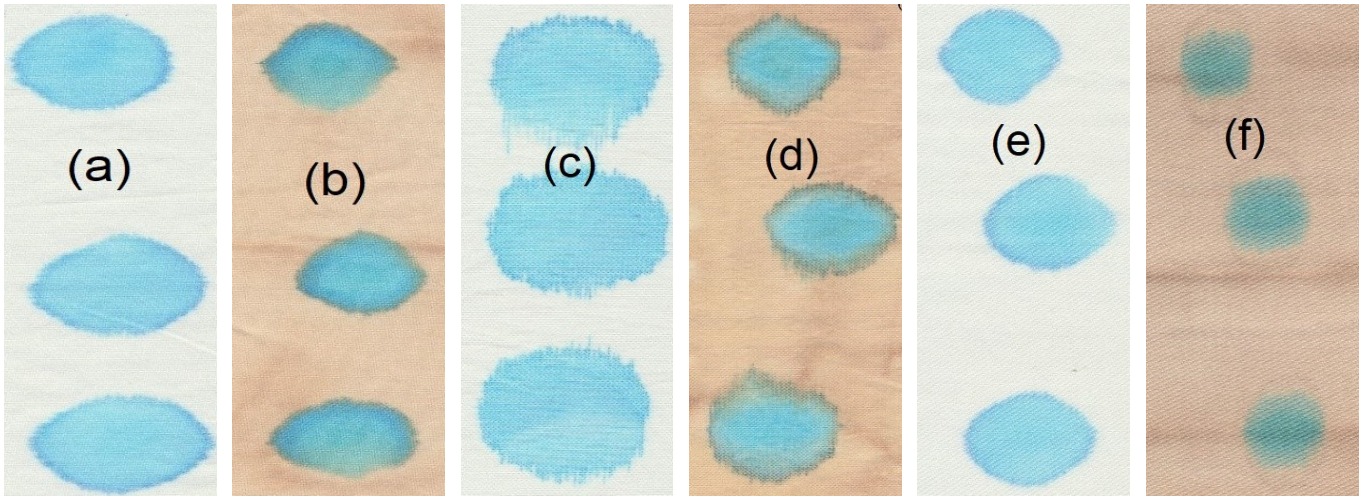


Fig. 6 Polyester samples after drop test; references for fabric (a) 1, (c) 2, (e) 3, and treated with 2% chitosan on samples (b) 1, (d) 2, (f) 3.

3.5 Detection of amino groups by ninhydrin dye

A ninhydrin test was performed on the untreated and chitosan-treated polyester fabrics. For this test, 0.35% ninhydrin solution was prepared in ethanol. The test samples were soaked for 5 minutes into the solution and the same solution was sprayed onto the surface of the fabric evenly followed by drying at 100 ºC for 4 minutes. After drying, the samples were visually examined under daylight. Figure 7 shows a clear visual difference between raw polyester and finished polyester samples after ninhydrin treatment. Research studies reported that a higher amount of free amino groups appear when treated with a higher amount of chitosan [20]. By this test, the applied chitosan can be determined. The HT process can be therefore used to apply chitosan from the solution onto PET fabrics.

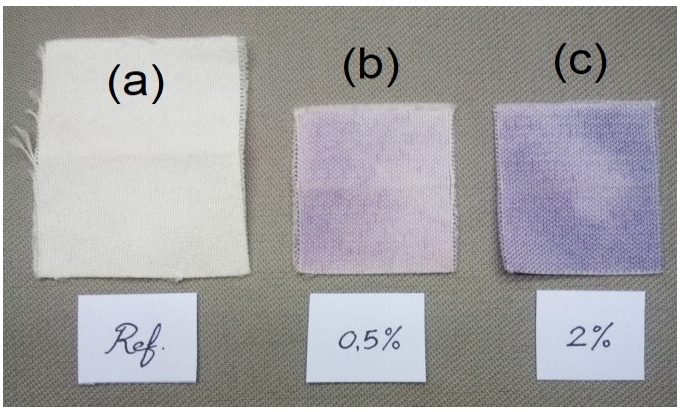
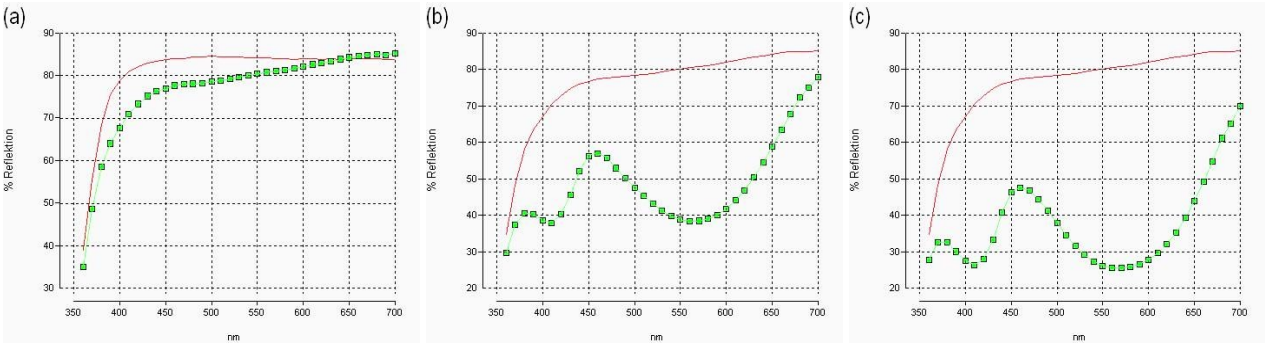


Fig. 7 Functionalized fabric 2 with 0.35% ninhydrin solution. (a) Fabric 2 – raw polyester, (b) fabric 2 with 0.5% chitosan, (c) fabric 2 with 2% chitosan.

To determine the effect of chitosan on finished polyester fabrics, additional measurements after the ninhydrin test was done by using the Datacolor device. The fabrics were folded in four, and the measurements were taken twice from each sample. Figure 8 shows the reflectance curves, a result of mean values from the measurements. Figure 8 exhibits obvious differences between two curves in 8a-c. The curves in Figure 8(a) are of two raw polyester specimens, where the green curve denotes the one treated with ninhydrin. Figures 8b and 8c show the deflections caused by different chitosan concentrations, and it can be stated that more chitosan on the surface of polyester results in less reflectance within the visible range.



(a) (b) (c)

Fig. 8 Reflectance curves according to Datacolor 400 spectrophotometer for fabric 2 treated with 0.35% ninhydrin solution. (a) Raw polyester fabrics with (red) and without (green) ninhydrin, (b) reference fabric (red) and finished fabric (green) with 0.5% chitosan, (c) reference fabric (red) and finished fabric (green) with 2% chitosan.

4 Conclusions

Chitosan-based recipes are applied by a HT process on polyester fabrics. Detecting the applied chitosan by SEM, EDS, and IR spectroscopy is challenging. These analytical methods are not enough evident to justify the chitosan presence. Therefore, drop-test and ninhydrin tests are performed on the finished polyester fabrics as the quickest and easiest way to detect chitosan presence. Chitosan can be applied from an acidic solution using an HT process on PET fabrics. By this, the liquid uptake and adsorption on the surface of treated PET fabrics are modified. The presented process can be the first step to new functional PET fabrics based on treatment with bio-based polymer chitosan.

Author Contributions

M.T. Hoque: main experimental work (especially HT process and analytics), data evaluation, and main writing of this paper. K. Klinkhammer: experimental work (mainly analysis), data evaluation, and writing; B. Mahltig: supervision of the related research project, data evaluation, and correction of this paper.

All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

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