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STUDY ON THE BIOSCOURING TREATMENT OF 50 % OF HEMP + 50 % OF COTTON FABRICS

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Abstract: *This work presents the study of the Bioscouring treatment applied on 50 % of hemp + 50 % of cotton blended materials. The goal of the treatment was the removing of morphological impurities present in cotton and hemp fibers in order to obtain cleaner materials with better properties.*
For enzymatic treatments different concentrations (1-3 % o.w.f) from a commercial product named Beisol PRO (a mixture of enzymes pectinases) were used. The reaction media was made of phosfate buffer solution of 0.1 M and pH 8. (sodium phosfate/disodium phosphate), 2 g/L sodium citrate (complexing agent) and 0.5 % Denimcol Wash RGN (wetting agent). All the experiments were carried out after a central, rotatable second order compound program with two independent variables: enzyme concentration (concentrations between 1-3 % o.w.f) and treatment time (15-55 minutes) at 20:1 liquid to fabric ratio and a temperature of 55 ^{0}C.
The reatment efficiency has been verified by the following analyses: weight loss, hydrophilicity, whiteness degree, yellowness degree, crystallinity, tensile strength, elongation at break, Scanning Electron Microscopy (SEM), spectrophotometric analysis in CIELAB system of the samples dyed with alizarin dye.
After all the investigations it was found that the bioscouring procedure of 50 % of hemp + 50 % of cotton blended materials conducted to a proper removal of the morphological impurities without affecting the internal structure of cellulose or any significant degradation of the material.

Key words: *hemp/cotton material, bioscouring treatment, enzymatic commercial product, weight loss, hydrophilicity, whiteness degree*

1. INTRODUCTION

The cotton and hemp fibers mainly consist of cellulose. In addition to cellulose, natural attendants like pectins, waxes, extractable substances, minerals, etc. are present in the fibers structure.

The pectin is mainly present in median lamella, accompanying the fiber in the growth process and giving elasticity to the fibers. It contains cycles of methylated D-galacturonic acid. D-galacturonic acid partially esterified is called pectic acid and has the following structure as shown in Fig. 1 [1].

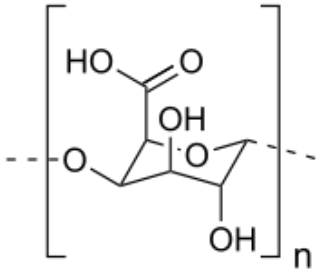


Fig. 1*: The structure of pectic acid*

By scouring treatment, the removal of natural attendances of cellulose is done by using sodium hydroxide which is usually replaced by enzymes, normally pectinases in the bioscouring treatment. Besides these agents, other auxiliaries are used: surfactants (anionic or non-ionic) and sequestrant agents in order to obtain a complete and uniform cleaning treatment. The role of the surfactants is to emulsify the unsaponifiable substances. The sequestrant agents bind the Ca^{2+} and Mg^{2+} ions which are present both in fiber's structure and water treatment, thus the detergent precipitation and staining of the fabric in the process is prevented. The sodium citrate belongs to the group of the hydroxycarboxylic acids and shows a very good sequestering activity [2].

Ideally, the scouring treatments have to be conducted in such a way that, the removal of natural attendants does not affect the structure of cellulosic fibers. Without these attendants, the material becomes hydrophilic and whiteness degree, crystallinity and mechanical properties are improved [3].

Still, over chemical or enzymatic treatments of textiles, different cellulose degradations may occur by hydrolysis or oxidation reactions, thermal, biochemical and photochemical actions, resulting hydrocelluloses, oxicelluloses, photocelluloses by the convertion of alcohol groups in the carbonyl or carboxyl groups [4].

2. EXPERIMANTAL PART

14 samples (13 for the enzymatic treatments and 1 for the conventional alkaline scouring treatment) were prepared from a fabric with the following characteristics: width (120 ± 3 cm), weight (220 ± 10 g/m^2), warp density (10 fibers/cm), weft density B (10 fibers/cm), 100 % of cotton yarn, Nm 14 for warp direction and 50 % of hemp + 50 % of cotton yarn, Nm 14 for weft direction.

Before the cleaning treatments, the samples were were washed with hot water at 100°C using a AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company - USA, followed by: drying, conditioning, weighing [5]

After drying, conditioning and weighing, the samples were subjected to Bioscouring and alkaline treatments. For enzymatic treatments concentrations between 1-3 % from the commercial enzymatic product Beisol PRO were used in phosfate buffer solution of 0.1 M and pH 8. (sodium phosfate/disodium phosphate) with the addition of 2 g/L sodium citrate and 0.5 % Denimcol Wash RGN. The liquid to fabric ratio was 20:1 and the temperature 55 ^{0}C for Bioscouring treatments and 100 ^{0}C for alkaline treatment, respectively. The variation of enzyme concentration (1-3 % o.w.f.)

and treatment time (15-55 minutes) was made by using a central, rotatable second order compound program with two independent variables. The alkaline treatment was done with 10 g/L sodium hydroxide, 5 g/L sodium carbonate, 1 g/L sodium bisulfite, 2 g/L sodium silicate and 2 g/L Sulfolen 148 (S-148, alkyl polyglicol ether) as a wetting agent.

Treatments efficiency was verified by the following analyses: weight loss, hydrophilicity, whiteness degree, yellowness degree, crystallinity, tensile strength, elongation at break, Scanning Electron Microscopy (SEM), spectrophotometric analysis in CIELAB system of the samples dyed with alizarin dye.

The results for weight loss and hydrophilicity after enzymatic and alkaline treatments are presented in Table 1.

Table 1: *Weight loss and hydrophilicity obtained for the samples subjected to the alkaline and bioscouring treatments for different conditions*

Sample	Enzyme concentration [%]	Treatment time [minutes]	Weight loss [%]	Hydrophilicity [s]
1	1.30	21.00	0.53	0.68
2	2.70	21.00	0.43	0.58
3	1.30	49.00	0.68	0.56
4	2.70	49.00	0.80	0.55
5	1.00	35.00	0.98	0.44
6	3.00	35.00	1.04	0.42
7	2.00	15.00	1.10	0.50
8	2.00	55.00	0.85	0.51
9	2.00	35.00	1.16	0.44
10	2.00	35.00	1.25	0.43
11	2.00	35.00	1.09	0.44
12	2.00	35.00	1.53	0.43
13	2.00	35.00	1.32	0.53
Alkaline	-	60.00	4.71	0.52
Control	-	-	-	>500

By analyzing the data presented in Table 1 it can be seen that for all coditions of enzymatic treatments, the weight loss does not exceed 2 %, which proves that the material was not degraded during treatments. For classic alkaline treatment, a higher weight loss of 5 % is observed, caused by the possible degradation of the fibers.

Regarding the hydrophilicity, for all 14 different treatments, values under 1 second were obtained, which show a good wettability of the treated material as a result of a proper cleaning. The wettability of the fabric being very important for further finishing processes.

The degree of structural organization of cellulose from treated fabric was evaluated by XRD analysis. A MiniFlex 600 diffractometer (Rigaku Corporation, Japan) was used. The operating conditions were: 40 kV, 15 mA, with CuKα monochromatic radiation, and using SC-70 detector and the automatic 6 position sample changer, ASC-6. The scan range was 5°-45°, with step width 0.05°, scan speed 1.2° / min. at room temperature and humidity. The PDXL2 Version 2.4.2.0 containing powder diffraction analysis package, PDXL Comprehensive Analysis, was used to analyze and calculate the cristallinity procent based on the diffraction intensity of the crystalline and amorphous phases.

For a better characterization of the treated samples from 50 % of cotton + 50 % of hemp material, determinations for tensile strength and elongation at break were made according to ASTM D 5035 – 06 "*Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)*" [6]. A testing machine 5KT from Tinius Olsen – United States with an interface running on a connected PC by Horizon software was used.

The crystallinity, tensile strength and elongation at break of the 50 % of cotton + 50 % of hemp analyzed samples are presented in Table 2.

Table 2: *The crystallinity, tensile strength and elongation at break of the treated samples*

Sample	Enzyme [%]	Treatment time [s]	Crystallinity	Tensile strength [N]	Elongation at break [%]
1	1.30	21.00	67.4	325.00	10.00
2	2.70	21.00	66.0	320.00	10.00
3	1.30	49.00	67.0	323.00	10.00
4	2.70	49.00	67.0	324.00	10.00
5	1.00	35.00	66.1	306.00	10.00
6	3.00	35.00	61.0	280.00	9.00
7	2.00	15.00	68.0	305.00	10.00
8	2.00	55.00	62.2	283.00	9.00
9	2.00	35.00	72.0	345.00	11.00
10	2.00	35.00	69.1	335.00	10.00
11	2.00	35.00	64.4	331.00	10.00
12	2.00	35.00	66.5	334.00	10.00
13	2.00	35.00	82.0	360.00	10.00
Alkaline	-	60.00	63.4	287.00	9.00
Control	-	-	65.0	333.00	10.00

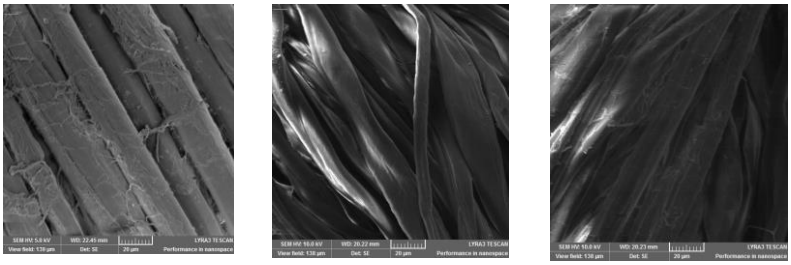
From data presented in Table 2 it can be seen as crystallinity varies depending on the treatment conditions, so that there was an increasing for concentrations up to 2.7 and 49 minutes and a decreasing of crystallinity for concentrations greater than 2.7 % and a higher duration of treatment (55 minutes). A good crystallinity seems to be at a concentration of 2 % enzyme and 35 minutes for treatment time. With the decreasing of crystallinity, the tensile strength of the material is decreasing.

For the majority of the treated samples, a slightly decreasing in tensile strength is observed compared to control (18 %), without significant changes in elongation at break. An increase in tensile strength of the material appears for the treatment with 2 % concentration of enzyme for 35 minutes.

The aspect of the fibre surface and structural changes were investigated by using Scanning Electron Microscopy (SEM). The samples were placed on a specimen support, then coated with Au using an auto fine coater (JFC-1200, JEOL Co., Japan). Observations were conducted using a SEM (LYRA 3, Tescan, Czech Republic) at 5 kV or 10 kV.

Figure 2 presents the SEM micrograph of 50 % of cotton + 50 % of hemp material for untreated sample (1), enzymatically treated sample at 2 % enzyme concentration and 35 minutes (2) and alkaline treated sample (3).

The SEM image (1) shows for untreated sample the presence of non-cellulosic cementing materials binding the fiber bundles together. No fiber damage was noticed for enzymatic treatment (2). The impurities were removed and the fiber surface is smooth and clean. The image of alkaline treated sample (3) presents peeling effect and some fibers degradations.



(1) (2) (3)

Fig. 2*: SEM micrographs for untreated sample (1), enzymatically treated sample (2% enzyme-35 minutes) (2), alkaline treated sample (3).*

Also, the treated samples were measured for whiteness and yellowness degree using a Datacolor 500 spectrophotometer. The reflectance (R %) at 420 nm was measured in comparison with a standard from barium sulphate of absolute white. The Hunter Whiteness Index and DIN 6170 Yellowness Index were calculated automatically by Datacolor Tools 2.0 software [7]. Bioscouring treatments led to a lower yellowness degree and to a 15 % enhancement of whiteness degree of the samples compared to control. A significant increase in whiteness degree of approximately 45 % appears for classic alkaline treated sample.

An effective cleaning of the material is also given by the removing of Ca^{2+} ions present in the pectin structure. Spectrophotometric analyses in CIELAB system were used for measuring the reflectance (R %) at 540 nm of the alizarin dyed samples in comparison to the control and K/S values were calculated. The color strength K/S value is a number related to the amount of the dyestuff present in a substrate. From these values, the percentage of residual calcium was used to establish the degree of Ca^{2+} ions removal. The results obtained for whiteness degree, yellowness degree and color strength (K/S) is shown in Table 3.

Table 3: *The whiteness degree, yellowness degree and color strength (K/S) of the treated samples*

Sample	Enzyme [%]	Treatment time [s]	Whiteness degree	Yellowness degree	Color strength (K/S) Alizarin
1	1.30	21.00	58.38	10.49	0.86
2	2.70	21.00	61.23	13.73	0.83
3	1.30	49.00	59.82	14.44	0.87
4	2.70	49.00	59.32	14.67	0.80
5	1.00	35.00	59.17	14.83	0.88
6	3.00	35.00	59.25	14.86	0.80
7	2.00	15.00	59.09	14.86	0.85
8	2.00	55.00	58.23	15.23	0.88
9	2.00	35.00	58.06	15.37	0.79
10	2.00	35.00	58.02	15.43	0.84
11	2.00	35.00	58.02	15.17	0.83
12	2.00	35.00	58.34	15.25	0.82
13	2.00	35.00	58.13	15.29	0.85
Alkaline			75.60	7.31	0.66
Control			52.00	16.45	1.01

A decreasing of the color strength (K/S) is observed for both enzymatically and alkaline treated samples, which demonstrates the removal of calcium ions from the system. For enzymatically treated samples, the color strength (K/S) was decreasing with 14-22 % compared to control. A 35 % decreasing of the color strength (K/S) is observed for alkaline treated sample.

5. CONCLUSIONS

After all the ivestigations carried out it was found that:

- For all enzymatic treatments, the weight loss does not exceed 2 %, what proves that the material has not suffered any degradation. For the alkaline treatment, a higher weight loss of 5 % is noticed, possible to some degradation of the fibres. The hydrophilicity values are under 1 second for all 14 different treatments, which show a good wettability of the treated material as a result of a proper cleaning.
- The crystallinity was varied depending on the treatment conditions, so that there was an increasing for concentrations up to 2.7 and 49 minutes and a decreasing of crystallinity for concentrations greater than 2.7 % and a higher duration of treatment (55 minutes). A good crystallinity was registered at a concentration of 2 % enzyme and 35 minutes for treatment time.
- With the decreasing of crystallinity, the tensile strength of the material was decreasing. For the majority of the treated samples, a slightly decreasing in tensile strength was observed compared to control (18 %), without significant changes in elongation at break. An increase in tensile strength of the material appeared for the treatment with 2 % concentration of enzyme and 35 minutes.
- Bioscouring treatments led to a lower yellowness degree and to a 15 % enhancement of whiteness degree of the samples compared to control. A significant increase in whiteness degree of approximately 45 % appeared for classic alkaline treated sample.
- A decreasing of the color strength (K/S) was observed for both enzymatically and alkaline treated samples, which demonstrates the removal of calcium ions from the system. For enzymatically treated samples, the color strength (K/S) was decreasing with 14-22 % compared to control. A 35 % decreasing of the color strength (K/S) was noticed for alkaline treated sample.

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