Enzymatic treated viscose fibers functionalized by chitosan

URŠKA VRABIČ BRODNJAK, DIANA GREGOR-SVETEC, AND MAJA KLANČNIK

ABSTRACT: Our research focused on the sorption properties of enzymatically treated viscose/chitosan and viscose fibers treated with enzymes and chitosan. To improve sorption properties of viscose fibers and to obtain the characteristics similar to viscose/chitosan fibers, we performed two different treatments. First, we treated both fibers with enzyme cellulase for 60 min and afterwards treated viscose fibers with the chitosan in an ultrasonic bath. In our research, structural characteristics and the accessibility of free adsorption places were investigated. We noted a noticeable change in the structure (degree of polymerization, crystallinity, and molecular orientation) of treated viscose and viscose/chitosan fibers. Changes that occurred in the morphology and in the structural properties of both types of tested fibers were also reflected in their physical and chemical properties. Research showed that the sorption properties of enzymatic treated fibers were improved.

Application: This study provides structure and sorption properties of viscose/chitosan fibers and viscose fibers treated with chitosan and analyzes the improvement of sorption properties of fibers, based on enzymatic treatment. Such treated fibers could be used in paper, packaging, hygiene towels, pads, and other applications.

Viscose fiber is regenerated cellulose fiber, made from wood pulp, usually from pine, spruce, or hemlock trees and cotton linters. It is biodegradable, produced from renewable source, with the properties similar to those of natural fibers. It has good moisture regain property, is hydrophilic and absorbent, feels soft and silky, has moderate dry strength and abrasion resistance, and is mechanically and chemically stable [1]. Viscose fibers can be modified in different ways, which indicates potential benefits of the fibers. Beside physical modifications, chemical modification to meet specific functionality is possible. A soft, smooth and also highly absorbent fiber is ideal for a wide range of very different applications, from apparel textiles to nonwoven materials for hygiene applications as well as special technical papers. [1] The addition of viscose fibers to wood pulp gives a sheet with improved dewatering ability, decreased density, and increased tear strength, but decreased tensile strength because of low interfiber bonding [2,3]. If instead of standard, round viscose fibers, very thin, flat fibers are used, a very high flatness of fiber, surface smoothness and good bendability give sufficient bonding area for the formation of strong paper [1]. As the bond strength is affected by the surface chemical composition and the swelling behavior, a chemical modification is another way to improve properties of viscose fiber. Bernt showed that fine-tuning of paper characteristics can be done with modification of the physical shape of viscose fibers or functionalization by anionic chemical modification [4]. Today, the surface modification of fibers is considered as the best route to obtain modern treated fibers [5]. Surface and bulk properties have an important role in paper products like hygiene towels and packaging applications.

Chitin derivatives have great adsorption characteristics and low cost, compared with other biopolymers used in the industry. Chitosan is the main derivative form of chitin. Chitosan, a commonly used biopolymer, has unique chemical and physical properties. It is produced by deacetylation of chitin, which is a biodegradable, nontoxic polysaccharide, soluble in acid, etc. There are many applications in pharmacy, biotechnology, and cosmetic industries [6]. Cellulose and chitosan have similar molecular structures, with the same β-glycoside linkages. The main difference is the presence of primary amino groups at the C-2 positions in chitosan, where cellulose has hydroxyl groups. The presence of active groups in chitosan molecular structure allows for easy chemical modification [7]. The presence of amino groups is responsible for the solubility in a diluted aqueous acid solution as a polycationic polymer [8]. In recent years, a lot of studies were done regarding different applications of chitosan, especially on cellulose functionalized by chitosan [9-15].

Chitosan treatments offer many advantages to regenerated cellulose fibers, such as biodegradability, non-toxicity, improved absorption ability, etc. Many techniques are available for introducing chitosan into cellulose fibers, such as treatments of cellulose fiber with cross-linking agents, soaking fiber in chitosan solution, and wet-spinning from blend [16]. In Japan, the representative commercial fiber derived from cellulose and chitosan is named Crabyon (Omikenshi Co.; Osaka, Japan) [17]. It is a fiber composed from a chitosan,

N,O-carboxymethylated chitosan, and viscose [18]. It is prepared by wet-spinning from a mixed solution of chitin viscose and cellulose viscose [19]. Along with improved antimicrobial activity, Crabyon fiber shows higher absorption ability and good mechanical properties, compared with regenerated cellulose fibers.

In response to environmental concerns about other treatments, enzymes have been widely used in many fields of industry. Many of the latest development studies on the enzyme treatments have been focused to improve the characteristics of fibers, among them regenerated cellulose fibers with cellulase treatment. There has been a considerable process in elucidating the mechanisms of the cellulolytic degradation. Better understanding is improving and extending the scope of finishing processes that use cellulase [20]. Enzymatic surface modification of cellulose fibers in textiles is a way to address issues of surface smoothness, pilling, and softness, all without the need to treat fabrics with traditional chemical methods [21].

Enzymes accelerate the rate of chemical reactions that occur with lower activation energy [22]. The result is formation of an intermediate enzyme substrate. Enzymes bind with the substrate by hydrogen, hydrophobic, and ionic bonds and also Van der Waals interactions. Cellulases are enzymes produced by microorganisms and plants, which have a great role in biodegradation of cellulose. Cellulase enzymes perform specific catalytic action on the 1,4-β-glucosidic bonds of the cellulose molecule [23]. The hydrolysis of this bond cleaves the molecule to smaller parts. These are not single enzymes, but complicated enzyme complexes composed of active subunits that cooperate synergistically. Cellulase enzymes are generally considered environmentally friendly and are usually dosed at low concentrations.

In recent decades, many studies have been conducted to determine the sorption properties of viscose and other regenerated cellulose fibers [16-21]. Viscose/chitosan fiber has great sorption properties, but is quite expensive. It can be used in many different products for single use, such as paper, packaging, hygiene towels, pads, etc., which is the same as viscose fibers. The aim of this research was to compare the structure and sorption properties of viscose/chitosan fibers to viscose fibers treated with chitosan, to then improve sorption properties of fibers based on enzymatic treatment.

EXPERIMENTAL

Materials

Viscose fibers (Lenzing Viscose) from Lenzing AG (Lenzing, Austria) were used throughout this work. The declared value of the linear density and the length of the fibers are 3.0 dtex and 29 mm, respectively. Viscose/chitosan fibers were obtained from Omikenshi Co. Ltd. The declared value of the linear density is 2.8 dtex and the length of the fibers is 28 mm. Both types of tested fibers have irregular cross sections.

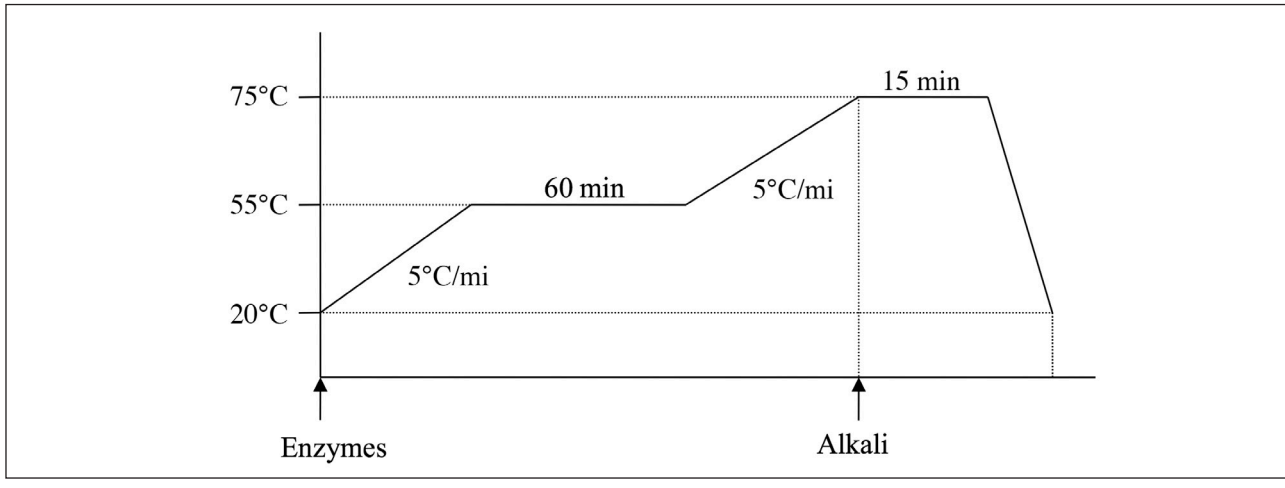
The enzyme cellulase used was Primasoft 100 from DuPont (Wilmington, DE, USA). Chitosan (low molecular weight, acetylation degree 85%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Chitosan solution was prepared by dissolving the chitosan in 2% aqueous acid solution. The acetic acid (99.8% assays) used was Honeywell Fluka (Honeywell; Morris Plains, NJ, USA).

Treatments

All tested fibers were first washed for 60 min in a bath containing 1 g/L of non-ionic surfactant with a liquor ratio 1:20. After washing, viscose/chitosan fibers were dried for 4 h at 105°C in a laboratory oven, then treated with the enzymes. The viscose fibers were first treated with the enzymes and afterwards with the chitosan.

Enzymatic treatment of viscose and viscose/chitosan fibers

The enzymatic treatment of fibers was performed with the enzymes cellulase in a launder-o-meter laboratory unit. Fibers of 2.5 g were treated for 60 min at 55°C in acetic acid buffer of pH 4.8 and liquor ratio of 20:1. The enzymes were deactivated by addition of soda (Na_2CO_3) and by increasing the temperature to 75°C for 15 min. **Figure 1** shows the enzymatic



1. Procedure of enzymatic treatment of tested fibers.

Sample	Treatment of Fibers
V	Untreated viscose fibers
V/C	Untreated viscose/chitosan fibers
$V_{-en.tr.}$	Enzymatic treated viscose fibers
$V/C_{-en.tr.}$	Enzymatic treated viscose/chitosan fibers
$V_{-en+ch.tr.}$	Viscose fibers treated first with enzymes and then with chitosan

I. Shows sample of the notation for untreated and treated viscose and viscose/chitosan fibers.

treatment procedure. After enzymatic treatment, samples were washed in distilled water to achieve the neutral pH of the fibers. Finally, fibers were dried in the laboratory oven for 4 h at 105°C.

Treatment of viscose fibers with the chitosan

A chitosan solution was prepared by dissolving 3.0 g of chitosan in 2% aqueous acetic acid at 60°C. Viscose fibers were immersed in the chitosan solution in the ultrasound bath for 120 min under constant frequency of 40 kHz and then washed with distilled water (20 mL × 100 mL) to remove the unreacted chitosan. The chitosan treated viscose fibers were first dried in the air for 12 h and then in the laboratory oven for 1 h at 50°C. **Table I** shows characteristics of the analyzed and treated samples.

METHODS

Determination of surface topography

To see the effects of different treatments on the surface of fibers, we used a JEOL (Tokyo, Japan) JSM-6060LV scanning electron microscope (SEM). The instrument was operated at 10 kV and magnifications of 5500× and 6000×.

Determination of the degree of polymerization

The degree of polymerization was determined using the viscosimetric method, according to the Schulz-Blaschke equation [24]. The degree of polymerization of the samples dissolved in cuoxam was determined using an Oswald shear dilution viscosimeter. In the research, four parallel measurements were done for each type of tested fibers.

Determination of crystallinity

We used the Schwertassek method to determine the crystallinity of the fibers from iodine sorption [24]. The fibers were first treated with KI_3 solution, after which the concentration of non-absorbed iodine was determined by titration. With this method, we took four parallel measurements for each type of tested fibers.

Iodine sorption value (IS) is the amount of iodine adsorbed by 1 gm of cellulose substrate. It was calculated by following equation:

$$IS = (a - b \cdot 1.33) \cdot F \cdot 2.5384/m \quad (1)$$

where a is volume [mL] of sodium thiosulfate ($Na_2S_2O_3$) solution (c = 0.01 mol/L) for a liquor of blank potassium iodide solution; b is volume (mL) of $Na_2S_2O_3$ solution (c = 0.01 mol/L) for a liquor of sample solution; F is a liquor factor of $Na_2S_2O_3$ solution, determined by potassium permanganate ($KMnO_4$) (0.02 mol/L); and m is weight of absolutely dry fiber sample [g].

From the given values of iodine sorption for amorphous cellulose (IS = 412 mg/g) the proportion of amorphous (x_a) and crystalline (x_c) phase was calculated [24].

Determination of molecular orientation

The average molecular orientation was determined from the birefringence measurement. The birefringence of the fibers was determined using a Meopta polarizing light microscope (Meopta; Prerov, Czech Republic)and an Ehringhaus compensator. The relative phase shift between the orthogonal wave fronts depends on the refractive index and thickness of specimen. The high relative standard variation of average molecular orientation obtained (**Table II**) is the consequence of irregular cross-sections of fiber, which has a big influence on the determined diameter under the microscope, resulting in high standard deviation of thickness. In the research, 50 measurements were done for each type of tested fibers.

Sample	DP, /	RSD, %	IS, /	RSD, %	X_c, %	RSD, %	f_{or}, /	RSD, %
V	510.58	0.05	100.95	0.99	75.50	1.29	0.4457	8.70
V/C	458.40	0.19	106.85	0.94	74.07	0.65	0.4603	31.42
$V_{-en.tr.}$	475.51	0.19	107.60	0.98	73.88	1.31	0.3890	13.11
$V/C_{-en.tr.}$	402.04	0.16	75.75	1.17	72.62	1.36	0.4979	21.13
$V_{-en+ch.tr.}$	439.76	0.08	104.13	1.08	62.59	0.45	0.3781	16.06

II. Degree of polymerization (DP), number for iodine sorption (IS), degree of crystalline part of the fibers (X_c), and factor of average molecular orientation (f_{or}) of untreated and treated viscose and viscose/chitosan fibers; RSD = relative standard variation.

Determination of the presence of carboxyl groups

The methylene blue method is a classic method for determining the presence of carboxyl groups in cellulose fibers. The methylene blue dye binds to acid carboxylic groups of fibers according to the principle of ion exchange. The share of carboxyl groups in the mass of the absolutely dry cellulose sample was calculated from the part of the unbound methylene blue dye, as follows [25]:

$$-COOH(absolutely\ dry\ sample) = {(7.5 - A) \cdot 0.00313}/{m} \quad (2)$$

where A is free, total amount of unbound methylene blue dye [mg] and m is mass of absolutely dry sample [g].

The amount of the dye in the dye bath was determined using the Perkin Elmer Lambda 2 UV/VIS spectrophotometer (PerkinElmer; Waltham, MA, USA) and the amount of dye concentration was calculated on the basis of the calibration curve. For each individual sample, three parallel measurements were taken.

Determination of contact angle and surface free energy

The wettability of fibers was determined by contact angle measurement. The measurement was carried out at room temperature, with Krüss apparatus using two different test liquids, water and heptane. The samples' mass changes, as a function of time during the water adsorption phase, were monitored. The initial slope of the function $m^2 = f(t)$ is known as the capillary velocity, from which the contact angle between the solid (polymer sample) and the water was calculated using a modified Washburn equation [26-28]:

$$cos\varphi = \left({m^2}/{t}\right) \cdot \left({\eta}/{\rho^2 \cdot \sigma \cdot c}\right) \quad (3)$$

where φ is the contact angle between the solid and liquid phase, m is the mass of the sample [kg], t is the time [s], η is the liquid's viscosity [mPa·s], ρ is the liquid's density [g/cm^3], σ is the surface tension of the liquid [mN/m], and c is a material constant or c factor. The constant c was determined for each sample from contact angle measurements using n-heptane, for which the contact angle on the nonwoven was zero, η = 0.4 mPa·s, ρ = 0.6836 g/cm^3, and σ = 20.4 mN/m [27].

Surface free energy can be determined from the measured contact angles with different liquids.

It is possible to determine the solid surface free energy (γ_s) as the sum of the polar (γ_s^p) and dispersive (γ_s^d) contribution [28]. Surface free energy was determined using the Zissman, Owens-Wendt-Raeble-Kaeble method.

Determination of zeta potential

The influence of different fiber composition on zeta potential value was investigated. An electrokinetic analyzer (EKA) (Anton Paar KG; Graz, Austria) was used to take streaming potential measurements. The detailed description of the method applied has been described by many researchers [26-31]. Potential measurements of fibers were always performed in the fiber cell using 0.001 n potassium chloride (KCl) as the electrolyte solution. The pH was adjusted using 0.1 n sodium hydroxide and 0.1 n hydrogen chloride. Zeta potential ζ was calculated from the streaming potential data using the Smoluchowski equation and the approach of Fairbrother and Mastin [21]. Surface conductivity was not taken into account.

We used the following equation for determining zeta potential [27]:

$$\zeta = {U_s \cdot \eta \cdot R_{0.1(KCl)} \cdot \chi_{0.1(KCl)}}/{\Delta p \cdot \varepsilon \cdot \varepsilon_0 \cdot R} \quad (4)$$

where ζ is zeta potential [mV], U_s is the streaming potential, η the liquid viscosity (mPa·s), $R_{0.1(KCl)}$ is the electrical resistance of the plug when the measurement cell is filled with KCl, whose specific conductance $\chi_{0.1(KCl)}$ is accurately known, Δp is the hydrodynamic pressure difference across the plug, ε is the liquid permittivity, ε_0 is the permittivity of free space, and R the electrical resistance across the plug.

Measurement was carried out by a computer program, where it was necessary to set the known parameters as follows: KCl (0.001 mol/L), concentration of the electrolyte (2.108 E^{-03}), fluid viscosity (0.826 mPa·s) and dielectric constant (77.335) [27].

Determination of adsorption capacity for dyes

For determination of the amount of dye adsorbed on fibers, methylene blue dye (Kemika; Ras el Khaimah, UAE) and bemacid yellow GR 200% (CHT Bezema; Tübingen, Germany) acid dye were selected. With adsorption of basic dye, the bonding on anionic groups of viscose fibers was evaluated. With acid dye, the adsorption on cationic amino groups of chitosan was determined.

Adsorption experiments were carried out with 2 g of fibers in 200 mL dye solution prepared with a dye concentration of 0.01 g/L at 25°C. In experiments of adsorption of basic dye on fibers, the dye alkaline solution of pH 9.5 (adjusted with solution of 2 g/L Na_2CO_3) was used. In experiments of adsorption of acid dye on fibers, dye solution of pH 5 (adjusted with solution of 3 mL/L acetic acid 30%) was applied. The adsorption was conducted at 25°C until the adsorption equilibrium was reached, which was in basic dye solution in 4 days and in acid dye solution in 3 days for all fibers.

By absorbance measurements of dye solutions and the calibration curve made on spectrophotometer Cary 1E UV-VIS (Varian; Palo Alto, CA, USA) at a wavelength of maximum absorbance (664 nm for basic dye and 401 nm for acid dye), the concentration of remaining dye in solution after adsorption was determined.

The percentage of adsorbed dye by the fiber was calculated using the following equation:

$$(\%) of\ dye\ adsorbed = {}^{C_o - C}/_{C_o} \cdot 100 \quad (5)$$

where C_o and C are the initial dye concentration and the remaining dye concentration in solution at adsorption equilibrium, respectively.

The adsorption capacity of fibers (q) for selected dyes was calculated by following equation:

$$q = {}^{(C_o - C) \cdot V}/_{m} \quad (6)$$

where C_o is the initial dye concentration (mg/L) and C is remaining dye concentration in solution at adsorption equilibrium (mg/L), V is the volume of solution (L), and m is the mass of fiber (g).

Determination of mechanical properties

Mechanical properties of fibers were determined in the standard atmosphere using an Instron 6022 (Instron; Norwood, MA, USA) tensile testing machine. The cross-head speed was 0.15 mm/s, pre-loading 0.5 cN/dtex and the gauge length 2.5 mm, respectively. The tensile data presented in this article are the average of 50 fibers.

RESULTS AND DISCUSSION

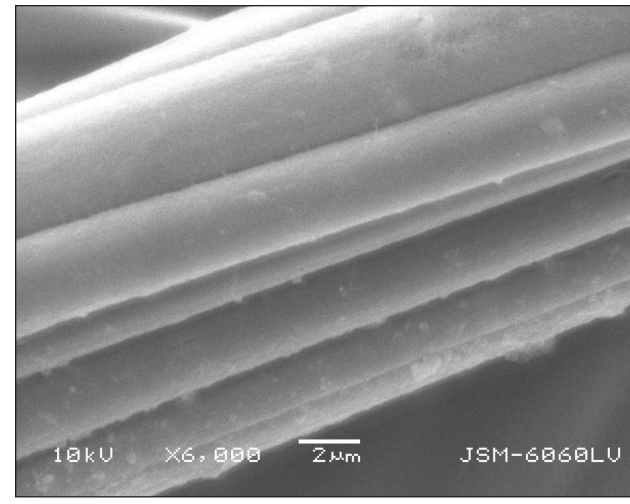
Surface topography

In our research, the effect of enzymatic treatment on the surface of the fibers was determined using SEM techniques. As seen from the SEM images in **Figs. 2-6**, the surface of enzymatically treated fibers (Figs. 4-5) was less even than the surface of untreated fibers (Figs. 2-3). There were some surface damages and irregularities, such as small holes and grooves along the fibers detected as the consequence of enzymatic treatment. Surface damages (e.g., longer holes) were more pronounced at viscose/chitosan than at viscose fibers. As seen from the micrograph (Fig. 6), chitosan that is bound on the surface of viscose fibers is clearly seen.

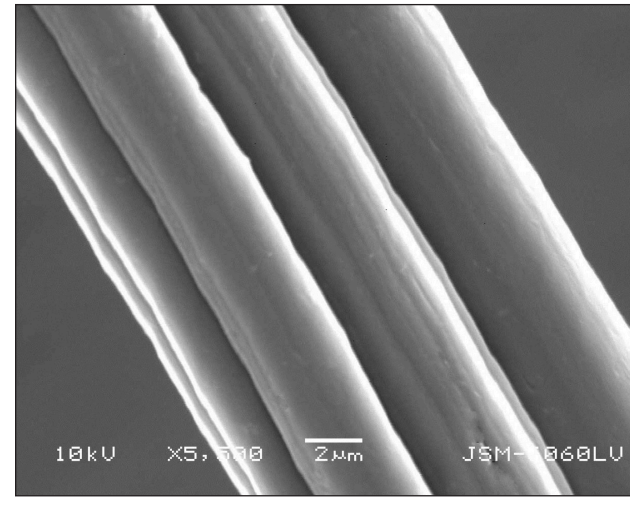
Structural characteristics

Generally, the structure of viscose/chitosan fibers is less ordered than that of viscose fibers. On average, viscose/chitosan fibers have shorter macromolecules, which result in a lower degree of polymerization, are less oriented, and have lower degree of crystallinity than viscose fibers (Table II). Because of the presence of α-cellulose and chitosan in viscose/chitosan fibers, the alignment and bonding of macromolecules in crystalline lattice is more difficult compared to pure cellulose molecules in viscose fibers.

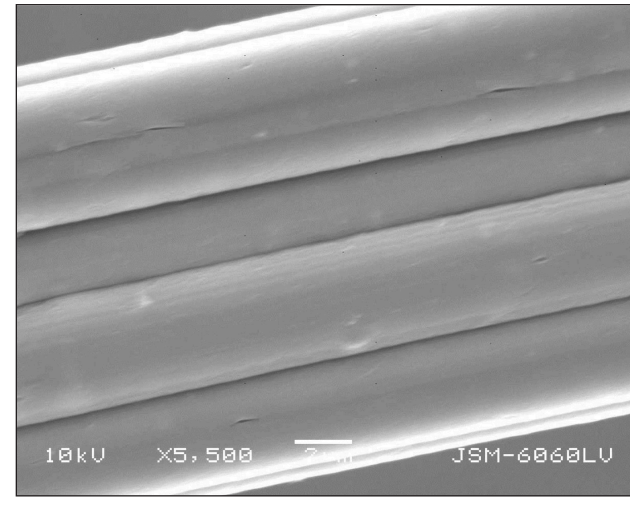
Treatment with the enzymes affects the orientation of macromolecules, and primarily tends to lower the orientation in



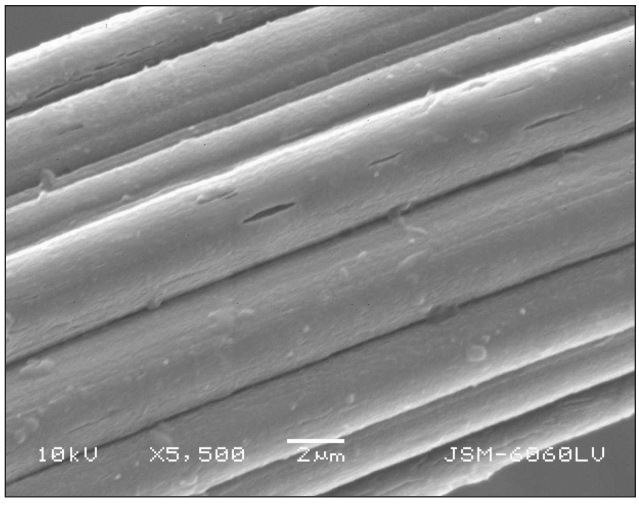
2. Untreated viscose fibers.



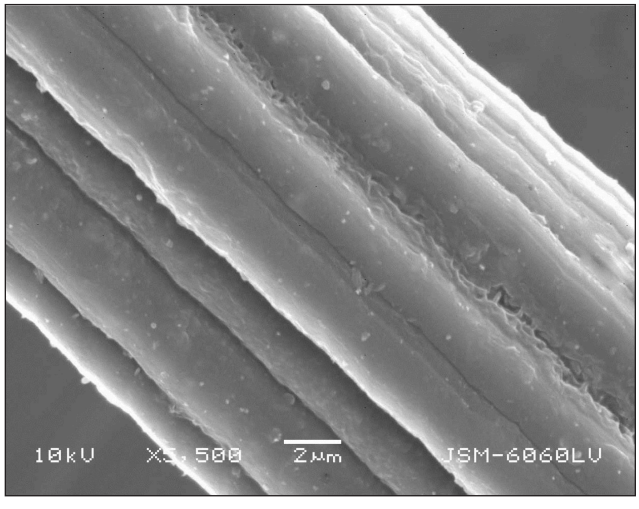
3. Untreated viscose/chitosan fibers.



4. Enzymatic treated viscose fibers.



5. Enzymatic treated viscose/chitosan fibers.



6. Viscose fibers treated with chitosan.

amorphous regions [21,22]. The average length of macromolecules is reduced, and cleavage of macromolecules occurs, particularly collapse of shorter molecules. In amorphous regions, arranged parts of macromolecules, long binding molecules and several shorter, accessible parts of the molecules (which can bind water) are present. Enzymes remove shorter molecules from the surface and cause rearrangement in amorphous and partly in crystalline areas, which leads to only a small lowering of the degree of crystallinity in the fibers. After 60 min of enzymatic treatment, the degree of polymerization of viscose fibers decreased by 6.9% and of viscose/chitosan fibers by 12.3%. The crystallinity of both fibers deceased by about 2%. The degree of polymerization of viscose fibers treated with chitosan also decreased, by 13.9%. The additional treatment of viscose fibers with the chitosan decreased the level of crystallinity and molecular orientation by more than 15%, suggesting that chitosan is bound not only on the surface of the fibers, but also interferes with the structure of viscose fibers.

Viscose fibers treated with the chitosan are less oriented and have a lower degree of polymerization and crystallinity than viscose/chitosan fibers. The reason lies in the different manufacturing routes. Viscose/chitosan fibers are manufactured from chitosan and cellulose pulp solutions, and the structure is formed by removing the solvent. The already formed structure of viscose fibers was treated with the chitosan that changed and partly destroyed the original structure of viscose fibers.

Results of structural measurements of viscose fibers treated with enzyme and chitosan show that macromolecules are shorter on average, which also indicates that the amount of ordered crystalline areas in fibers should be smaller. We assumed that the cleavage of cellulose molecules starts in the amorphous regions, releasing cellulose fragments, and then proceeds with the cleavage of the accessible cellulose molecule on the crystalline surface, leading to a lower degree of polymerization and lower orientation of molecules in amorphous regions.

Sorption characteristics

The results of the methylene blue dye method show that all fibers, untreated and treated, possess a considerable part of the carboxyl group. The higher the content of -COOH groups, the greater the amount of methylene blue dye is bound to the fibers. However, in addition to monovalent binding of dye cations to the carboxyl groups of cellulosic fibers, binding of the hydroxyl groups also occurs. Therefore, the ion-exchange interactions depend on the content of -COOH groups.

As expected, and seen in **Table III**, untreated viscose and viscose/chitosan fibers have fewer carboxyl groups. Likewise, enzymatic treatment causes an increase of carboxyl groups and free functional groups, which leads to lower zeta potential and higher values of surface free energy, resulting in a higher hydrophilic character of the fibers. Methylene blue dye is also adsorbed at other accessible places in the amorphous regions of fibers, not only by the carboxyl groups.

The results of the methylene blue dye method confirm the changes of structural characteristics of fibers determined

	V	V/C	$V_{-en.tr.}$	$V/C_{-en.tr.}$	$V_{-en+ch.tr.}$
-COOH, mmol/kg	46.43	46.66	48.91	47.36	47.28
RSD, %	0.39	0.73	0.72	0.23	2.05

III. Carboxyl content (-COOH) of untreated and treated viscose and viscose/chitosan fibers, determined using methylene blue dye method; RSD is relative standard variation.

Solvent	Sample									
	V		V/C		$V_{-en.tr.}$		$V/C_{-en.tr.}$		$V_{-en+ch.tr.}$	
	φ, °	RSD, %	φ, °	RSD, %	φ, °	RSD, %	φ, °	RSD, %	φ, °	RSD, %
Water	84.43	0.85	81.79	1.10	82.33	1.26	81.44	1.08	83.45	1.09
Heptane	88.09	1.93	83.06	1.09	85.76	0.87	82.76	1.49	86.11	0.39

IV. Values of contact angles (φ) of water and heptane on untreated and treated viscose and viscose/chitosan fibers; RSD = relative standard variation.

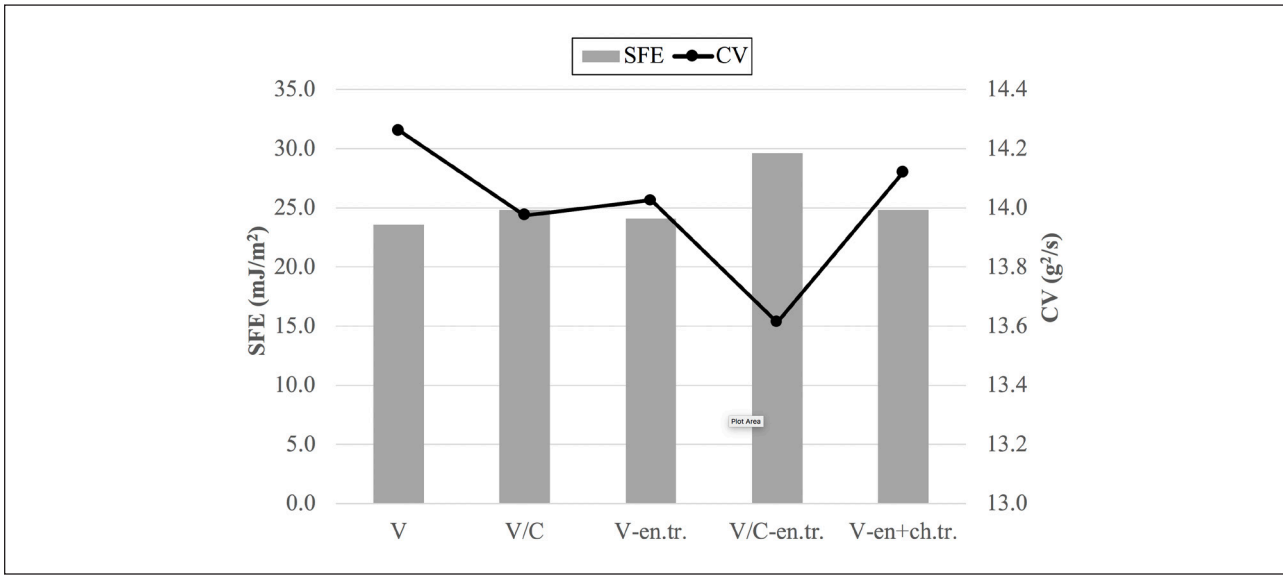
after enzymatic treatment and treatment of viscose fibers with chitosan.

The hydrophilic/hydrophobic character of fibers was determined using tensiometry. **Table IV** presents the contact angles of two different solvents with untreated and treated fibers. Contact angles were determined from the measured sorption velocities using the Washburn equation. The results represent the ability to determine the wetting behavior of fibers with two different reagents. The lowest contact angle with water was obtained at untreated viscose/chitosan fiber, which is 3.1% lower than untreated viscose fibers. The same trend is detected with heptane solvent. As expected, the enzymatic treatment of fibers lowers the contact angles for both solvents used. Lowering of the contact angle with the water of enzymatic treated viscose and viscose/chitosan fibers is the consequence of the structural changes, which resulted in more hydrophilic character of fibers. The differences are not significant, but still detected. Fibers tested in water have contact angles lower than tested with the heptane. The reason for this is the polar contribution of surface tension of each solvent, which reacts with the polar contribution of surface tension of the fibers.

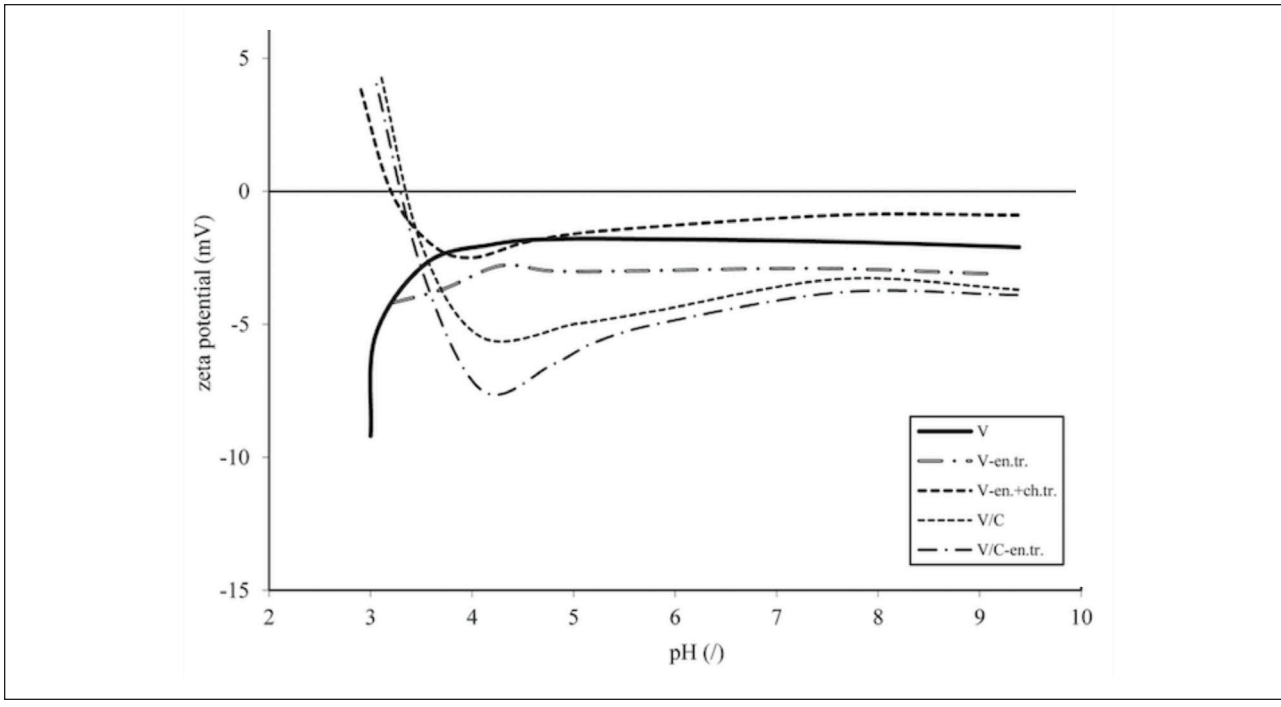
Surface free energy was determined on the basis of the Wendt Owens approximation procedure used for determining the interaction between the surface of the substrate and the liquid phase. As seen from **Fig. 7**, there are no significant differences among fibers. It appears that untreated viscose/chitosan fibers have a higher value of surface free energy (24.825 mJ/m²) than untreated viscose fibers (23.582 mJ/m²). The same trend is shown for enzymatic treated viscose/chitosan fibers, which reached the highest value among all treated samples (29.672 mJ/m²).

Capillary velocity for untreated and treated viscose fibers is higher in comparison with untreated and enzymatic treated viscose/chitosan fibers. Among all viscose fibers, the untreated sample achieved the highest value (14.26 g²/s). That correlates with structural characteristics; viscose fibers have the highest degree of polymerization and crystallinity among tested fibers, resulting in reduced absorption and wettability. Treatment with enzymes and chitosan changed the availability and amount of functional groups, as well as the mechanism of interaction. The lowest value of capillary viscosity (13.61 g²/s) was seen in the viscose/chitosan fibers treated with enzymes.

Zeta potential depends on the chemical structure, surface



7. Surface energy (SFE) and capillary velocity (CV) determination of untreated and treated viscose and viscose/chitosan fibers.



8. Zeta potential as function of pH of untreated and treated viscose and viscose/chitosan fibers.

polarity, fiber diameter, porosity, and specific surface interactions with water and swelling in water [30]. Low zeta potential is the result of adsorption of water and anions, with a simultaneous potential drop in the surface layer. In our research, measurements showed the lowest zeta potential in the alkaline pH region for viscose/chitosan fibers (**Fig. 8**). Adsorption of water and electrolyte solution causes swelling of the surface, thereby reducing the activity area. Negative charge of viscose/chitosan and viscose fibers is caused by the presence of -COOH and -OH groups.

Higher values of zeta potential indicates less hydrophilic character of the fibers. Because of the presence of chitosan in viscose/chitosan fibers and viscose fibers treated with chitosan, a positive zeta potential occurs at a pH between 3 and 4, which decreases at a higher pH. Figure 8 shows that the untreated viscose/chitosan fibers are more hydrophilic and have more anionic groups (mostly OH groups) than do untreated viscose fibers. Because of that, untreated fibers have a lower zeta potential. Enzymatic treatment of viscose increases the number of anionic groups (OH and COOH), which is noticed from lower zeta potential in the alkaline region. After enzymatic treatment of viscose/chitosan fibers, the zeta potential is slightly lower, mostly because of a slightly higher number of COOH groups. The number of anionic groups of viscose fibers treated with enzyme and chitosan is very similar as in enzyme-treated viscose fibers. At the lowest pH levels, all fibers with chitosan have positive zeta potential because of protonated ammonia groups.

The adsorption of basic (cationic) dye in alkaline pH is carried out on anionic dissociated hydroxyl in carboxyl groups of fibers. Although the differences in the adsorption of the basic dye between the fibers are very small, the highest adsorption capacity has viscose/chitosan fibers with 81.1% of adsorbed dye (**Table V**). These fibers are more hydrophilic and, according to zeta potential measurements (Fig. 8), have more anionic groups and are 3% more adsorptive for

Parameter	Sample				
	V	V/C	$V_{-en.tr.}$	$V/C_{-en.tr.}$	$V_{-en+ch.tr.}$
q, mg/g RSD, %	0.7834	0.8065	0.7976	0.7996	0.7759
	0.15	0.13	0.14	0.33	0.15
% of adsorbed dye RSD, %	78.81	81.14	80.24	80.44	78.06
	0.15	0.13	0.04	0.26	0.14

V. Adsorption capacity of fibers (q) and percentage of adsorption of basic dye (methylene blue); RSD is relative standard deviation.

Parameter	Sample				
	V	V/C	$V_{-en.tr.}$	$V/C_{-en.tr.}$	$V_{-en+ch.tr.}$
q, mg/g RSD, %	0.0089 /	0.8301 0.09	0.0345 /	0.7242 0.11	0.7994 0.16
% of adsorbed dye RSD, %	0.89 /	83.04 0.08	3.48 /	72.45 0.17	79.97 0.14

VI. Adsorption capacity of fibers (q) and percentages of adsorption of acid dye (Bemacid yellow GR 200%); RSD = relative standard variation.

Sample	σ, (cN/dtex)	ε, (%)	A_{sp}, J/g	σ_y, (cN/dtex)	E_o, GPa
V	2.51	33.20	64.99	0.80	4.59
V/C	2.15	36.71	65.01	0.81	4.60
$V_{-en.tr.}$	2.59	42.00	67.00	0.37	4.14
$V/C_{-en.tr.}$	2.12	38.55	64.87	0.75	4.55
$V_{-en+ch.tr.}$	2.68	37.44	54.55	0.78	4.39

VII. Mechanical properties: stress at break (σ), strain at break (ε), specific work at break (Asp) yield stress (σ_y), and elastic modulus (E_0) of fibers.

basic dye than viscose fiber. Enzymatic treatment of viscose/chitosan fiber practically has no effect on the adsorption of dye. Measurements (Table V) show only a slight (less than 0.9%) decrease in the adsorption capacity. After enzymatic treatment of viscose fiber, the adsorption on viscose is a little bit higher, with 80.2% of adsorbed dye, as on untreated viscose with 78.8% of adsorbed dye, because of having a more open and hydrophilic structure of enzymatically treated fiber with a higher number of anionic groups. The viscose treated with enzyme and chitosan has the same adsorption capacity for basic dye as viscose fiber. It has higher numbers of carboxylic groups (Table III). However, according to zeta potential (Fig. 8), the number of anionic groups (-OH) at alkaline pH is lower than in viscose.

The anionic acid dye of a small molecule adsorbs in acid medium on the cationic ammonium groups of chitosan in fibers. Adsorption does not occur on viscose, which does not have amino groups, although enzymatically treated viscose, which is more wettable, takes slightly more dye than does untreated viscose (**Table VI**).

The viscose/chitosan has the highest adsorption capacity for acid dye among all fibers with chitosan; it adsorbed 83% of dye. Enzymatically treated viscose/chitosan has 13% lower adsorption capacity for acid dye than does untreated viscose/chitosan fiber, suggesting a lower number of amino groups in viscose/chitosan treated with enzyme, which is also seen from zeta potential measurements (Fig. 8). The adsorption of acid dye on viscose treated with enzyme and chitosan is a little bit lower (3.7%) than on viscose/chitosan fiber.

Mechanical properties

Table VII shows tensile properties of the fibers. Tensile properties depend on the degree of crystallinity, degree of polymerization, and molecular orientation. In general, the influence of enzymatic treatment on the tensile properties of fibers is quite small, the changes in stress at break and specific work at break are below 5%. Depolymerization of macromolecules first occurs in amorphous regions. The influence on the strength of fibers is small, as strength is mainly determined from the crystalline regions. Shorter macromolecules and less ordered structure has more influence on the stretchability of fibers, resulting in an increase in the strain at break and decrease of yield stress and elastic modulus for both fibers treated with the enzyme. These changes are more evident in enzymatically treated viscose fibers. The treatment of viscose fiber with the enzyme and chitosan had no influence on fiber strength. Even a small increase in stress at break was noted. The treatment influenced the deformability, the strain at break increased, and the resistance to deformation, elastic modulus, and work at break were lowered.

CONCLUSIONS

In this study, we compared the sorption properties of viscose and viscose/chitosan fibers, first on untreated and afterwards on enzymatic treated fibers. Because of the higher zeta potential, capillary velocity, and contact angle with water, the untreated viscose fibers had lower wettability and were less adsorptive for basic dye than were untreated viscose/chitosan fibers.

Viscose fibers treated with enzyme cellulase have im-

proved sorption properties because the enzymes caused changes not only on the surface, but also in the amorphous parts of fibers. Enzymatic treatment reduced the orientation of macromolecules, the degree of crystallinity, and the degree of polymerization. More functional groups became available, which in turn resulted in a greater absorbency. Similarly, viscose/chitosan fibers treated with enzymes were less crystalline, had a lower degree of polymerization and a higher amount of carboxylic groups, lower zeta potential, and a higher value of surface free energy than did untreated fibers.

Viscose fibers treated with chitosan after enzymatic treatment had the improved sorption properties of enzyme-treated viscose fibers. The research has shown that treatment with enzymes and chitosan improved sorption properties, without significant damage to the fibers. Fibers showed sorption behavior similar to that of viscose/chitosan fibers; therefore, chitosan-treated viscose fibers could be a good substitute for viscose/chitosan fibers. **TJ**

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ABOUT THE AUTHORS

We chose this topic to research because of our interest in biobased materials. Our research is focused on fibers, paper, packaging, and textiles and the characterization of these materials. The most challenging aspect of the study was the functionalization process.

One lesson we learned from this study was that a literature review gives you the starting point for the experimental work, which then has to be done with a lot of trials. We were surprised to be able to obtain better fiber characteristics than expected.

Mills might benefit from this functionalization of regenerated cellulose fibers, which could lead to new products with added value. Our next step is to try different treatments and functionalizations of various substrates and optimization of processes.

Brodnjak

Gregor-Svetec

Klančnik

Brodnjak is assistant professor, Gregor-Svetec is professor, and Klančnik is assistant professor,University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Slovenia. Email Gregor-Svetec at diana.gregor@ntf.uni-lj-si.

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