BIOACTIVE TEXTILE MATERIALS BASED ON CELLULOSE AND CHITOSAN

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ABSTRACT: *Here, we present a detailed review of recent research and achievements in the field of bioactive textile materials based on cellulose and chitosan. The most important properties of cellulose and chitosan are outlined, giving rise to the interest in their combining. Their combination is particularly attractive because both cellulose and chitosan are not harmful to human beings and the environment. Rising living standards and increased environmental awareness are driving forces for the development of bioactive textile materials based on cellulose and chitosan. We present various types of bioactive textile materials based on cellulose and chitosan that we have developed recently. In this review, we have shown that the field of bioactive textile materials based on cellulose and chitosan is an inexhaustible source of ideas and opportunities for further development.*

Keywords: *cellulose, chitosan, textile materials, bioactivity.*

BIOAKTIVNI TEKSTILNI MATERIJALI NA BAZI CELULOZE I HITOZANA

APSTRAKT: *Ovde predstavljamo detaljan pregled novijih istraživanja i dostignuća u oblasti bioaktivnih tekstilnih materijala na bazi celuloze i hitozana. Navedena su najvažnija svojstva celuloze i hitozana, koja izazivaju interesovanje za njihovo kombinovanje. Njihovo kombinovanje je posebno atraktivno jer i celuloza i hitozan nisu štetni za ljude i životnu sredinu. Rastući životni standard i povećana ekološka svest su pokretačke snage za razvoj bioaktivnih tekstilnih materijala na bazi celuloze i hitozana. Predstavljamo različite vrste bioaktivnih tekstilnih materijala na bazi celuloze i hitozana koji su razvijeni u našim laboratorijama. U ovom pregledu smo pokazali da je oblast bioaktivnih tekstilnih materijala na bazi celuloze i hitozana nepresušan izvor ideja i mogućnosti za njen dalji razvoj.*

Ključne reči: *celuloza, hitozan, tekstilni materijali, bioaktivnost.*

1. INTRODUCTION

Increased environmental awareness, the predicted reduction of fossil resources as well as the increased costs of their extraction, have fueled a surge of interest in renewable and sustainable resources. The greatest interest was attracted by polysaccharides due to their renewability, recyclability and biodegradability, as well as the fact that they represent the most abundant fraction of biomass. Cellulose and chitosan are the most widespread natural polysaccharides and have been used for a long time in various applications [1].
However, the number of reports on the successful combination of these two polysaccharides has only become significant since the 1990s. The consideration of combining these two polysaccharides was based on the fact that both have a similar molecular structure, but different properties that can be advantageously combined. Cellulose primarily offers good structural, mechanical, and hydrophilic properties, while chitosan offers a wide range of bioactive properties [2].
Knowledge of interactions at the molecular level between cellulose and chitosan was crucial for the development of bioactive textile materials based on cellulose and chitosan. The research groups of *Holmberg* [3] and *Laine* [4] provided some essential information about such interactions. Based on these theoretical studies, various bioactive textile materials based on cellulose and chitosan have been developed to date.
In this review, we aim to present the scope and complexity of the combination of these two exceptional polysaccharides, cellulose and chitosan, and their importance for the development of bioactive textile materials based on them. Special attention is given to viscose fabric and various approaches to combining it with chitosan.

2. CELLULOSE

Cellulose is the most abundant natural polymer on Earth with ~1.5×10^{12} tons of cellulose produced each year. The molecular structure of cellulose, isolated from plant cell walls, was first discovered and determined by the French scientist *Anselme Payen* in 1838. In addition to plants, cellulose is also produced by some types of algae, fungi, and bacteria [5].
Cellulose is an organic compound consisting of a linear chain of β (1→4) linked D glucose units (Figure 1.). A single D glucose unit is a hexose that takes on one of α or β forms, depending on the position of the hydroxyl groups. As a result of the glucose structure, cellulose contains a large amount of free hydroxyl groups located at the C2, C3, and C6 atoms. The main hydroxyl groups along polysaccharide chains can be easily modified by oxidation, esterification, acylation, grafting, and etherification resulting in a wide range of cellulose derivatives [6]. Native cellulose or cellulose I is the most crystalline type of cellulose which exists in two forms: Iα and Iβ. Cellulose Iα crystal has a triclinic unit cell, and cellulose Iβ crystal has a monoclinic unit cell. Both, cellulose Iα and Iβ are present in native cellulose structures but in different ratios depending on the source of cellulose. Other allomorphs of cellulose are possible, the most common of which are cellulose II, III, and IV. Cellulose II can be prepared by mercerisation or regeneration of cellulose I. Cellulose

III can be prepared from cellulose I or cellulose II by treatment with liquid ammonia, resulting in cellulose III1 or cellulose III2. Cellulose IV1 and IV2 can be prepared by heating cellulose III1 or cellulose III2 in glycerol [7].
Single cellulose macromolecules interconnect via hydrogen bonds to form cellulose microfibrils that exhibit highly-ordered crystalline and low-ordered amorphous regions. The intermolecular hydrogen bonds in the crystalline regions are strong, which ensures the good structural and mechanical properties of cellulose, as well as its insolubility in most solvents. They also provide prevention of cellulose melting. The cellulose macromolecules are usually longer than the crystalline regions. As a consequence, one cellulose macromolecule can run from one crystalline region to another, passing through amorphous regions, and thereby holding the crystalline and amorphous regions together. Due to the large distance between cellulose macromolecules in amorphous regions, fewer intermolecular hydrogen bonds are established between cellulose macromolecules, which allows cellulose macromolecules to form hydrogen bonds with other molecules, such as water. This gives macromolecular cellulose its hygroscopic and hydrophilic characteristics [8].

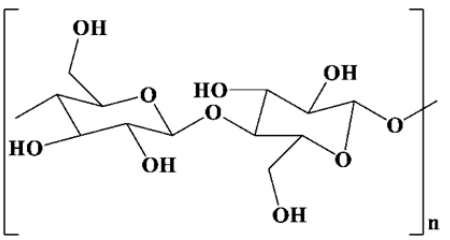


Figure 1: Molecular structure of cellulose [6]

3. CHITOSAN

Chitosan is a polysaccharide obtained by alkaline deacetylation of chitin and is the second most commonly used natural polymer. Chitin was discovered in 1811. when the French chemist and pharmacist *Henri Braconnot* studied fungi. It is the main structural component of the exoskeleton of crustaceans (such as spiders, butterflies, ladybirds, lobsters, prawns, and crabs) as well as the cell walls of certain fungi. According to its molecular structure, chitin is poly-N-acetyl-D-glucosamine, which is formed during biosynthesis. The molecular structure of chitin is similar to the molecular structure of cellulose, with the difference that the hydroxyl group on the C2 atom of each glucosidic unit of chitin is replaced by an acetylated amino group. Given that the mutual packing of chitin macromolecules in the crystal lattice takes place in a manner analogous to cellulose, the supramolecular structure of chitin is extremely similar to the supramolecular structure of cellulose. But, unlike cellulose, which exists in nature in only one form, chitin appears in nature in three different forms: α, β, and γ [9].
Complete alkaline deacetylation of chitin is impossible by conventional procedures, so commercial chitosan typically contains 15-25% acetylated amino groups. Therefore,

chitosan is a heteropolysaccharide consisting of β (1→4) linked units of 2-acetamido-2-deoxy-β–D-glucopyranose and 2-amino-2-deoxy-β–D-glucopyranose units (Figure 2.) [9].

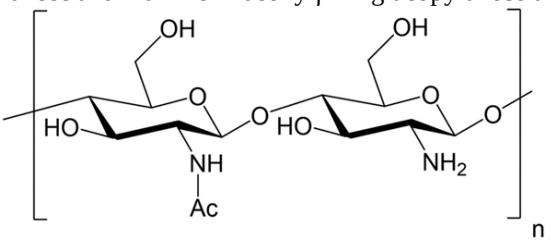


Figure 2: Molecular structure of chitosan [10]

Unlike most polysaccharides that are neutral or negatively charged, chitosan is positively charged due to the presence of a large number of free amino groups in its structure. Consequently, chitosan can only be dissolved in dilute acid solutions, which limits its application in various fields. To overcome this limitation, many scientists have focused their research on the chemical modification of chitosan to obtain water-soluble chitosan derivatives [10].

Regardless of solubility limitations, chitosan stands out among numerous bioactive compounds due to its biocompatibility, biodegradability, non-toxicity, and wide range of bioactive properties. Its antibacterial, antifungal, antiviral, antioxidant, anti-inflammatory, analgesic, hemostatic, anticoagulant, and anticancer properties have made it very suitable for obtaining products used in health care and medicine [11, 12]. In recent years, the most attention has been devoted to studying its antimicrobial and antioxidant properties. Chitosan has been found to possess a broad spectrum of antimicrobial activity against fungi, and Gram-positive and Gram-negative bacteria. However, the exact mechanisms of chitosan's antimicrobial activity have not yet been fully elucidated. The most accepted hypothesis is based on the disruption of the cell membrane/cell wall of the microorganism due to the interactions between the positively charged chitosan and the negatively charged membrane of the microorganism [13].

Generally accepted mechanisms of antimicrobial action of chitosan are based on:

- disruption of the cell membrane/cell wall,
- interactions with the DNA of microorganisms,
- chelation of nutrients necessary for the survival of microorganisms, and
- the formation of a dense polymer film on the surface of microorganisms [13].

Protonated amino groups of chitosan play a key role in disrupting the cell membrane/cell wall of microorganisms. When the pH value of chitosan's environment is lower than its pKa value, amino groups are protonated giving chitosan a positive charge. The cell wall of Gram-positive bacteria is negatively charged due to the presence of teichoic acid located in the thin peptidoglycan layer, while the cell wall of Gram-negative bacteria is extremely negatively charged due to the presence of lipopolysaccharides located in the outer layer of the membrane. Also, in the case of fungi, the cell wall contains components that make it negatively charged. Electrostatic interactions between positively charged chitosan

molecules and negatively charged components of the microorganism's cell wall can lead to blocking intra/extracellular exchange or even rupture of the cell wall and, ultimately, leakage of cytoplasmic contents [13]. *Fu* et al. [14] showed that teichoic acids found in the cell wall of *S.aureus* interact with chitosan derivatives and thus inhibit bacterial growth, in some cases up to almost 100%. Using electron microscopy, *Li* et al. [15] recorded damage to the cell membrane and leakage of the cytoplasmic content of *E.coli* in the presence of chitosan. Interactions of chitosan with the DNA of microorganisms are particularly related to low molecular weight chitosans. Hydrolysis products of low molecular weight chitosan can establish interactions with the DNA of microorganisms, which affects protein synthesis and inhibition of mRNA of microorganisms [13]. This mechanism of antimicrobial action of chitosan was confirmed by *Liu* et al. [16] against *E.coli*, and by *Sebti* et al. [17] against *A. niger*. Chelation of nutrients necessary for the survival of microorganisms is based on the ability of chitosan to complex with metal ions. Cell wall components of both Gram-positive and Gram-negative bacteria attract divalent metal ions that are essential for their survival. Phosphate groups of teichoic acid found in the peptidoglycan layer of Gram-positive bacteria particularly attract Mg^{2+} and Ca^{2+} ions, which participate in maintaining enzyme functions and membrane integrity. Lipopolysaccharides, components of the outer membrane layer of Gram-negative bacteria, also have a strong affinity for divalent metal ions due to their negative charge. In this regard, chitosan negatively affects the survival of microorganisms by chelating metal ions and nutrients that are necessary for the growth of microorganisms. The formation of a dense polymer film on the surface of microorganisms is characteristic of chitosans of high molecular weight, which can be deposited on the surface of microorganisms and thus prevent the intake of nutrients and oxygen into them, which has a particularly negative effect on the survival of aerobic bacteria [13]. The deposition of chitosan on the outer membrane of *E.coli* was recorded by *Helander* et al. [18] using electron microscopy.

Chitosan has the ability to activate antioxidant mechanisms in human cells that prevent oxidative stress responsible for the creation of reactive oxygen species (ROS) at diseased sites in the body. Chitosan as a ROS scavenger has distinctive antioxidant activity that can prevent peroxidation and degradation of cell membranes, lipids, proteins, and genomes. This unique feature results from the reaction of ROS with the free amino and hydroxyl groups of chitosan leading to an increase in the stability of ROS [13]. *Sun* et al. [19] reported that chitosan and its derivatives act as hydrogen donors for ROS neutralization.

The latest research has shown that chitosan nanoparticles have superior permeability and immune modulation, without toxicity to human cells, and enhanced antibacterial activity compared with bulk chitosan. Withal, much research effort has been devoted to the chitosan nanoparticles/metals hybrids development, to connect the chelating properties of chitosan with the antibacterial properties of metals. Metal chelation with chitosan increases the positive charge density of chitosan nanoparticles, which leads to their enhanced adsorption onto the negatively charged bacterial cell wall, and thus to the inhibition of bacterial cell growth. Zinc is one of these metals, which show great antibacterial properties. An additional advantage of using chitosan nanoparticles/metals hybrids is the US-FDA

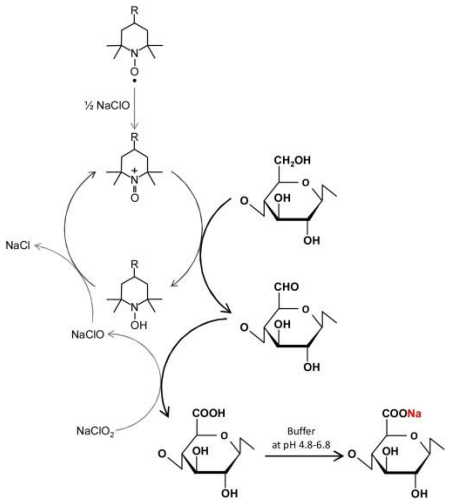
approval of chitosan and zinc as safe for many dietetic and wound dressing applications [20].

3. TEXTILE MATERIALS BASED ON CELLULOSE AND CHITOSAN

Similarities between the chemical and molecular structures of textile materials based on cellulose and chitosan/chitosan-based nanoparticles enable high affinity between them. The most likely intermolecular interactions between textile materials based on cellulose and chitosan/chitosan-based nanoparticles are based on H-bonds and *Van der Waals* forces. However, for more intense and irreversible binding between textile materials based on cellulose and chitosan/chitosan-based nanoparticles, it is necessary to introduce carboxyl and/or aldehyde groups into/onto the textile materials based on cellulose, which are then potential anchoring sites for chitosan/chitosan-based nanoparticles. Carboxyl groups of textile materials based on cellulose as host material can provide electrostatic attraction between them and chitosan/chitosan-based nanoparticles as adsorbate, while aldehyde groups are an excellent choice because they can allow covalent binding of chitosan/chitosan-based nanoparticles by forming a *Schiff*'s base. These bounds, when present at the same time, may serve as a starting point for irreversible binding of chitosan/chitosan-based nanoparticles onto textile materials based on cellulose [20, 21].
2,2,6,6-tetrametilpiperidin-1-oksil (TEMPO) oxidation and coating with TEMPO-oxidized cellulose nanofibrils (TOCN) proved to be very effective in introducing a large number of functional groups (carboxyl and aldehyde) in/on the textile materials based on cellulose. In this way, subsequent improved binding of chitosan/chitosan-based nanoparticles in/on the textile materials based on cellulose is enabled. It is important to point out that the coating of textile materials based on cellulose with TOCN has an advantage over the TEMPO oxidation of textile materials based on cellulose in terms of preserving mechanical properties. It is known that the structure of cellulose changes during TEMPO oxidation, which generally leads to a significant deterioration of the mechanical properties of TEMPO-oxidized textile materials based on cellulose. In contrast, it was found that coating textile materials based on cellulose with TOCN improves their mechanical properties [21]. The section below provides a brief overview of the TEMPO oxidation of the textile materials based on cellulose as well as the obtaining of TOCN and the coating of textile materials based on cellulose with TOCN.
TEMPO oxidation of textile materials based on cellulose in TEMPO/NaClO/$NaClO_2$ system under weakly acidic conditions is a complex reaction. The mechanism of TEMPO oxidation of textile materials based on cellulose in the TEMPO/NaClO/$NaClO_2$ system is shown in Figure 3. (a). As can be seen from Figure 3. (a), the reaction starts by oxidation of TEMPO to the oxoammonium ion ($TEMPO^+$) with NaClO. $TEMPO^+$ oxidizes the hydroxyl groups at the C6 atoms of textile materials based on cellulose to aldehyde groups and is reduced to the N-hydroxy-TEMPO. The aldehyde groups are directly oxidized to the sodium carboxylate groups with $NaClO_2$, and then NaClO generated *in situ* from $NaClO_2$ oxidizes the N-hydroxy-TEMPO, again to the TEMPO+. In addition to aldehyde groups formed as intermediates at the C6 atoms cellulose, a low amount of aldehyde groups can

also be formed as reducing ends of cellulose due to the cleavage of the 1,4-glycosidic bond by β-elimination of cellulose during TEMPO oxidation of textile materials based on cellulose in TEMPO/NaClO/$NaClO_2$ [22].

a)



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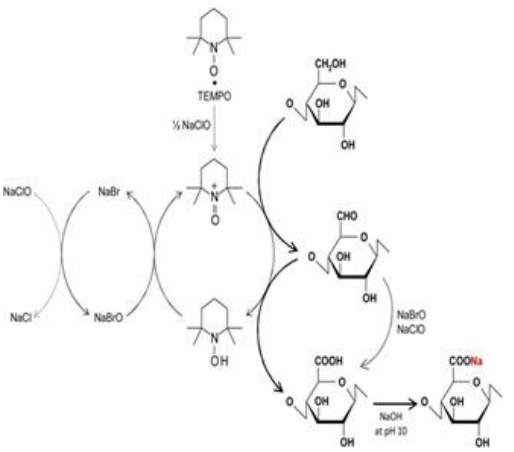

Figure 3: TEMPO oxidation of textile materials based on cellulose in TEMPO/NaClO/$NaClO_2$ system under weakly acidic conditions (a), TEMPO oxidation of cotton in TEMPO/NaBr/NaClO system under alkaline conditions (b) [22]

The most promising way to obtain TOCN is a combination of TEMPO oxidation of cotton in a TEMPO/NaBr/NaClO system under alkaline conditions, and subsequent mechanical

disintegration of TEMPO-oxidized cotton to nanofibrils using an ultrasonic homogenizer [13]. The mechanism of TEMPO oxidation of cotton in the TEMPO/NaBr/NaClO system under alkaline conditions is shown in Figure 3. (b). The reaction starts with the oxidation of TEMPO to the oxoammonium ion ($TEMPO^+$) with NaClO. $TEMPO^+$ oxidizes the hydroxyl groups at the C6 atoms of cotton to aldehyde groups. The reduced TEMPO or N-hydroxy-TEMPO is then oxidized by NaBrO, formed from NaBr by oxidation with NaClO. The aldehyde groups are directly oxidized to the sodium carboxylate groups with NaClO and/or NaBrO. Compared to TEMPO oxidation of cellulose in TEMPO/NaClO/$NaClO_2$ system under weakly acidic conditions, during TEMPO oxidation of cellulose in TEMPO/NaBr/NaClO system under alkaline conditions a larger amount aldehyde groups are formed as reducing ends of cellulose due to more pronounced cleavage of the 1,4-glycosidic bond by β-elimination of cellulose. In other words, during TEMPO oxidation of cellulose in TEMPO/NaBr/NaClO system under alkaline conditions leads to more pronounced depolymerization of cellulose, which is desirable for facilitated mechanical disintegration of TEMPO-oxidized cotton to nanofibrils [13, 22].

After TEMPO oxidation in TEMPO/NaBr/NaClO system under alkaline conditions oxidation, the nanofibrils inside the cotton are more easily separated from each other. Namely, the repulsive forces between the ionized carboxyl groups overcome the attractive forces between the hydroxyl groups that hold the nanofibrils inside the cotton together. It was established that after TEMPO oxidation in the TEMPO/NaBr/NaClO system under alkaline conditions oxidation, mechanical defibrillation of the same raw material is achieved with drastically lower energy consumption. Until now, after TEMPO oxidation in the TEMPO/NaBr/NaClO system under alkaline conditions oxidation, mechanical treatments were most often used with the use of a kitchen blender and the ULTRA-TURRAX® systems. However, it was found that mechanical treatment with the use of an ultrasonic homogenizer is the fastest and requires the least energy consumption. The operating principle of the ultrasonic homogenizer is based on the generation of hydromechanical forces that lead to the defibrillation of TOCN from the starting material with a yield of over 95% [13].

Coating of textile materials based on cellulose with TOCN is based on immersing textile materials based on cellulose in a water dispersion of TOCN. Then excess water is removed by squeezing it onto a laboratory padder. *Korica* et al. [13] investigated the stability of the adsorbed TOCN on the textile materials based on cellulose by monitoring the zeta potential changes with the time of exposure of textile materials based on cellulose coated with TOCN to the aqueous solution. The obtained results showed that the exposure of textile materials based on cellulose coated with TOCN to an aqueous solution does not lead to changes in the zeta potential that could indicate the release of TOCN. In other words, the obtained results indicated that during the coating of textile materials based on cellulose with TOCN, an extremely strong connection between textile materials based on cellulose and TOCN was achieved, based on the system of hydrogen and *Van der Waals* bonds.

In previous research in this area, *Korica* et al. [13, 20, 21, 23] obtained TEMPO-oxidized and TOCN-coated viscose fabrics with increased content of carboxyl and aldehyde groups. TEMPO.oxidized viscose fabric has 438 mmol/kg cellulose carboxyl groups and 440

mmol/kg cellulose aldehyde groups, while TOCN-coated viscose fabric has 86 mmol/kg cellulose carboxyl groups and 27 mmol/kg cellulose aldehyde groups. Compared to raw viscose fabric, TEMPO-oxidized and TOCN-coated viscose fabrics achieved improved binding of chitosan/chitosan-based nanoparticles. In addition, TEMPO-oxidized and TOCN-coated viscose fabrics also showed improved persistence of bound chitosan/chitosan-based nanoparticles during multiple washing cycles.

Korica et al.[13] conducted experiments on a model of ultra-thin films to determine which pH values are most suitable for improved binding of chitosan/chitosan-based nanoparticles on textile materials based on cellulose. It has been proven that pH 5.5 is the most suitable in terms of simultaneously establishing electrostatic and covalent interactions between textile materials based on cellulose and chitosan/chitosan-based nanoparticles. In their further research [13, 20, 21 23], raw, TEMPO-oxidized, and TOCN-coated viscose fabrics were functionalized with chitosan (CH), and chitosan nanoparticles without and with embedded zinc (NCH and NCH+Zn, respectively) at pH 5.5. Compared with raw viscose fabric, TEMPO-oxidized, and TOCN-coated viscose fabrics bound a higher amount of CH, NCH, and NCH+Zn. Accordingly, TEMPO-oxidized and TOCN-coated viscose fabrics functionalized with CH, NCH, and NCH+Zn achieved higher antibacterial and antioxidant activity than raw viscose fabric functionalized with CH, NCH, and NCH+Zn.

The washing durability of raw, TEMPO-oxidized, and TOCN-coated viscose fabrics functionalized with CH, NCH, and NCH+Zn was monitored after one, three, and five washing cycles. As a consequence of a higher amount of irreversibly bound CH, NCH, and NCH+Zn, TEMPO-oxidized and TOCN-coated viscose fabrics contributed more efficient and durable antibacterial and antioxidant activity than raw viscose fabric. TEMPO-oxidized viscose fabric functionalized with CH achieved the most efficient and durable antibacterial activity: up to five washing cycles in the case of *S.aureus*, and up to three washing cycles in the case of *E.coli*. The antioxidant activity of all viscose fabrics functionalized with CH, NCH, and NCH+Zn was not significantly deteriorated after multiple washing cycles.

3. CONCLUSION

The development of bioactive textile materials based on cellulose and chitosan represents a particularly interesting and promising strategy in the context of new sustainable and environmentally friendly products obtained from renewable resources. As shown in this brief review, chemical modification and intelligent combination of these polysaccharides can be exploited to develop of new bioactive textile materials based on cellulose and chitosan with improved and tailored properties and therefore with potential applications as medical textiles.

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