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REVIEW PAPER

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NEW FUNCTIONALITIES IN CELLULOSIC FIBERS DEVELOPED BY CHEMICAL MODIFICATION*

This paper gives an overview of the current state in the field of cellulosic fibers functionalization by chemical modification. The emphasis is placed on the selective (periodate and TEMPO oxidation) and non-selective (permanganate and peroxide) cellulose oxidation, non-conventional methods for obtaining man-made cellulosic fibers, methods for obtaining antimicrobial cellulosic fibers, as well as method for obtaining two-component polysaccharide fibers. To provide evidence on the achieved functionalities we mainly used capillary rise method, moisture and iodine sorption method, water retention power, NaOH uptake, different ions sorption, Cu-number, carbonyl- and carboxyl-selective labelling and antimicrobial tests.

Cellulose is one of the oldest natural polymers and hemp (*Cannabis sativa*) was most likely the first plant cultivated by humankind for its textile use. Today is more than clear that chemical fibers, created to replace natural fibers, after quite a long period of intensive application, are considered inferior to natural ones, especially in respect to physiological, hygienic, and health properties, as well as comfort and ecological properties. Further advantages of cellulosic fibers are that they are renewable, biodegradable, and can be derivative to yield additional values to improve quality of life and thus to tap new markets with the product. Regarding new directions in cellulose research, we can identify three main topics. The first is the field of analytical problems and routes of derivatization reaction; the second topic is the search for completely new products and uses, and the third topic is that of mass production [1–3].

This paper gives an overview of the current state in the field of cellulosic fibers functionalization by chemical modification. Emphasis is placed on the selective (periodate and TEMPO oxidation) and non-selective (permanganate and peroxide) cellulose oxidation, non-conventional methods for obtaining man-made cellulosic fibers, methods for obtaining antimicrobial cellulosic fibers, as well as method for obtaining two-component polysaccharide fibers. To provide evidence on the achieved functionalities we mainly used capillary rise method, moisture and iodine sorption method, water retention power, NaOH uptake, different ions sorption, Cu-number, carbonyl- and carboxyl-selective fluorescence labelling and antimicrobial tests.

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CELLULOSE OXIDATION

The oxidation of cellulosic materials is a quite frequent procedure in cellulose chemistry, used to impart special properties on the cellulosic fibers. Cellulose, because of its polyhydric alcohol structure, is very sensitive to oxidizing media. The extensive modifications, which accompany this reaction, give rise to products whose chemical and physical properties depend upon the oxidizing reagent used, and the acidity or basicity of the medium in which oxidation occurs. The chemical structure of cellulose is altered in a way that hydroxyl groups are oxidized into the corresponding carbonyl structure, i.e. an aldehyde at C-6 and a ketone at C-2 and C-3, or carboxyl moiety (at C-6). Oxidation can also be accompanied by a change in the carbon skeleton of the cellulose backbone: a carbon-carbon bond cleavage between C-2 and C-3, for instance, allows for the introduction of aldehyde or carboxyl structures also at C-2 and C-3, which otherwise would not be possible. Cellulose degradation (chain cleavage) often accompanies the oxidation, but is actually caused by subsequent reactions and not by the oxidation itself.

The functionalities introduced by oxidation of cellulose are either used directly because of their special properties, e.g. hydrophilization or even water solubility by introduction of carboxyl groups, or they are used as reactive "chemical hooks" for further chemical modification.

Selective cellulose oxidation

There are two common procedures frequently applied for selective oxidation of cellulose, the TEMPO oxidation and the periodate oxidation. Oxidative conversion of glucans by the system 2,2',6,6'-tetramethylpiperidine-1-oxyl (TEMPO) / sodium hypochlorite / potassium bromide was first reported in 1994 [4,5] and has been the subject of several studies since then [6,7]. The reaction was described to cause selective oxidation at C-6 of the anhydroglucose

units to carboxylic groups via the intermediate aldehyde stage, finally producing water-soluble polyglucuronic acids [7] (Figure 1). The nitroxyl radical affects the oxidation from the alcohol to the aldehyde oxidation state, while the hypobromide generated *in situ* from hypochlorite and bromide performs the further oxidation of the aldehyde to the carboxylic acid. TEMPO oxidation is usually accompanied by a drastic change of the molecular weight [8], due to β -elimination starting from C6 aldehyde. The reaction is usually carried out around pH 10–11 since at lower pH, hypochlorite becomes an overly aggressive and non-selective oxidant, and TEMPO reactivity is decreased.

In order to introduce new functionalities, remove lignin and hemicelluloses, as well as improve sorption properties of hemp fibers, they were selectively oxidized with TEMPO. By changing the parameters of the oxidation (i.e. HOCl concentration and treatment time), it is possible to obtain hemp fibers with a different amount of cation exchange functions (0,09 to 0,80 mmol of carboxylic groups per gramme of fibers). Amount of cation exchange functions into the fibers depends directly on the time of modification, as well as concentration of oxidizing agents. In the case of TEMPO oxidation of lyocell fibers, applying severe conditions results in losing fibrous structure and for textile applications only oxidations under mild conditions should be used [9].

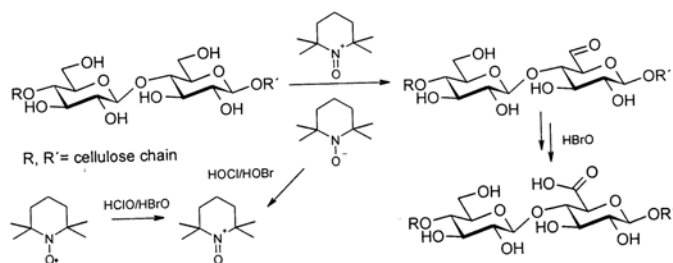


Figure 1. Mechanism of TEMPO oxidation with the intermediate formation of the C6-aldehyde.

Periodate oxidation of cellulose effects bond cleavage between C-2 and C-3 of the anhydroglucose units with concomitant introduction of aldehyde functionalities at those two positions (*cf.* Figure 2). The reaction is thought to proceed via a cyclic diester of per-iodic acid with geminal hydroxyls, which subsequently undergoes an intramolecular redox process with simultaneous C-C bond cleavage according to a concerted mechanism [10]. The reaction is quite selective for cellulose as the only geminal hydroxyls available are located at C-2 and C-3 of the anhydroglucose units.

The effect of periodate concentration on the rate of oxidation of cellulose by potassium periodate has been studied by means of experiments in which li-

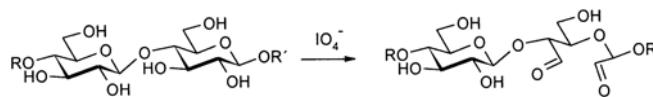


Figure 2. Periodate oxidation at cellulose

ocell fibers were treated at RT with 0,2% and 0,4% solutions of the oxidant buffered at pH 4 with 0,1M acetic buffer. The amount of periodate consumed under these conditions was taken as an empirical measure of the reaction rate (Figure 3). The quantification of carbonyl groups in oxidized fibers can be done by determination of the so called copper number but this method has drawbacks: the data of the copper number cannot be directly linked to the quantity of a specific oxidized function. Group-selective fluorescence labelling in combination with multi-detector gel permeation chromatography (multi-angle laser light scattering, refractive index, fluorescence) has become a powerful tool in cellulose analytics [11]. The possibility to accurately determine carbonyl and carboxyl contents and, in the case of DMAc/LiCl soluble cellulose, to assign them to specific molecular weight regions renders these approaches especially powerful.

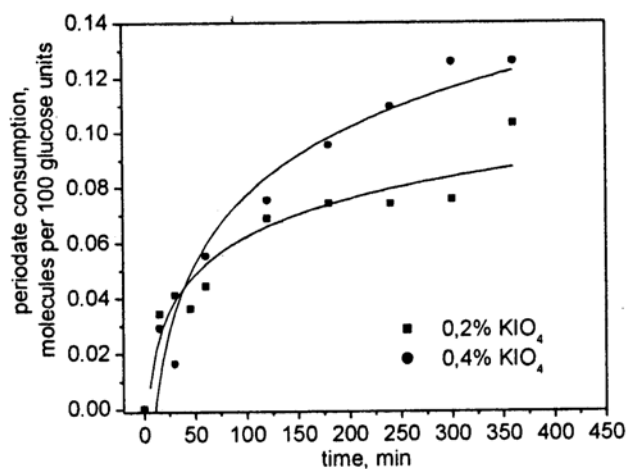


Figure 3. Periodate consumption vs. reaction time

The oxidation by potassium periodate breaks to some extent the crystalline structure of cellulose in the original lyocell fibers, therefore, it may weaken the tensile properties. Figure 4 shows the relationship of the breaking force of the modified fibers versus oxidant concentration and treatment time. As we expected, the breaking force of modified fibers did not change remarkably during the first 50 min of the oxidation. However, it decreased sharply after this period, probably due to breaking down the cellulose crystallization.

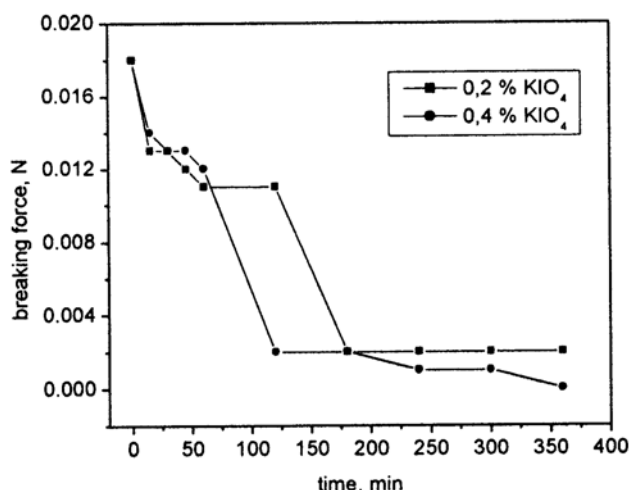


Figure 4. Breaking force of the periodate oxidized cellulose fibers vs. oxidant concentration and treatment time

Non-selective cellulose oxidation

In order to improve sorption properties of hemp fibers, they were modified with non-selective oxidizing agents, hydrogen peroxide and potassium permanganate [12]. Oxidation of hemp fibers was chosen because of both – improving sorption properties and removing lignin. By changing the parameters of the oxidation (concentration of oxidizing agents, pH, reaction time and temperature) it is possible to obtain hemp fibers with a different amount of cation exchange functions (2.48 to 5.88 mmol Na⁺ per gramme of fibers), Figure 5. Amount of cation exchange functions into the fibers depends directly on the time of modification, pH value of solution, temperature, as well as concentration of oxidizing agents. In addition, higher values were obtained in the case of permanganate oxidation.

A hydrogen atom present in carboxylic groups can be easily replaced with another cation, so the fi-

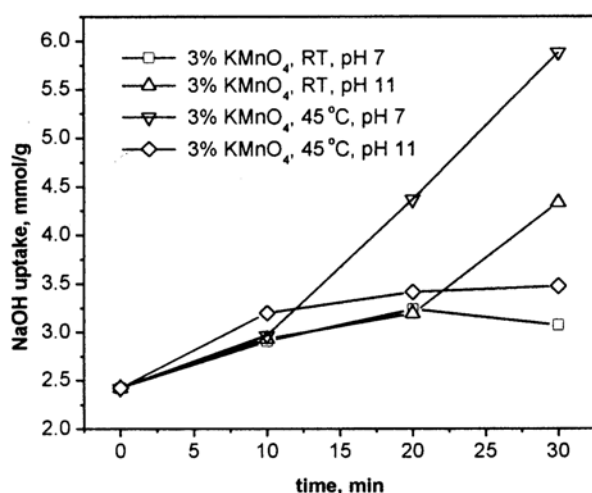


Figure 5. NaOH uptake by oxidized hemp fibers vs. sorption time, concentration and pH value of oxidizing agent solution

bers can be used for effective isolation of different cations from solutions and gasses, and as the basis for obtaining of biologically active fibers. Cation-exchange hemp fibers allow chemotherapeutic agents with basic properties to bond chemically with the fiber.

HEMP FIBERS WITH ANTIMICROBIAL PROPERTIES

The treatment of textiles with antimicrobial agents is necessary to avoid the microbial degradation of textile fibers, limit the incidence of bacteria, reduce the formation of odour following the microbial degradation of perspiration, and protect users by avoiding the transfer and spread of pathogens. Silver in various forms has a long history as an antimicrobial agent, and in our research, silver nitrate was chosen as antimicrobial agent. The optimal conditions for silver ions sorption from aqueous silver nitrate solution by hemp fibers with improved chemisorption properties were determined by changing sorption conditions: pH value, concentration of aqueous silver nitrate solution and duration of sorption. The quantity of Ag⁺ ions sorbed by hemp fibers depends directly on the duration of sorption, as well as concentration of AgNO₃ solutions [13,14]. The results show an increase from 0.018 mmol/g for unmodified hemp fibers to 4.74 mmol/g for oxidized hemp fibers, some results are presented in Figure 6. Obtained results are much higher than the value found in literature [15] for sulphhydryl hemp fibers (0.1 mmol/g), which proves that oxidation of hemp fibers is suitable for improving sorption properties of hemp fibers, and other complicated methods can be avoided.

Results of antimicrobial tests show that incorporation of silver ions in hemp fibers leads to the generation of antimicrobial materials having activity against a broad spectrum of microbes (Gram-negati-

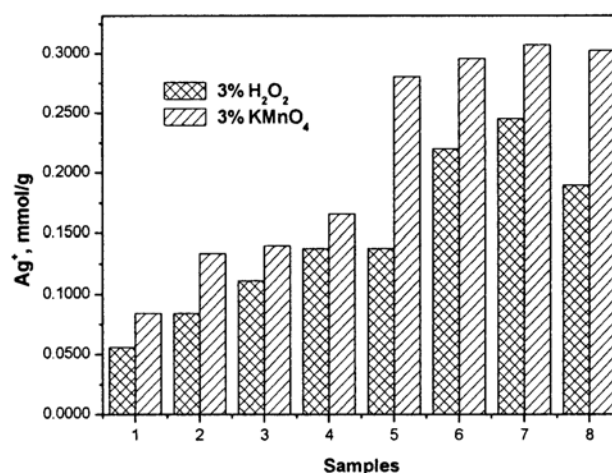


Figure 6. Quantity of Ag⁺ sorbed by oxidized hemp fibers (samples 1-4 oxidized at RT, samples 5-8 oxidized at 45°C)

ve bacteria strains – *Escherichia coli*, Gram-positive bacteria strains – *Staphylococcus aureus*, and yeast – *Candida albicans*) [13].

NON-CONVENTIONAL METHODS FOR OBTAINING MAN-MADE CELLULOSIC FIBERS

The increased production of bast fibres (especially hemp fibres) brought about an increase in the amount of waste, namely shive (hemp stalks) and short fibres. This waste presents a potential significant source of high quality cellulose suitable for the production of high-quality papers and chemical cellulose fibres [16]. Modern approaches to obtaining cellulose hydrate fibres are based on the direct dissolution of cellulose in a tertiary amine-N-oxide, specifically in N-methylmorpholine-N-oxide (NMMO) [17,18]. This solvent may be completely returned to the process, after regeneration, and enables relatively high operating speeds. This procedure, compared to the viscose one, may be considered to be very "ecological". New prospects in the production of cellulose fibres, films and other cellulosic materials have been opened by applying the direct dissolution of cellulose in NMMO.

Bearing in mind both actual field of research: direct cellulose dissolution in NMMO, and hemp as new source of cellulose, which gives the high yield (per units of time and square) in comparison with wood, here we address shortly the possibility of dissolving hemp fibres directly in NMMO. The results of the investigation of the solubility of cellulose from hemp fibres indicated, as in the case of the dissolution of technical beech cellulose, that this process is gradual and time dependent. The beech cellulose and hemp fibres dissolved similarly, and in the simple fashion described by Chanzy et al. [19]. The accompanying substances in hemp fibres (residual hemicelluloses, pectin, waxes, lignin) influence cellulose solubility and self-association of solvated macromolecules in solution [20]. These substances decrease the surface tension of the cellulose solution, thereby affecting the conditions and rate of sample dissolution. This phenomenon may explain fact that hemp fibres with higher DP than the beech cellulose dissolved at the similar dissolution rate. It should be noted that previous removing of accompanying substances in hemp fibres results in degradation of cellulose, i.e. DP is reduced to 1100.

Comparative analysis of the solubility of cellulose from hemp fibres and technical beech cellulose and the rheological characteristics of the obtained solutions indicated the following possibilities: the successful dissolution of cellulose from hemp fibres; the preparation of solutions with similar rheological properties to those of technical beech cellulose in NMMO (both solutions behave as non-Newtonian liquids with similarly shaped flow curves and similar activation energies of viscous flow); the formation of

films and fibres from solutions of cellulose from short hemp fibres of the same or improved quality compared to those made of technical beech cellulose [20,21].

In our recent research we also investigate the possibilities of obtaining bicomponent biologically active cellulose-chitosan fibres by dissolving cellulose from hemp fibres and chitosan in NMMO and the mixing of cellulose and chitosan solutions in different ratios [22]. Preliminary results show that it is possible to obtain composite or biocomposite cellulose/chitosan fibre from a mixture of cellulose and chitosan solutions. The obtained bicomponent fibres are characterized by enhanced sorption capacity and satisfactory tensile characteristics.

SHORT HEMP FIBERS BASED SORBENT MATERIAL

Removal of heavy metals from waste waters is a major ecological problem. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content. A search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial byproducts, as potential metal sorbents. Hence, we have tested the short hemp fibers as metal ions adsorbents. In order to improve sorption properties hemp fibers were modified with sodium hydroxide and sodium chlorite [23], or by dielectric barrier discharge [24]. Cadmium (II), lead (II) and zinc (II) were rapidly adsorbed in 15 minutes by the short hemp fibers. Sorption equilibrium was then reached in 60 minutes, and maximum cadmium, lead and zinc uptake was 10, 17,8 and 13,6 mg/g respectively. The order of metal affinity for the short hemp fibers was $Pb > Zn > Cd$. The systems under study offer some new attractive possibilities of selective sorption of various pollutants from aqueous effluents [25].

INSTEAD CONCLUSION

We can agree with Z.A. Rogovin's words that chemists can and should make cellulose better than it has been created by nature. Cellulosic fibres will again play a major role in the future due to growing market of hydrophilic fibres and tendency to develop production of natural, light, renewable and biodegradable fibres. Actually, it is expected that cellulosic fibres only for clothing, will be in demand up to 38 mil.ton/year in the year 2050.

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IZVOD

CELULOZNA VLAKNA NOVIH FUNKCIONALNIH SVOJSTAVA DOBIJENA HEMIJSKIM MODIFIKOVANJEM

(Pregledni rad)

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U ovom radu dat je prikaz sadašnjeg stanja u oblasti funkcionalizacije celuloznih vlakana hemijskim modifikovanjem, sa posebnim osvrtom na selektivnu oksidaciju perjodatima i TEMPO-m, neselektivnu oksidaciju celuloznih vlakana permanganatom i peroksidima, nekonvencionalne postupke dobijanja hemijskih celuloznih vlakana, postupcima dobijanja antimikrobnih celuloznih vlakana, kao i mogućnostima za dobijanje dvokomponentnih celuloznih vlakana na bazi polisaharida. Kapilarnost, sorpcija vlage i joda, sposobnost zadržavanja vode, sorpcija različitih jona, bakrov broj, selektivno obeležavanje karbonilnih i karboksilnih grupa, kao i antimikrobni testovi su neke od metoda korišćenje za karakterisanje postignutih efekata modifikovanja.

Ključne reči: Celulozna vlakna • Hemijsko modifikovanje • Antimikrobna vlakna • Dvokomponentna polisaharidna vlakna •

Key words: Cellulosic fibers • Chemical modification • Antimicrobial fibers • Two-component polysaccharide fibers •