Silver-Loaded Lyocell Fibers Modified by TEMPO-Mediated Oxidation

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Received 3 July 2009; accepted 17 January 2010
DOI 10.1002/app.32128
Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The purpose of this research was to accomplish antimicrobial properties in lyocell fibers by Ag^+ ions sorption from aqueous silver nitrate solution. Sorption properties of lyocell fibers were improved by the selective TEMPO-mediated oxidation, i.e. oxidation with sodium hypochlorite and catalytic amount of sodium bromide and 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO). The most suitable experimental conditions for the selective TEMPO-mediated oxidation were determined by changing oxidation conditions: concentration of sodium hypochlorite, as well as duration of sorption. The obtained results showed that the maximum sorption capacity (0.809 mmol of Ag^+ ions per gram of fibers) of modified lyocell fibers was obtained for the sample modified with 4.84 mmol NaClO per gram of cellulose, during 1 h. The antifungal activity of the TEMPO-oxidized lyocell fibers with silver ions against fungi from the Candida family, *Candida albicans* (ATCC 24433), and antibacterial activity against two strains: *Staphylococcus aureus* (ATCC 25923) and *Escherichia coli* (ATCC 25922) were confirmed *in vitro*. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1772–1779, 2010

Key words: lyocell fibers; TEMPO-modification; silver ion sorption; swelling; antimicrobial activity

INTRODUCTION

Contamination of textile materials by microorganisms like pathogenic bacteria, odor-generating bacteria, molds, fungi, and viruses is likely to occur, which is of a great concern to public health.[1,2] Additionally, the development of body odor itself cannot be avoided, even with optimally designed clothing. Hence, the use of new textiles 'treated with antimicrobial agents', has become necessary to protect customers, to reduce odor by decreasing the number of germs on the skin and with the aim to avoid the loss of performance properties as a result of microbial fiber degradation.[3,4]

As antimicrobial agents, silver ions and inorganic silver salts (especially nitrate) have been known since ancient times. Silver ions have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities[5] (i.e. silver is one of a few antimicrobial preparations, which possess both antibacterial and antifungal activity, and bacteria are not able to develop their resistance to the silver, as in the case of antibiotics). All mentioned unique properties together with high thermal stability; odor control; good fabric compatibility, etc., have been established silver ions as a topical agent in several of today's medical areas.[6–8]

According to the actual eco friendly criteria, cellulose, as the most abundant and renewable biopolymers; is widely used as one of the promising raw materials for the preparation of various functional materials.

Among cellulose fibers, lyocell fibers, has attracted great attention in the field of textiles as it was developed in the mid 1970s because of the following: as man-made cellulose fibers they are more homogenous in structure and properties than natural cellulose fibers, with better sorption properties, and what is very important among man-made cellulose fibers they distinguish themselves by some unique properties (very high strength in comparison with other man-made cellulose fibers, high crystallinity, specific luster and handle, optimum conditions for the skin).[9,10] Special features - the dissolving of cellulose without chemical modification, ability of solvent to attain exceedingly high concentration of cellulose (e.g., 35% w/w in DP 600), and nearly complete recovering of the nontoxic solvent NMMO, have established lyocell process as an environment friendly, relatively simple, economically viable, product-enhancing, and highly flexible technology (for example: antibacterial lyocell fibers Sea Cell® Active are produced by incorporation of antibacterial substances into the spinning solution).[11,12]

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Contract grant sponsor: Ministry of Science and Technological Development of the Republic of Serbia; contract grant number: TR - 19009.

TABLE I
Sample Marks, TEMPO-Mediated Oxidation Conditions, and COOH Groups Content (2.5 mg TEMPO/g of Cellulose, RT, pH 10.5)

	Oxidation conditions		COOH groups content (mmol/g cell)	
Lyocell samples	Conc. NaClO (mmol/g cell)	t (h)	Ca-acetate method	Potentiometric titration
LO	0	0.00	0.061	0.035
LI_1	0.30	1.00	0.111	0.049
LI_2		2.00	0.125	0.090
LI_3		3.00	0.122	0.092
LI_4		4.00	0.299	0.121
LII_1	2.42	1.00	0.584	0.401
LII_2		2.00	0.693	0.581
LII_3		3.00	0.657	0.618
LII_4		4.00	0.413	0.499
$LIII_{0.25}$	4.84	0.25	0.174	0.071
$LIII_{0.50}$		0.50	0.432	0.212
$LIII_1$		1.00	0.607	0.579
$LIII_2$		2.00	0.294	0.189
$LIII_4$		4.00	0.159	–
$LIV_{0.25}$	9.67	0.25	0.154	0.059
$LIV_{0.50}$		0.50	0.303	0.119
LIV_1		1.00	0.537	0.434

In this article, we combined the aforementioned unique properties of lyocell fibers and silver ions to obtain antimicrobial lyocell fibers; silver ions were incorporated into lyocell fibers by chemisorption from aqueous silver nitrate solution. Sorption properties of lyocell fibers were improved by the selective TEMPO-mediated oxidation, i.e. oxidation with sodium hypochlorite and catalytic amount of sodium bromide and 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO). According to literature[13–18] catalytic TEMPO-mediated oxidation, using water soluble and stable nitroxyl radicals such as 2,2,6,6-tetramethylpyperidine-1-oxy radical (TEMPO) under aqueous conditions, has been recently proposed as one of the most promising methods for cellulose functionalization, where carboxyl and aldehyde functional groups can be effectively introduced into solid cellulose under aqueous and mild conditions. The most noticeable points of this TEMPO-mediated oxidation of polysaccharides are the following; highly regioselective oxidation of primary hydroxyl groups in polysaccharides to carboxyl groups can be achieved, and this selective oxidation proceeds under aqueous mild conditions around room temperature at pH 10–11.[19]

A series of the TEMPO-mediated oxidations, under different conditions, were done to determine the most suitable experimental conditions for "the activation" of lyocell fibers. The moisture sorption, water retention, carboxyl groups content, and silver ions uptake were used to assess the changes in lyocell fibers due to the oxidation. The antimicrobial activity of silver-loaded lyocell fibers against different pathogens: *Staphylococcus aureus, Escherichia coli,* and *Candida albicans* was evaluated *in vitro.*

EXPERIMENTAL

Materials

The man-made cellulose fiber–lyocell fiber (Lenzing AG, Austria, fineness: 1.3 dtex, length: 38 mm; without spin finishing), was used in this study. All used chemicals obtained from commercial sources are p.a. grade.

Methods

Preparation of TEMPO-oxidized cellulose fibers

The oxidation procedure was based on the literature methodology.[18,20] In brief, lyocell fibers (10 g) were suspended in water (750 mL) containing TEMPO (0.025 g) and sodium bromide (0.25 g). Subsequently, a designed amount of NaClO solution containing 13% available chlorine, corresponding to 0, 0.30, 2.42, 4.84, and 9.67 mmol/g cellulose, was added to the cellulose slurry under continuous stirring. The pH of the slurry was maintained to be 10.5 at room temperature by adding 0.5*M* NaOH for 0.25–4 h. After stirring for a designed time, the oxidation was quenched by adding ethanol (ca. 5 mL). The oxidized cellulose was washed thoroughly with water and then ethanol on a filter paper set in a Büchner funnel. The water insoluble fractions thus obtained were then dried at room temperature for 48 h. Sample marks and TEMPO-mediated oxidation conditions are shown in Table I.

Determination of moisture sorption

Moisture sorption of oxidized lyocell fibers was determined according to standards (ASTM D 2654-76, 1976).[21–23] Fibers were exposed to standard atmosphere: 20 ± 2°C, 65 ± 2% relative humidity, for 24 h (ASTM D 1776-74, 1974). Moisture sorption was calculated as weight percentage of absolute dry material. Reported values are the mean values of three separate determinations.

Determination of water retention value

Water retention of lyocell fibers was determined in triplicate by standard centrifuge method (ASTM D 2402-78, 1978).[23]

Determination of carboxyl groups (COOH) in the TEMPO-oxidized lyocell fibers

Calcium acetate method. The carboxyl groups of the oxidized cellulose react with the salts of weaker acids, such as calcium acetate, forming a salt of the oxidized cellulose and releasing an equivalent amount of the weaker acid. On this basis as well as by the modification of published calcium acetate method,[18,24] for determination of carboxyl content in oxidized cellulose fibers, the following method was applied. Cellulose samples (0.5 g) were treated with 0.01*M* HCl during 1 h and washed thoroughly with water. In the next step to the oxidized cellulose 50 mL of distilled water and 30 mL 0.25*M* of calcium acetate solution were added. After standing during 2 h with frequent shaking, to facilitate completion of the interchange, 30 mL portions of the liquid were titrated with 0.01*M* sodium hydroxide, using phenolphthalein indicator. The carboxyl contents are calculated as follows:

$$\mathrm{COOH} = \frac{\frac{80}{30} \times 0.01M \times \mathrm{V(NaOH)}}{m\left(1 - \frac{w}{100}\right)} (\mathrm{mmol/g}) \quad (1)$$

where 0.01*M* – concentration of NaOH; *V*(NaOH) – volume of NaOH solution used for titration, (mL); *m* – weight of treated fibers, (g); and *w* – moisture content, (%).

Potentiometric titration. Cellulose samples (0.5 g) were added to 100 cm^3 of 0.5*M* NaCl. The titration was started with a neutral fibers suspension to which 10 cm^3 of 0.1*M* HCl in 0.5*M* NaCl was added using a precision burette. The titration was carried out by adding of 0.1*M* NaOH in 0.5*M* NaCl from a precision burette. During titration, the solution was stirred with a glass propeller and kept in airtight titration vessel. All experiments were carried out under thermostatically controlled conditions at 25°C. An inert atmosphere was maintained by continuous flow of argon. After each addition, the potential was recorded automatically with Methrohm 848 titrino plus. The stability criterion for recording of the potential after each addition was a drift of less than 0.5 mV/min. The amount of impurities not stemming from the fibers was determined by performing blank titrations. All presented values are the mean values of five parallel measurements.[25]

Silver ions sorption by TEMPO-oxidized lyocell fibers

Silver ions were incorporated into previously TEMPO-oxidized lyocell fibers and control one by chemisorptions under following conditions: fibers (0.1 g) were immersed in 100 mL of 0.01 mol/dm^3 $AgNO_3$ solution, and shaken at room temperature for 240 min in the dark, that were optimized earlier.[26] The change in concentration of Ag^+ after sorption was determined by NH_4SCN titrations employing $Fe(NH_4)(SO_4)_2$ as an indicator according to Volhard's method.[27,28]

Determination of antimicrobial activity of silver-loaded TEMPO-oxidized lyocell fibers

Agar diffusion test[29,30] was used to assess the antimicrobial activity of silver–loaded TEMPO-oxidized lyocell fibers. Three test organisms were used: Gram-positive *S. aureus* ATCC 25,923, Gram-negative *E. coli* ATCC 25,922, and yeast *C. albicans* ATCC 24,433. The agar diffusion test consists in placement of 1.0 cm × 1.0 cm samples (0.05 g of parallelized and pressed fibers) onto an agar support inoculated with tested microorganisms and, after 24 h incubation at 37°C, measuring the width of the zone of inhibition (clear) or suppression (diffuse) of growth against the indicator organisms in comparison to a control sample.

RESULTS AND DISCUSSIONS

Obtaining of silver-loaded TEMPO-oxidized lyocell fibers

The first stage of obtaining of antimicrobial silver-loaded lyocell fibers was TEMPO-mediated oxidation; conditions of oxidation are presented in Table I. The TEMPO-mediated oxidation presents selective oxidation at C-6 of the anhydroglucose units to carboxyl groups via the intermediate aldehyde stage.[17] The nitroxyl radical affects the oxidation from the alcohol to the aldehyde oxidation state, while the hypobromite generated *in situ* from hypochlorite and bromide performs the further oxidation of the aldehyde to the carboxylic acid.[13–16] Introduced hydrophilic carboxyl groups were used as reactive "chemical hooks" in the second stage of obtaining of antimicrobial lyocell

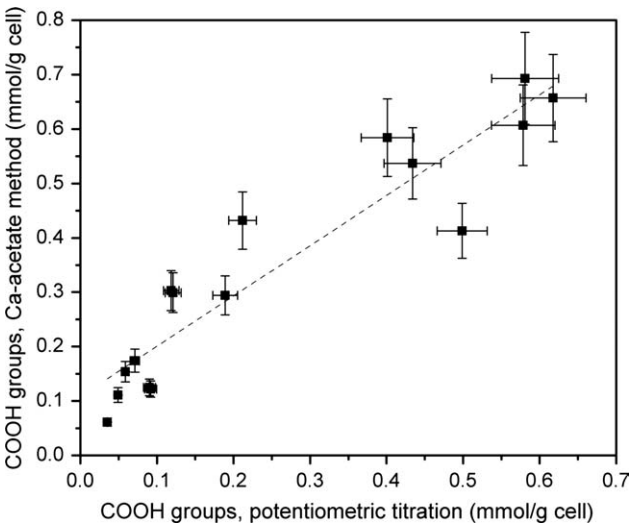

Figure 1 Relationship between COOH groups (mmol/g cell) determined by the potentiometric titration and Ca-acetate method (mmol/g cell). Error bars represent the ± one standard deviation.

fibers, i.e. a hydrogen atom present in carboxyl groups could be easily replaced with another cation, in this case with silver ions. In our previous article,[18] correlation between NaClO concentration, oxidation time, and introduced carboxyl groups into TEMPO-oxidized lyocell fibers were shown in detail. Here we discuss relationships between introduced COOH groups and Ag^+ ions sorption capacity.

To better understand and correlate the amount of sorbed Ag^+ ions and amount of the accessible COOH groups in the complex fibrous systems, we decided to use two analytical methods for determination of COOH groups: the indirect Ca-acetate method and the potentiometric titration as a direct method. Results obtained by these two methods are given in Table I and compared in Figure 1.

The amount of the COOH groups in unmodified and TEMPO-oxidized lyocell fibers, determined by Ca-acetate method, are generally higher in comparison with those determined by potenciometric titration. The reason for that can probably be attributed to experimental uncertainties: the Ca-acetate method is indirect method and the potentiometric titration is direct method. However, the two methods correlate reasonably well, and the general trend is that an increase in the amount of carboxyl group determined by potentiometric titration is accompanied by an increase in the amount of acidic group determined by Ca-acetate method. The reproducibility of potentiometric titration, which is a direct method, was much better (coefficients of variation less then 8.57%) than the reproducibility of Ca-acetate method, which is an indirect method (coefficients of variation less then 12.20%). Because of that in further discussion, we compare the amount of sorbed Ag^+ ions and amount of the accessible COOH groups determined by the potentiometric titration. The relationship between the amount of sorbed Ag^+ ions and amount of the COOH groups is shown in Figure 2.

The predictable result is that one carboxyl group react with one silver ion by the ion exchange technique; but in our case situation looks a little bit complicated. Concerning to data presented in Figure 2, for the oxidized lyocell fibers with lower amount of COOH, the amount of sorbed Ag^+ ions, toward the COOH group content, is in predictable stoichiometry of 1 : 1. But, in the case of oxidized lyocell fibers with higher amount of COOH groups, the amount of sorbed Ag^+ ions is larger than amount of carboxyl groups. The possible explanation for such behavior could be, acording to the literature,[31] fact that cellulose absorbs metal ions by groups other than carboxyl as well as fact that, the ion excange of silver with the carboxyl groups is affected by sample size.

Obviously, besides introduced COOH groups, other changes in lyocell fibers caused by TEMPO-oxidation, have influence on Ag^+ ions sorption. Therefore we further analyzed the correlation between Ag^+ ions sorption capacity and TEMPO-oxidation conditions.

Figure 3 shows the effect of oxidation time and amount of the primary oxidant (NaClO) added on Ag^+ ions sorption capacity of the water insoluble fractions of TEMPO-oxidized lyocell fibers.

For unmodified lyocell fibers, the amount of sorbed Ag^+ ions is the lowest (0.014 mmol/g cell), while in all other cases, where TEMPO-mediated oxidation was applied, results show increase in the Ag^+ ions sorption by modified fibers, ranging from

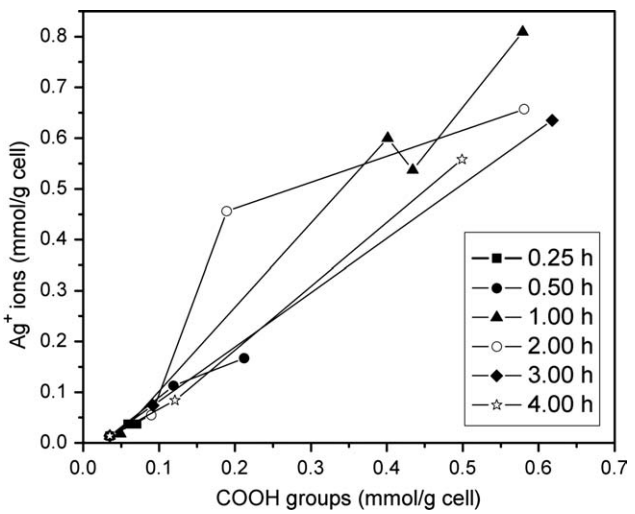

Figure 2 Relationships between COOH groups (mmol/g cell), determined by the potentiometric titration, into TEMPO-oxidized lyocell fibers and Ag^+ ions sorption capacity (mmol/g cell).

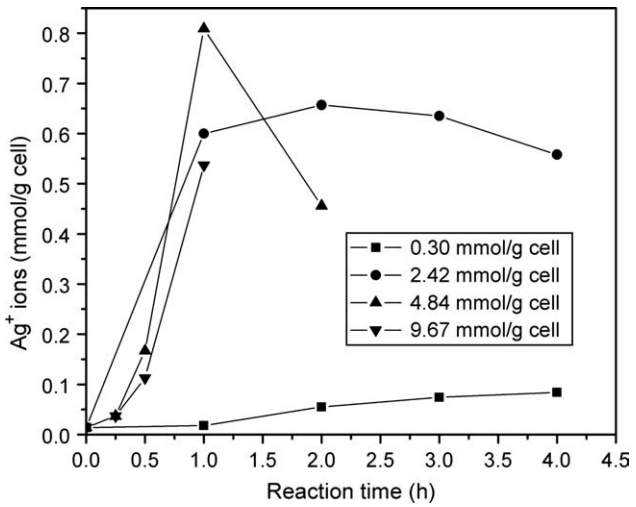

Figure 3 Relationships between oxidation time (h) and Ag^+ ions sorption capacity (mmol/g cell) of the water insoluble fractions of TEMPO-oxidized lyocell fibers, where 0.30, 2.42, 4.84, and 9.67 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, at room temperature and pH 10.5.

0.018 mmol/g cell to 0.809 mmol/g cell. Modification with the lowest concentration of oxidative agent NaClO (0.30 mmol/g cell), causes slight increase of the Ag^+ ions sorption with prolonged oxidation time (up to 4 h), from 0.018 mmol/g cell to 0.084 mmol/g cell. In the case of lyocell modification with the higher concentration of NaClO (2.42, 4.84, and 9.67 mmol/g cell), the amount of Ag^+ ions sorbed by oxidized fibers slightly increase during the first 30 min. When reaction was prolonged for additional 30 min (total time = 1 h), in all cases, the rapid jump in Ag^+ ions uptake was observed and considerable amount of Ag^+ ions were loaded into lyocell fibers. This can be explained by the fact that, according to the literature[13–16] the TEMPO-oxidation presents conversion of OH groups into COOH groups via the intermediate CHO stage,[17] and in the first 30 min, there is not enough COOH groups that can react with silver ions.

Modification with 2.42 mmol NaClO/g cell, during 2 h, leads to increase of the amount of sorbed Ag^+ ions, while prolonged oxidation time (3 and 4 h) causes slight decrease of the Ag^+ ions sorption capacity of oxidized fibers. Observed decrease of the Ag^+ ions sorption capacity can be explained by dissolution of highly oxidized cellulose fractions, that leads to decrease the amount of COOH groups, which react with silver ions.

The maximum increase of the amount of sorbed Ag^+ ions by oxidized lyocell fibers (0.809 mmol/g cell), is obtained for the sample oxidized in the presence of 4.84 mmol NaClO/g cellulose during 1 h (sample $LIII_1$). With prolonged oxidation time, up to 2 h, under the same oxidation conditions, the amount of sorbed Ag^+ ions decreases very sharply (0.456 mmol/g cell). Decrease in Ag^+ ions sorbtion and COOH groups content are consequence of the dissolution of highly accessible fractions and degradation of fibrous form of lyocell, weight loss up to 26.27%, that can be seen from the data for the weight loss for the oxidized lyocell fibers presented in our previous publications.[18]

Oxidation with 4.84 cell and 9.67 mmol NaClO/g cell, longer than 2 h and 1 h, respectively, should be avoided, because the oxidative conditions are too severe for lyocell fibers, i.e. followed by high weight loss, strong decrease in tenacity (preliminary results show drop from 27.3 cN/tex for unmodified to 4.0 cN/tex for modified lyocell fibers), and losing fibrous structure in the case of the most severe conditions. Regenerated cellulose lyocell fibers, are much more reactive toward TEMPO-oxidation mainly due to the lower crystallinity index and less complex fine and micro structure than natural cellulose fibers (for example, cotton), as well as higher accessibility of cellulose II crystal structure (regenerated and mercerized cellulose) as compared with cellulose I (native cellulose).[13–16,18]

It is known that, together with the introduction of aldehyde and carboxyl groups into cellulose, by the TEMPO-mediated oxidation, the fibrous morphology of cellulose fibers has been changed, depending on the oxidation conditions.[13–16,18] Changes in cellulose chemical composition, crystallinity, and void system (diameter, volume, and inner surface of voids)[32] during the TEMPO-oxidation, affect the sorption properties. As we mentioned earlier, besides introduced COOH groups, other changes in lyocell fibers caused by TEMPO-oxidation have influence on Ag^+ ions sorption. To better understand obtained results, we tried to figure out relationship between Ag^+ ions uptake capacity and sorption properties of TEMPO-oxidized lyocell fibers; sorption properties of oxidized lyocell fibers were evaluated by determination of water retention power and moisture sorption (Figs. 4 and 5). Furthermore, these two properties are also very important for possible application of textile materials, especially textiles which are intended for wound care applications. If we correlate the content of introduced Ag^+ ions into TEMPO-oxidized lyocell fibers and their water retention values – WRV (Fig. 4), it is obvious that, generally, with increase of water retention values, the Ag^+ ions sorption capacity also increases. In this correlation, we have the similar appearance like in Figure 2, where we correlated the amount of introduced COOH groups and Ag^+ ions sorption capacity; i.e. two area of dependency between WRV and Ag^+ ions uptake, and jump between them. In the first area, the Ag^+ ions sorption capacity is changed between 0.018 and 0.167 mmol/g cell, while value

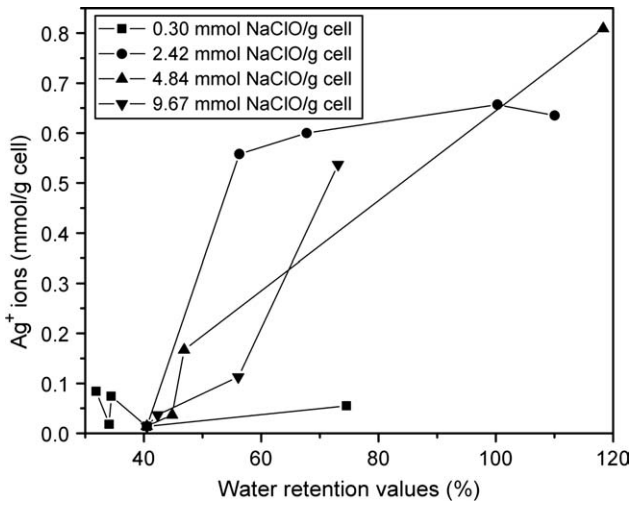

Figure 4 Relationships between water retention values (%) and Ag^+ ions sorption capacity (mmol/g cell) of the water insoluble fractions of TEMPO-oxidized lyocell fibers, where 0.30, 2.42, 4.84, and 9.67 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, at room temperature and pH 10.5.

for WRV is changed from 31.86 to 74.55%. In the second area, we have values from 0.537 to 0.657 mmol/g cell, for Ag^+ ions sorption capacity and from 56.28 to 110.03% for WRV. Reason for such behavior of oxidized lyocell fibers can be fact that in the second area, when fibers sorbed more water, they swell more and the fiber structures become "opened" and accessible for Ag^+ ions sorption. Sample denoted as $LIII_1$ (oxidized 1 h, with 4.84 mmol NaClO/g cell), shows the maximum values for both, Ag^+ ions sorption capacity (0.809 mmol/g cell) and WRV (118.32%).

The obtained results and our conclusions are additionally confirmed by relationship between the content of introduced Ag^+ ions in TEMPO-oxidized cellulose fibers and moisture sorption values – MS. The moisture sorption values and the Ag^+ ions sorption capacity have the same trend of change for all modified samples. This relationship for the group of samples (LII_1, LII_2, LII_3, LII_4), oxidized with 2.42 mmol NaClO/g cell for different oxidation time, is shown in Figure 5. With increase or decrease of moisture sorption values, the Ag^+ ions sorption capacities increase or decrease, too.

As it has been reported earlier[18] free hydroxyl and carboxyl groups at the cellulose fibers amorphous regions and at the crystallites' surface are responsible for the sorption properties, and the carboxyl groups introduced by TEMPO-oxidation are present on the crystal surfaces and in disordered regions of celluloses, without any introduction into the inside of the cellulose crystallites. The ordered regions (crystalline) do not contribute significantly to the process of water adsorption[32–34] because water is able to permeate into the noncrystalline portion of cellulose. Those correlation between introduced COOH groups, WRV, MS, and sorbed Ag^+ ions, leads to conclusion that Ag^+ ions were also sorbed in amorphous regions of cellulose.

Antimicrobial activity of silver-loaded TEMPO-oxidized lyocell fibers

The antifungal activity of the TEMPO-oxidized lyocell fibers with incorporated silver ions were tested against fungi from the Candida family, *C. albicans* (ATCC 24,433), and antibacterial activity against two strains: *S. aureus* (ATCC 25,923) and *E. coli* (ATCC 25,922), which have a pathogenetic effect,[6–8] and frequently cause infections in hospital environment but also in daily life.

Table II shows the antimicrobial activity for unmodified lyocell fibers (LO), TEMPO-oxidized lyocell fibers (LI_1 and LIV_1) and silver-loaded TEMPO-oxidized lyocell fibers (Ag^+ ions + LI_1, LII_1, $LIII_{0.25}$, $LIII_1$, $LIII_2$, and LIV_1).

As it can be seen, there is no antimicrobial activity of untreated lyocell (LO) and of TEMPO-oxidized lyocell fibers (LI_1 and LIV_1). Incorporation of silver ions in TEMPO-oxidized lyocell fibers generally inhibited growth of tested microbes. Among tested microorganisms, Gram-positive bacteria strain, *S. aureus* is the most sensitive to the silver-loaded TEMPO-oxidized lyocell fibers, then the yeast *C. albicans* and at the end Gram-negative bacteria strain *E. coli*, which is in agreement with literature data.[9]

For gram-positive bacteria *S. aureus*, the silver-loaded TEMPO-oxidized lyocell fibers containing

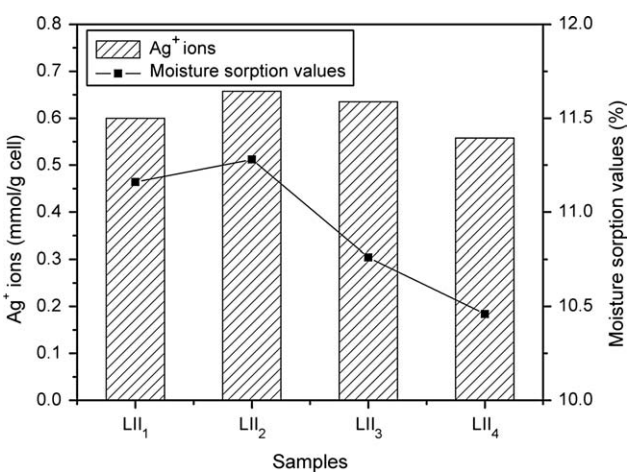

Figure 5 Relationships between moisture sorption values (%) and Ag^+ ions sorption capacity (mmol/g cell) of the water insoluble fractions of TEMPO-oxidized lyocell fibers, where 2.42 mmol NaClO (per gram of cellulose) was applied to the cellulose slurry, at room temperature and pH 10.5.

TABLE II
The Antimicrobial Activity of Silver-Loaded TEMPO-Oxidized Lyocell Fibers

Sample marks	Ag^+ ions (mmol/g cell)	Width of the inhibition zone after 24 h (mm)		
		S. aureus	*E. coli*	*C. albicans*
LO	–	0	0	0
$LI_1 + Ag^+$	0.018	2.0–2.5	1.5	2.5
$LII_1 + Ag^+$	0.600	3.5–4.0	2.5	3.0
$LIII_{0.25} + Ag^+$	0.037	2.0	1.5	2.0
$LIII_{0.50} + Ag^+$	0.167	3.5	2.0	2.5
$LIII_1 + Ag^+$	0.809	2.5	2.5	3.0
$LIII_2 + Ag^+$	0.456	1.5	1.5	1.5
$LIV_1 + Ag^+$	0.537	2.5	1.5	1.5–2.0
LI_1	–	0	0	0
LIV_1	–	0	0	0

0.600 mmol Ag^+/g cell and 0.167 mmol Ag^+/g cell, namely samples denoted as LII_1+Ag^+ and $LIII_{0.5}$+Ag^+, were the most effective, whereas for gram-negative bacteria *E. coli* and yeast *C. albicans*, samples denoted as LII_1+Ag^+ and $LIII_1$+Ag^+ were the most effective. The last sample ($LIII_1$+Ag^+) also shows the maximum value for silver ions sorption capacity (0.809 mmol/g cell). There is no clear dose dependant antimicrobial activity, however, the quantity of bonded silver ions, in all cases, is enough to develop desirable antimicrobial activity in the silver-loaded TEMPO-oxidized lyocell fibers. This can be explained by the fact that the silver does not attack microorganisms directly; it operates as a catalytic agent, and moreover, it is not consumed in this process, as it was proposed by Davis and Etris.[35] The antimicrobial mechanism of action of silver is not yet fully understood, but among several proposals developed to explain the inhibitory effects of silver ions on microorganisms (silver may react with microorganisms by any or all of the following mechanisms: destruction of microorganisms by oxidation catalyzed by silver; disruption of electron transfer in microorganism, and/or preventing the unwinding of DNA with the substitution of hydrogen ions by monovalent silver; and interaction with cell wall membrane without entering the cell forming reversible sulfhydryl or histidyl complexes on the cell surface and the preventing dehydro-oxygenation process) only the destructive oxidation catalyzed by silver is not dose dependant.[35–37]

CONCLUSIONS

The obtained results demonstrate possibility of obtaining biologically active lyocell fibers using TEMPO-oxidized lyocell fibers. Herein, the lyocell fibers were first oxidized by TEMPO-mediated oxidation. As a result of TEMPO-mediated oxidation, lyocell fibers exhibited (beside other changes), generally increase in carboxyl groups content ranging from 0.049 to 0.618 mmol/g cell, that present "chemical hooks" for silver ions sorption. TEMPO-mediated oxidation improves wettability and silver ions sorption onto oxidized lyocell fibers. It is found that the maximum silver sorption (0.809 mmol/g cell) is obtained for sample ($LIII_1$), modified with 4.84 mmol NaClO per gram of cellulose, during 1 h.

The silver-loaded TEMPO-oxidized lyocell fibers generally show antimicrobial activity against tested pathogens (*S. aureus*, *E. coli*, and *C. albicans*). These fibers indicate different activity against different microorganisms; Gram-positive bacteria strain, *S. aureus* is the most sensitive to the silver-loaded TEMPO-oxidized lyocell fibers. There is no clear dose dependant antimicrobial activity, however, the quantity of bonded silver ions, in all cases, is enough to develop desirable antimicrobial activity in the silver-loaded TEMPO-oxidized lyocell fibers.

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