CELLULOSE CHEMISTRY AND TECHNOLOGY

INFLUENCE OF PERIODATE OXIDATION ON SORPTION PROPERTIES OF VISCOSE YARN

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Viscose yarn was submitted to oxidation using different sodium periodate concentrations for various periods of time in order to investigate the influence of oxidation on the chemical and sorption properties of the resulting yarns. The oxidation progress was monitored through periodate consumption, aldehyde group content and weight loss of the modified samples. The aldehyde groups were introduced into the oxidized viscose up to 1.284 mmol/g, while the weight loss was generally of about 5%. Compared to the untreated yarn, the oxidized samples exhibited lower water retention and iodine sorption values – of 32.4% and 53.6%, respectively, while moisture sorption values decreased for an oxidation time up to 180 min and increased when the time of oxidation was longer, up to 360 min. The changes in viscose yarn wettability, because of the oxidation treatment, were evaluated based on the parameters determined by the capillary rise method, which are related to the coefficient of diffusion and radius of pores.

Keywords: viscose fibers, periodate oxidation, structure – property relations, wettability, capillarity

INTRODUCTION

The social concern for global environmental problems encourages the search for alternatives to fossil-based polymeric materials. Novel materials based on abundant, biodegradable and renewable natural polymers, such as cellulose, could replace these non-renewable materials. Modifications of cellulose may lead to derivatives with new chemical and physical properties, and by that to new cellulose-based products.[1]

Among the wide variety of methods available for cellulose modification,[1-5] oxidation is of particular significance, as through it different functionalities can be introduced into the cellulose structure. Cellulose hydroxyl groups are sensitive to various oxidizing agents, however, most of them have non-selective character, as opposed to the sodium periodate and nitroxyl radicals, which are the most selective oxidizing reagents for cellulose.[2]

The periodate oxidation is an attractive and widely used method to modify cellulose and other polysaccharides.[5-7] This is due to its highly selective nature, ease of application and only minimal degradation of the starting material.[6] Sodium periodate exclusively oxidizes the secondary hydroxyl groups of the cellulose glucopyranoside rings to aldehyde groups, while keeping the primary hydroxyl group intact.[7-13] The oxidation involves the cleavage of the C2–C3 bond, *i.e.* the ring opening, which increases the flexibility of oxidized cellulose molecules.[14] The created aldehyde groups could form stable, covalent hemiacetal linkages with adjacent hydroxyl groups.[11,12] The resulting compound, dialdehyde cellulose, can be further derivatized owing to the high reactivity of the aldehyde groups. For instance, it is a suitable intermediate for immobilization of enzymes[15] and amino polysaccharides.[16] Dialdehyde cellulose can be transformed into a more hydrophilic dicarboxyl form[17] or into hydrophobic cellulose-based material.[18-20]

The periodate oxidation treatment changes the properties of starting cellulose (*e.g.* chemical, mechanical, sorption properties[15,21]), depending on the degree of oxidation, which may affect its final use. Knowledge of changes in the sorption properties of cellulose materials could be of great importance since the aqueous medium is most commonly used in their processing and practical application. The sorption properties of fibers can be examined by using various methods, such as those for determining water vapor sorption,[22,23] water retention power,[24] or iodine sorption.[25] Water and iodine penetrate into the available less ordered areas of cellulose fibers; however, their sorption mechanisms are different. While the iodine adsorbs in a monomolecular layer, water forms multimolecular layers filling up all the available voids of fiber.[22]

Water sorption and retention power represent a measure of fiber ability to sorb and retain a certain amount of water in the form of vapor or water in liquid state, as well as its accessibility to an aqueous medium, whereas iodine sorption is a measure of fiber accessibility and crystallinity index.[21]

Another important property of fibers is wettability. This ability of fibers and other solid materials to attract testing liquids is characterized by the contact angle,[20,26] which can be easily measured on flat and smooth surfaces. In the case of solids with curved and heterogeneous surface and porous structure, such as fibers and other textile materials, their wetting properties are commonly quantified using capillary rise experiments.[27-30] This method allows measurement of the liquid rise rate in a tested material. The results of capillarity measurements, liquid height and time of ascent can serve for calculation of wettability parameters: diffusion coefficient D, coefficient related to pore radius C and coefficient R, which represents the ratio of wetting angles at a given height and the maximum (equilibrium) height.[30]

Viscose fibers are widely used in clothing, but also in other areas, such as medical and healthcare textiles and construction industry. Being a bio-based, highly versatile man-made fiber, it can be expected that new areas of application of this fiber will be found as new properties are imparted to it. In this paper, the influence of oxidation with sodium periodate on the sorption properties of viscose yarn was investigated. By studying the changes in moisture sorption, water retention power, iodine sorption and wettability, an attempt was made to get more insight into the changes in the structure of man-made cellulose fibers during periodate oxidation.

EXPERIMENTAL

Materials

Viscose filament yarn (nominal fineness of 10 tex/f 20) was obtained from Ites Rilon-Lorison (Odzaci, Republic of Serbia). Sodium periodate was purchased from Fluka (Buchs, Switzerland). All chemicals used were of analytical grade.

Periodate oxidation of viscose yarn

Viscose yarn samples were immersed in solutions of sodium periodate in 0.1 M acetic buffer (ratio of 1:50, w/v) pH 4.0, at concentrations of 2.0 mg/mL and 4.0 mg/mL, *i.e.* 0.2% and 0.4% (w/v). The solutions of periodate with the samples of viscose yarn were stirred in the dark at room temperature, for various times, *i.e.* 15, 30, 45, 60, 120, 180, 240, 300 and 360 min. After completion of the oxidation reaction, the yarn samples were washed with ice-cold distilled water several times to remove the oxidant (the conductivity of residue water after washing should be around 2 μS/cm). The obtained oxidized viscose samples were then dried at room temperature for 72 h.

Taking into account that the consumption of one periodate molecule produces two aldehyde groups, the rate of oxidation of viscose fibers may be identified with the rate of periodate consumption (*i.e.* the decrease in the periodate content of the solution, referred to the weight of fibers immersed in it and expressed as molecules of periodate per 100 glucose units). Titrimetry was used to calculate the periodate consumption.[5]

Weight loss after oxidation

The formation of soluble fragments as a result of chemical treatment was determined by measuring the weight loss of oxidized viscose samples by applying the direct gravimetric method.[31]

Determination of aldehyde group content

The aldehyde group content was determined according to the method described in the literature.[32-34] The aldehyde groups were selectively oxidized to carboxyl groups with sodium chlorite at pH 4-5 at room temperature for 48 h, and the carboxyl group content was determined by the modified calcium-acetate method.[34] Before titrations, all the viscose samples were ion-exchanged into acid form by suspension in 0.01 M HCl for 1 h, followed by washing with distilled water. The aldehyde group content was calculated by subtracting the carboxyl content value determined in the starting viscose sample from that of chlorite-oxidized samples. The oxidation level of oxidized viscose fibers was expressed as the percentage value of oxidized glucose units, assuming the presence of two aldehyde groups per oxidized sugar.

Determination of moisture sorption

Moisture sorption was measured using an Infrared Moisture Analyzer MA35 and calculated automatically as weight percentage of absolute dry material according to the standard.[35] Viscose samples were exposed to standard atmosphere (20 ± 2 °C, 65 ± 2% relative humidity) for 24 h before measurement.[36] The reported values for each viscose sample (raw and oxidized) are the mean values of three separate determinations.

Determination of water retention value

The water retention power of the viscose samples was determined in triplicate by the standard centrifuge method[37] and expressed as the ratio between the mass of water retained in the sample after soaking and centrifuging, and the mass of the absolute dry sample.

Determination of iodine sorption value

The iodine sorption of the viscose samples was evaluated using the Schwertassek method.[24,25,38] Viscose sample (0.3 g) was treated with 2 mL of iodine solution KI_3 (prepared from 5 g I_2, 40 g KI and 50 mL H_2O) for 3 min and then 100 mL saturated sodium sulphate (200 g/L) was added and shaken for 1 h. The iodine concentration of the sample and blank was determined by titration with 0.02 M sodium thiosulphate and the iodine sorption value (*ISV*) in mg I_2 per g of sample was calculated as follows:

$$ISV = \frac{(b-t)\cdot 2.04 \cdot 2.54}{m_a}\,(mg/g) \tag{1}$$

where b is the volume (mL) of the $Na_2S_2O_3$ solution for blank titration, t is the volume (mL) of the $Na_2S_2O_3$ solution for the titration of the sample solution and m_a is the weight of the absolute dry viscose yarn (g).

According to Schwertassek, the absorption takes place in the amorphous phase. A ratio of ISV per g cellulose to 412 (mg iodine absorbed per 1 g of methyl cellulose) determines the amorphous fraction. The crystallinity index (*CrI*) was calculated using the following equation:[25]

$$CrI = 100 - \left(\frac{ISV}{412}\cdot 100\right)(\%) \tag{2}$$

Determination of wettability parameters values

A simple experimental apparatus for measuring capillarity, which included a sample stand, test tubes in a holder and a ruler, was described in detail in a previous paper.[30] Viscose yarn samples (300 mm) were suspended from the stand with the preloaded lower end dipped into a red colored eosin solution. The aqueous solution of eosin (0.1%) was used instead of water owing to its better visibility. The liquid rise height (h) was measured as a function of time (t) at defined intervals of 10 s in the first minute, of 1 min in the following 9 min and of 10 min until the maximum height (h_{eq}) was reached. For each sample, five measurements were made and the average height values at the same time were determined. Based on the experimental data, three wettability parameters can be determined by using the following equations:[27,39]

$$h^2 = D \cdot t\ (mm^2) \tag{3}$$

where D (mm^2/s) is the capillary diffusion coefficient;

$$H = C \cdot t\ (mm) \tag{4}$$

where C (mm/s) is a coefficient related to the mean hydrodynamic pores radius and the liquid nature,[27] while H values were determined as:

$$h_{eq} \cdot \ln\frac{h_{eq}}{(h_{eq}-h)} - h \tag{5}$$

Coefficient R, which confirms the validity of the assumption $\theta \cong \theta_{eq}$, is given by:

$$R = \frac{\cos\theta}{\cos\theta_{eq}} = \frac{D}{2\cdot C\cdot h_{eq}} \tag{6}$$

where θ (°) and θ_{eq} (°) are the advancing (dynamic) and equilibrium (static) contact angle of the liquid on the solid.

Scanning electron microscopy (SEM) analysis

The fiber surface morphology was investigated using a JEOL JSM-5300 scanning electron microscope, after sputtering the samples with gold.

RESULTS AND DISCUSSION

Influence of periodate oxidation conditions on the level of viscose yarn oxidation

The effect of periodate concentration and reaction time on the rate of oxidation of the viscose yarn was studied. Since the consumption of one periodate molecule produces two aldehyde groups, the rate of oxidation may be identified with the rate of periodate consumption. The course of the reactions, which was followed by measuring sodium periodate consumption by the viscose samples from 0.2% (Fig. 1a) and 0.4% $NaIO_4$ solutions (Fig. 1b), can be divided into two different phases. The rate of oxidant consumption is relatively high in the first 60 min. In the second phase, periodate consumption still increases continually, almost linearly with time, but the rate is lower than in the first phase.

As it was expected, the slope of the curve illustrating oxidant consumption from the 0.4%

$NaIO_4$ solution is approximately twice higher than the curve slope for 0.2% $NaIO_4$.

The viscose yarns exhibited a significant increase in the aldehyde group content with the increase of the reaction time and periodate concentration. The highest aldehyde group amount of 1.284 mmol/g was introduced into the yarn oxidized under the most severe conditions (0.4% $NaIO_4$, 360 min, Fig. 1b), corresponding to 10.4% of glucose units oxidized. The aldehyde content obtained for this viscose sample was 13 times higher than the corresponding value obtained for cotton fiber oxidized under the same conditions,[15] while the periodate consumption value was only 1.3 times higher. To explain this result, there are several factors to be considered. It is well known that the degree of crystallinity of viscose fiber is lower than that of cotton fiber, and this strongly influences the rate of periodate oxidation of cellulose.[8] Higher accessibility of the cellulose II crystal structure compared to the cellulose I structure also contributes to the higher reactivity of the viscose fiber toward periodate oxidation, compared to cotton fibers. Besides that, cellulose molecules containing oxidized units are prone to scission, *i.e.* glycoside bond cleavage, leading to newly-formed end aldehyde groups. Taking into account that periodate cleaves the C2–C3 bond of the pyranoside ring and not the glycoside bond itself, the cellulose depolymerization is probably caused by solution acidity[40] and it could be expected to be more pronounced for viscose than for cotton fibers. This could be attributed to the higher content of oxidized glucose units in the viscose fiber's cellulose molecules, as well as to differences in the structure of man-made and natural cellulose fibers. Finally, in the case of cotton oxidation treatment, a portion of periodate was consumed by non-cellulosic material.[15]

Partial cellulose destruction, *i.e.* cellulose chain scission causes the formation of low-molecular weight fractions. A portion of fractions is soluble corresponding to the weight loss of oxidized viscose yarns. The loss in weight of the above-mentioned most oxidized viscose sample was of 4.73%. However, all the other samples showed similar weight loss values, in a narrow range of 4.47-5.04%, in spite of different oxidation levels. According to this result, the majority of the fractions are most likely intermolecularly linked through the hemiacetal bonds and stay in the fibers. This can be also inferred from the results showing a much higher increase in the aldehyde group content than in periodate consumption (Fig. 1a, b). Also, the presence of a high amount of aldehyde groups introduced suggests extensive crosslinking[11,40] taking place in the viscose fibers due to the formation of hemiacetal linkages between adjacent cellulose chains.

Moisture sorption and water retention value of viscose yarn

Periodate oxidation causes changes in the supramolecular structure of the viscose fibers, along with the conversion of the secondary hydroxyl groups of cellulose to aldehyde groups, thus affecting their sorption properties. Since the sorption ability of cellulose fiber manly depends on the portion of amorphous regions and the void system,[22] studying the changes in the sorption properties of oxidized fibers would enable us to better understand the changes in their structure. For this purpose, interactions of fibers with water are often employed.

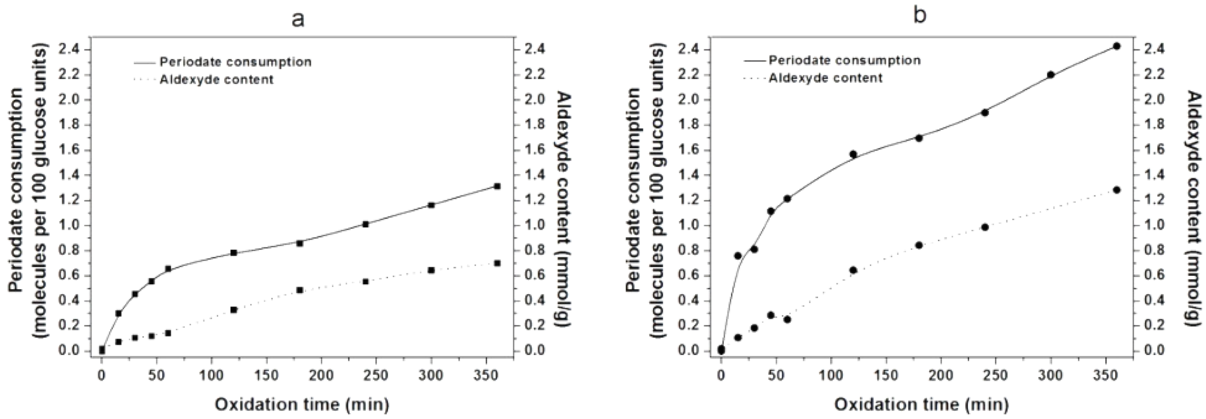

Figure 1: Relationship between periodate consumption or aldehyde group content and oxidation time of viscose fibers modified with (a) 0.2% and (b) 0.4% $NaIO_4$

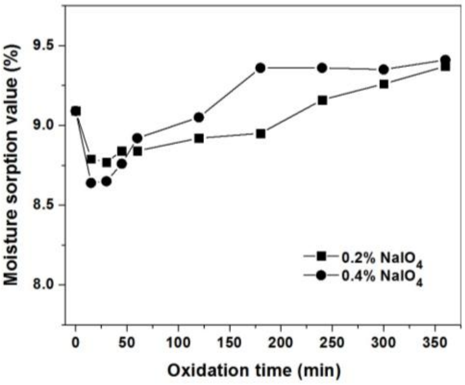

Figure 2: Moisture sorption values of viscose fibers oxidized with 0.2% and 0.4% $NaIO_4$ during 15-360 min

Figure 2 presents the moisture sorption values of unmodified viscose yarns and of those oxidized under different conditions. In comparison with the unmodified yarn, the viscose oxidized with 0.2% and 0.4% sodium periodate during the first 180 and 120 min, respectively, adsorbed lower amounts of moisture, while all the other oxidized samples exhibited slightly higher moisture sorption values. Generally, the modified viscose showed small changes in the moisture content, ranging from a 5.0% decrease, obtained for the sample oxidized with 0.4% periodate for 15 min, to a 3.5% increase for the sample oxidized with the same solution for 360 min.

A number of hydroxyl groups in the periodate oxidized fibers are converted to aldehydes, which are less prone to interacting with water molecules than with hydroxyl groups. Additionally, hemiacetal crosslinks improve the fiber integrity and remove possible sites for water sorption. These factors are most probably responsible for the decrease in moisture sorption. On the other hand, the cellulose molecules' scission leads to an increase in the amount of moisture-adsorbing groups. Cellulose destruction that takes place in a thin reaction surface layer of the viscose fibers, which is confirmed by SEM analysis of oxidized fiber microstructure, also contributes to the increase in moisture sorption.

As it can be seen in Figure 3, the oxidation progress is followed by fiber damage in the form of cracks because of deeper oxidant penetration, but it also influenced the worsening of mechanical properties, which was already presented in our previous work.[41] This makes the fiber structure more open, enhancing its accessibility for water vapor. With the oxidation progress, these effects were probably more dominant than those reducing water-adsorbing sites, which could explain the increase in moisture sorption values with longer oxidation time. The changes in the fiber morphology and aldehyde group content induced by periodate oxidation affect the amount of adsorbed liquid water. Generally, cellulose fibers can absorb a large quantity of water that fills up their available voids. This is accompanied by fiber swelling, mainly because of the expansion of amorphous regions. In order to estimate the water holding capacity, the quantity of water that is absorbed and retained by the oxidized fibers, *i.e.* their water retention values (WRVs) were determined.

As shown by the data in Figure 4, periodate oxidation reduces the water retention power of the viscose samples. The lowest WRV, recorded for the sample treated with 0.4% $NaIO_4$ during 300 min, is 32.4% lower than that of the unmodified yarn. It is noticeable that the decrease in WRV is more pronounced for the samples oxidized with higher periodate concentration, which also had higher aldehyde group contents. The decrease in WRV, despite the increased microporosity of the oxidized fibers because of the cracks formed on their surface, could be mainly the result of the crosslinking effect. According to the literature,[42,43] crosslinked fibers have less available absorption sites for water and are less able to swell.

Iodine sorption of viscose yarn

As reported earlier[22,23,44] iodine sorption takes place in the amorphous regions of cellulose fibers in such a way that iodine adsorbs to available hydroxyl groups forming a monomolecular layer. Therefore, the iodine sorption value (ISV) is a measure of the accessibility of the fiber's less ordered regions to aqueous solutions.

The ISV of the unmodified viscose yarn was 291.1 mg I_2/g cellulose. A strong decrease in ISV after the first 15 min of periodate treatment can be seen in Figure 5. After that, iodine sorption continues to diminish with oxidation time, reaching the minimum value of 135.0 mg/g (decrease of 53.6%) after 360 min. Since available hydroxyl groups are required for iodine sorption, the obtained results mean that their number diminished with the oxidation progress. This is due to either their conversion to aldehyde groups or their inclusion into the crystalline regions by crosslinking; the latter makes them inaccessible for iodine anions. Thus, the increase in aldehyde group content is followed by the reduction of ISV (Figs. 1 and 5). The viscose yarns showed a greater decrease in the ISV in comparison with cotton fibers oxidized under the same conditions,[19] which is in agreement with the higher amounts of aldehyde groups introduced by periodate oxidation in the accessible areas of viscose fibers.

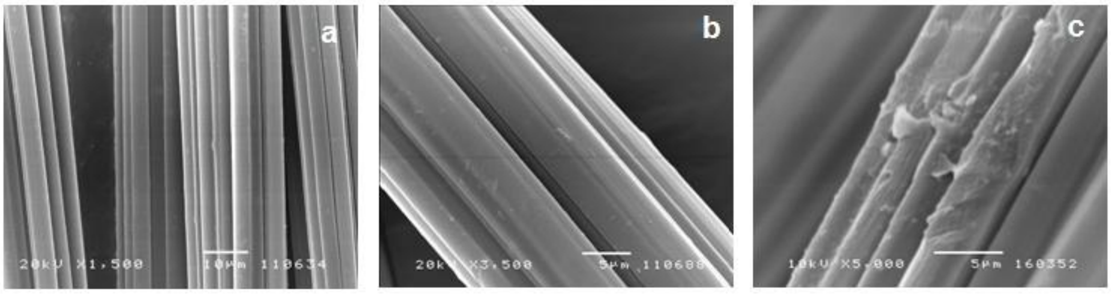

Figure 3: SEM photographs of a) untreated viscose fibers, b) viscose oxidized with 0.4% $NaIO_4$ for 180 min and c) viscose oxidized with 0.4% $NaIO_4$ for 360 min

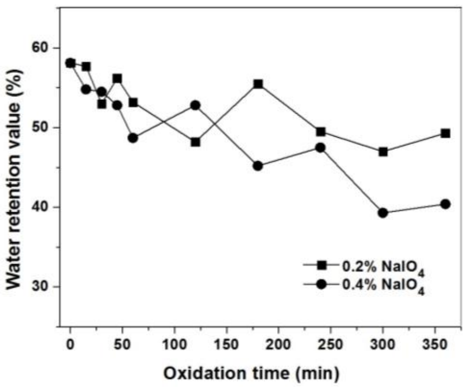

Figure 4: Water retention values of viscose fibers oxidized with 0.2% and 0.4% $NaIO_4$ during 15-360 min

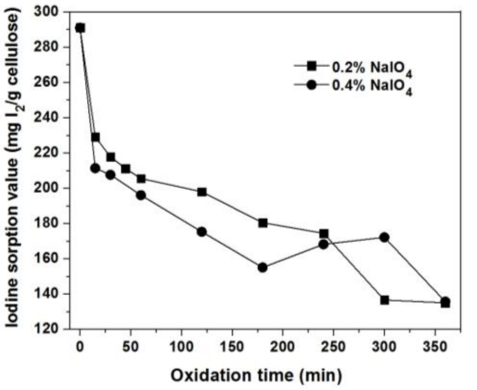

Figure 5: Iodine sorption values of viscose fibers oxidized with 0.2% and 0.4% $NaIO_4$ during 15-360 min

Since iodine anions absorb only to fiber’s amorphous regions, the ISV is inversely proportional to the crystalline regions, expressed by the crystallinity index.[23] Hence, the smallest amount of iodine should be bound by fibers with the highest portion of crystalline regions.[22,44] Due to the introduction of aldehyde groups and subsequent crosslinking, the degree of crystallinity of the viscose fibers increased during the oxidation, as indicated by a lowering of ISV. The crystallinity index of the viscose samples, calculated on the basis of the ISV (Eq. 2), increased from 29.4% for the unmodified viscose to 44.4-67.3% for the oxidized viscose. It could be supposed that a higher increase in crystallinity involves the reorganization of the less ordered amorphous fraction of the oxidized samples due to the crosslinking effect, especially when the oxidation is carried out with higher periodate concentration and longer oxidation time.

Wettability of viscose yarn

The advance of the liquid front with time for some samples is shown in Figure 6. The wettability of the viscose yarn is clearly affected by periodate oxidation.

Equilibrium heights were higher for the samples oxidized with 0.2% periodate for up to 60 min than for the unmodified sample, whereas they were lower for the samples treated with higher concentration or for longer oxidation time. The lowest h_{eq} value was found in the sample modified with 0.4% $NaIO_4$ for 360 min, which was expected since the highest amount of aldehyde groups was introduced under these oxidation conditions.

It can be seen in Figure 7 that h^2 values vary linearly with time in the initial 60 s. This is in accordance with Eq. (3) and allows determining coefficient *D*, which is directly related to both the size of capillaries and the contact angle.[27] Straight lines are also obtained when the values of *H* are plotted as a function of time up to 600 s (Fig. 8), giving satisfactory correlation coefficients, except in one case (0.94).

The values of parameters *D*, *C* and *R* for the unmodified viscose yarn and those oxidized under different conditions are given in Table 1. Significantly higher values of coefficients *D* and *C* are obtained for the samples oxidized with 0.4% periodate, compared with the untreated one and the samples oxidized with 0.2% periodate. Coefficients *D* and *C* obtained for the viscose samples oxidized with 0.4% periodate are about 3 times higher than coefficients *D* and *C* obtained for the untreated sample and about 1.5-2 times higher than the same coefficients obtained for the samples oxidized with 0.2% periodate. On the other hand, the variation of the coefficients' values with oxidation time, within the same group of samples, means that during oxidation not only a significant amount of aldehyde groups was introduced, but also the morphology of the samples was affected, in terms of changed pore radius. The *R* values (Table 1) mostly range between 0.73-0.89, which confirms the validity of the assumption $\theta = \theta_{eq}$.

The formation of hemiacetal linkages in the early stage of oxidation may cause the reduction of the radius of pores, which can lead to the increase of liquid rise height. With the oxidation progress, occlusion of small pores may occur because of more extensive crosslinking, resulting in lower h_{eq} values. Moreover, the equilibrium height for most of the oxidized samples was established after 1800 s (Fig. 6).

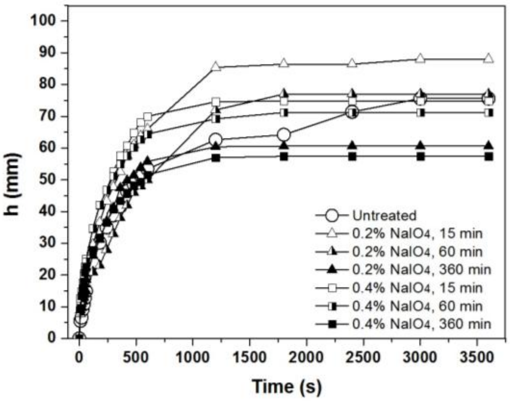

Figure 6: Capillary rise for viscose yarn oxidized with different periodate concentration and oxidation time

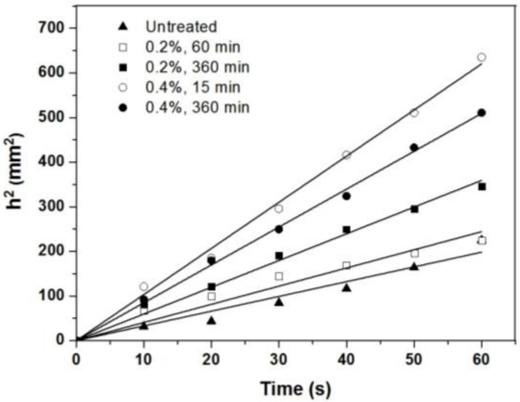

Figure 7: Variation of h^2 values with time for viscose samples oxidized with different periodate concentration and oxidation time

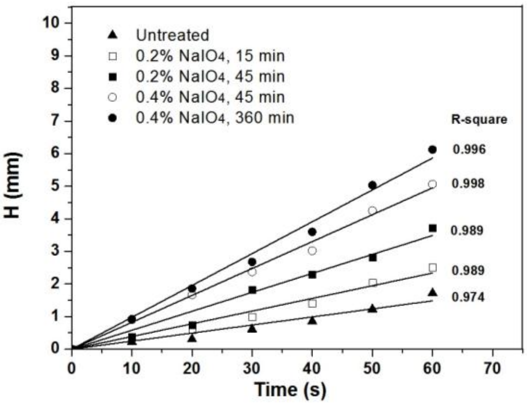

Figure 8: Variation of *H* values as a function of time for oxidized viscose samples with given coefficients of determination *R*

Table 1
Coefficients *D*, *C* and *R* determined for viscose samples oxidized with different periodate concentration and oxidation time

Oxidation conditions	Untreated	0.2% $NaIO_4$					0.4% $NaIO_4$				
		15 min	30 min	45 min	60 min	360 min	15 min	30 min	45 min	60 min	360 min
D, mm^2/s	3.31	5.95	6.95	9.99	4.07	5.99	10.34	10.81	10.00	9.83	8.49
C, mm/s	0.03	0.04	0.05	0.06	0.03	0.06	0.09	0.09	0.08	0.09	0.10
R	0.73	0.85	0.89	0.82	0.88	0.82	0.77	0.79	0.83	0.77	0.74

This could be related to their more compact, crosslinked structure, which is also recognized as an important factor that contributes to the reduction of WRV and ISV. The large cracks on the fiber surface formed when the oxidation was performed under severe conditions probably had a significant role in decelerating the movement of liquid and lowering the h_{eq} values.

CONCLUSION

Viscose yarn was gradually oxidized by adjusting sodium periodate concentration and oxidation time. The process was followed by an increase in aldehyde group content, up to 1.284 mmol/g, corresponding to 10.4% of glucose units oxidized, and by an alteration of the supramolecular structure and surface morphology. As a result, the sorption properties of the viscose yarns changed significantly, especially when severe oxidation conditions were applied. The most pronounced changes were seen in the water retention power and iodine sorption of the oxidized samples, which decreased with the oxidation level to 32.4% and 53.6%, respectively. Compared to the unmodified viscose, a decrease of moisture sorption and increase of wettability was found for the samples with a lower oxidation level, and *vice versa*. Such sorption behavior of the periodate oxidized viscose can be attributed not only to the conversion of hydroxyl to aldehyde groups, but also to improved fiber integrity with less accessible cellulose hydroxyl groups caused by the crosslinking effect and increased microporosity resulting from the cracks formed on fiber surfaces.

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