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Depolymerization During Nitroxide-Mediated Oxidation of Native Cellulose

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ABSTRACT: The kinetics and mechanism of depolymerization during nitroxide-mediated oxidation of native cellulose has been studied under various conditions. The physical heterogeneity of the native cellulose and its complicated hypermolecular and supramolecular structure exerts a remarkable influence on the kinetics of oxidation and depolymerization. A strong influence of external tension applied on cellulose gauze reactivity during its oxidation has been proven, which is caused by its complicated hypermolecular structure. Celluloronic acids were obtained by the application of external tension during selective oxidation of native cellulose textiles. The cellouronic acids contained the higher amount of carboxyl groups but they also had a lower intrinsic viscosity, i.e., the average degree of polymerization (DP). The mathematical model—so-called DP-peeling off model—has been derived to describe the kinetics of cellulose depolymerization based on experimental data obtained. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3641–3647, 2007

Key words: cellulose aging; cellouronic acid; oxidized cellulose; degradation; nitroxide oxidation

INTRODUCTION

Knowledge of nitroxide-mediated oxidation of cellulose accompanied by its degradation is important not only for celluloronic acid preparation for biomedical or technical applications, but predominantly, as a novel approach to understand and control the aging of cellulose materials, e.g., in paper and paper products. Logically, it seems reasonable to suppose that these types of reactions are also evoked during the degradation and the destruction of cellulose in natural atmosphere contaminated with high amounts of pollutants.

The nitroxide-mediated oxidation, in which dimeric nitroxide is applied in acidific aqueous media, is a well known method e.g., Ref. 3,10,15,19–23 to oxidize cellulose to get (1→4)-linked β-D-glucuronan (C-6-oxycellulose). The pH value (1% extract in water) of oxidized cellulose varies from about 3 to 4. This oxidation enables almost selective conversion of C6 primary hydroxyl groups in the polysaccharides to carboxyl groups, and thus the corresponding polyuronic acids, i.e., celluloronic acid—PAGA(poly 1,4-β-D-anhydroglucuronic acid)—with different degree of substitution (DS) and degree of polymerization (DP), are obtained quantitatively. However, as remarked by Painter et al.,[12] the oxidation by this method is not absolutely specific for position 6. Under the conditions required for complete oxidation of the primary alcohol groups, approximately 8% of the units are also oxidized at secondary positions.

The oxidation of native cellulose by HNO_3/H_2SO_4-$NaNO_2$ or HNO_3/H_3PO_4-$NaNO_2$ mediated oxidation[3,4] is an older alternative to oxidation of regenerated cellulose.[18] It is known that an oxidation of native cellulose gives products with different uniformity and hypermolecular structure due to complicated morphology of its fiber walls. The reaction of cellulose fibers usually takes place in heterogeneous system. While some functional groups and glycosidic bonds are immediately accessible for reactions with aqueous reagents, some groups can react only after they have been made accessible to the reagents. However, the reagents can only reach these functional groups after they have overcome the forces that hold the structural building units together and determine their ''accessibility.''

Cellulose is characterized by highly ordered repeating units, linear molecular chains, moderate

chain flexibility, abundant and reactive hydroxyl groups, and strong interchain forces. Intra- and intermolecular hydrogen bonds, together with dipole and van der Waals forces, but predominantly hydration bonds in water medium[8,9] determine the physical and chemical characteristics of native cellulose with commonly high level of crystallinity and moderate to low levels of accessibility. It can be also envisaged that the hydrogen bonds holding the chain molecules together in the dry solid network and hydrogen bonds operating among the functional groups within the molecules may—to some extent—even influence the nature of reactions,[6] i.e., progressive oxidation and degradation. It was suggested that polysaccharides in their native, crystalline state are more stable to aqueous reagents than in that amorphous state. Crystallinity decreases and accessibility increases in a sequence such as: *Valonia ventricosa*, ramie, cotton, and regenerated cellulose as rayon.[5] When solid (fibrous) cellulose is treated with acids quite often its physical (supramolecular) structure changes and it can be expected that this change also affects the response of acid treated cellulose to oxidation.

The hydrolysis may precede or follow the oxidation if aqueous solutions of oxidants are used (see Fig. 1). So the result of oxidation of cellulose may be masked by or superimposed upon hydrolytic effects. The selective acidific oxidation of cellulose as a polysaccharide involves both a progressive stepwise reaction commencing at the oxidation of methylol group of glucose unites and a direct hydrolytic cleavage of the glycosidic bonds. Since usually solid (fibrous) cellulose and not molecularly dispersed cellulose is exposed to the action of acidific solutions, the availability or ''accessibility'' both of the methylol groups and of the glycosidic bonds can be expected to affect the rate of the reactions. Because of supramolecular structural effects of fibrous cellulose with different accessibilities in the crystalline and amorphous areas, the oxidation of hydroxyl groups in one area may go as far as the aldehyde stage, whereas in another area it may go as far as the carboxylic stage.[7] Oxidized celluloses, thus, are chemically heterogeneous compounds, consisting of unoxidized and differently oxidized building units.

It is well known, in the presence of aqueous mineral acids (and commonly at elevated temperature in clean water), microstructural units of cellulose are attacked with the formation of glucose and soluble oligosaccharides along with an insoluble fraction. It has been observed that, among physical and chemical factors, mechanical tension has an influence on the behavior of native cellulose during acid hydrolysis.[16] However, the kinetics of heterogeneous acid degradation of cellulose fibers during their oxidation, except[13] for TEMPO-mediated oxidation, has received comparatively a little attention.
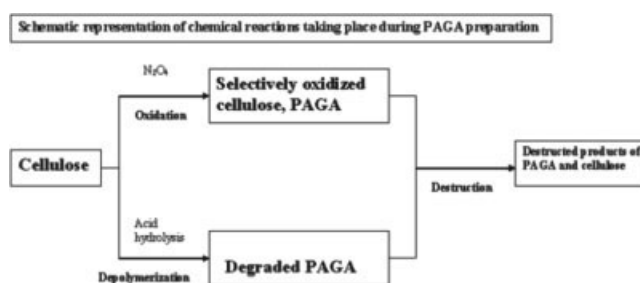
Figure 1 Schematic representation of chemical reactions taking place during selective acid oxidation of cellulose.

The purpose of this work was to examine behavior of native cellulose during its selective oxidation in acid environment and to explain this mechanism. Because of the practical importance of this methodology, the response of cellulose to mechanical action and especially the impact of external tension on cellulose in form of textile was the main interest. The kinetics of oxidation was investigated by measurement of carboxyl group content, while an influence of the acid hydrolysis was determined by DP (decreasing tendency in a sample of cotton filament during its oxidation).

EXPERIMENTAL

Materials

The commercial cotton textiles (gauzes) for medical application (VLT-INVAZ, Kocléřov, Czech Republic) were used as native cellulose knitted fabric materials. Nitric acid, sodium nitrite, and sulfuric acid were of a pure grade (Synthesia, Pardubice-Semtin) and used without any further purification.

Methods

The native cellulose in the form of gauze was fixed on a special grooved cylindrical device enabling us to apply the external mechanical tension within the knitted fabric. The oxidation was started by diving the cylinder with fixed gauze into oxidation bath consisted of 58–60 wt % HNO_3, 3–5 wt % H_2SO_4, and 4.2–4.6 wt % HNO_2. The bath was tempered at $20 \pm 2°C$. By putting back, the oxidation was quenched immediately by washing (twice in centrifuge) thoroughly with water and finally with ethanol and dried at $40°C$ in a vacuum oven. The blank experiments simulated only acid hydrolysis without the presence of HNO_2.

Analyses

The viscosity-average DP of oxidized cellulose were calculated from their intrinsic viscosities in cadoxen[14] using Mark–Houwink equation

$$DP = 148.3[\eta_{CAD}]^{1.105},$$

where $[\eta_{CAD}]$ limit viscosity number of nitrous oxidized cellulose in cadoxen solution. Although Blaha et al.[2] exactly described the determination of DP in the iron tartrate complex (FeTNa) solution, we used the cadoxen method because of its good solvating properties and relative stable, clear, and colorless solutions.[1]

Determination of the carboxyl content in oxidized cellulose was performed according to the method employed by Kumar and Yang.[15] About 0.5 g of oxidized cellulose gauze was accurately weighed and soaked in 50 mL of 2% (w/v) calcium acetate solution for 30 min. The mixture was titrated with a $0.1M$ NaOH solution using phenolphthalein as an indicator. The carboxyl content in oxidized cellulose was calculated as follows:

$$\text{carboxyl groups (\% w/w)} = \frac{N.V.45 \times 100}{\text{weight of sample (mg)}},$$

where N is the molarity of NaOH, and V is the volume (mL) of NaOH consumed in titration after correcting this one for the blank.

RESULTS AND DISCUSSION

Acid hydrolysis

Through random acid hydrolysis in solid cellulose, the glycosidic linkages are split, and for each splitting one hemiacetal and one hydroxyl end group are formed, thus yielding shorter chains. The mechanism of the acid-catalyzed hydrolysis is well known. It is described in detail in a comprehensive study of Szejtli.[17] The depolymerization of cellulose during its degradation by acid hydrolysis is often described by two rate mechanisms.[11] In the presence of excess of water environment, the reaction is first order, but if measurements are done at the very early stages of the reaction, this is indistinguishable from zero order. As demonstrated by Nevell,[11] both of these kinetics are possible to describe with equations for first order and zero order reactions with mathematical solution resulting in the so called Ekenstam eq. (1):

$$1/DP - 1/DP_0 = k.t \tag{1}$$

where DP_0 and DP are degree of polymerization at start and after time t of cellulose depolymerization, respectively. The eq. (1) is only one being utilized generally for description of cellulose depolymerization in both regenerated and native form. However, this equation describes the kinetics of depolymeriza-

tion including all of experimental data if the depolymerization is fully randomly controlled process, i.e., the degraded polymer is homogeneous.

If the mass concentration, y of a monomer unit ($M_{monomer}$) in polymer ($M_{polymer}$) is defined as

$$y = 1/DP = M_{monomer}/M_{polymer},$$

then we can describe a depolymerization kinetics of the homogeneous polymers in terms of the simplest following formula (2).

$$dy/dt = k. \tag{2}$$

Again, by integration of (2), one obtains above-mentioned Ekenstam eq. (1). To verify experimental data we have further utilized the rearranged form of eq. (1) denoted as a reciprocal kinetic model of depolymerization (3):

$$DP = 1/(a + b.t), \tag{3}$$

where $a \equiv y_0 = 1/DP_0$ and $b = k$. According to eq. (2), the rates of random splitting of polymer are constant at each stage of depolymerization. Such behavior is typical for homogeneous polymer, not so for native cellulose. There is supposed some more slowly depolymerization rate of less accessible crystalline localities and rapid degradation of easily accessible amorphous parts of cellulose.

Thus, a heterogeneous degradation of cellulose is characterized by two distinct process phases[24]—an initial fast reaction followed with a slow process. The initial phase associated with a small cellulose dissolution (7%) and a sharp DP reduction has been generally attributed to degradation in the easily accessible areas of cellulose (see Fig. 2). The simple mathematical model, called as simple DP-peeling off
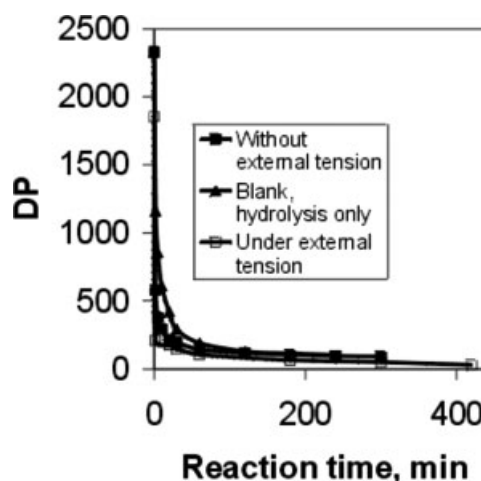
Figure 2 Kinetic of PAGA depolymerization taking place during selective acid oxidation of cellulose.

TABLE I
Verification of Cellulose Depolymerization Kinetic

Model	General DP-peeling model	Reciprocal kinetic model	Simple DP-peeling model
Sample	Cotton gauze without external tension		
s	16.80206	108.6025	20.65740952
$r_{x,y}$	0.999735	0.987475	0.999550
a	0.0004289	0.000431	0.00042916
b	0.0009952	0.000561	0.0009132
c	0.45325	1	0.5
K	1.07861 E^{-7}	0.000561	4.16967 E^{-7}
N	1.206287921	0	1
k (min^{-1})	4.95212 E^{-7}	1.57 E^{-7}	4.16967 E^{-7}
Sample	Cotton gauze under external tension		
s	29.1042354	90.83845	52.76130759
$r_{x,y}$	0.99908274	0.989525	0.996479
a	0.000538735	0.000539	0.000539061
b	0.00346082	0.001737	0.002103921
c	0.27495985	1	0.5
K	3.0869 E^{-10}	0.001737	2.21324 E^{-6}
N	2.636894623	0	1
k (min^{-1})	5.98864 E^{-6}	1.51 E^{-6}	2.21324 E^{-6}
Sample	Cotton gauze, blank, acid hydrolysis only		
s	22.51314161	111.1203	86.8063361
$r_{x,y}$	0.99959372	0.988626	0.993074
a	0.00042935	0.000441	0.00042447
b	0.00025931	0.000148	0.000384278
c	0.68376784	1	0.5
K	3.89201 E^{-6}	0.000148	7.38348 E^{-8}
N	0.462484694	0	1
k (min^{-1})	3.36208 E^{-8}	1.1 E^{-8}	7.38348 E^{-8}

The $r_{x,y}$ and s are the correlation coefficient and standard deviancy coefficient of estimation, respectively.

model, enabling us to describe this behavior we can deduced by similar but more complicated application of eq. (2). Thus, the eq. (4) is obtained:

$$dy/dt = k/(y - a), \qquad (4)$$

where $a \equiv y_0$, because for $t = 0$ is $y = y_0$; $k = b^2/2$.

By integration of (4) and rearranging, the eq. (5) which is useful for experimental data verification has also been obtained

$$DP = 1/(a + b.t^{0.5}), \qquad (5)$$

where $b = \sqrt{2k}$. Moreover, it is possible to rewrite this model in the form of general eq. (6) called as general DP-peeling off model:

$$dy/dt = K/(y - a)^n, \qquad (6)$$

where $n = (1 - c)/c$, $K = c.b^{1/c}$, and again $b = \sqrt{2k}$ and $a \equiv y_0 = 1/DP_0$. Logically, if the exponent $n \to 1$ then the value of $c \to 0$, .5. In the case $c \leq 0$, .5, the value of coefficient $n \geq 1$ and the polymer degradation, characterized by DP decrease, is more significant. The equation following the solution of differential eq. (6) at boundary conditions:

if $t = 0$ $y = y_0$ or $1/DP_0$

if $t = t$ $y = y$ or $1/DP$

and useful for verification of experimental data has then a form (7).

$$DP = 1/(a + b.t^c) \qquad (7)$$

All equations, i.e., (3), (5), and (7) have been further utilized for experimental data verification and comparison.

By comparing all of these models (Table I), obviously, DP-peeling off models are suitable for a quantitative description of cellulose hydrolysis processes. Especially the general DP-peeling off model is the most useful. The results given in Table I:

-a strong influence of oxidative reactants on acid cellulose hydrolysis (compare both the rate constancy k and the exponent coefficient n of usual acid hydrolysis in blank experiments with both oxidative experiments);

-a strong influence of external tension on acid cellulose hydrolysis (compare both the rate constancy k and the exponent coefficient n of acid
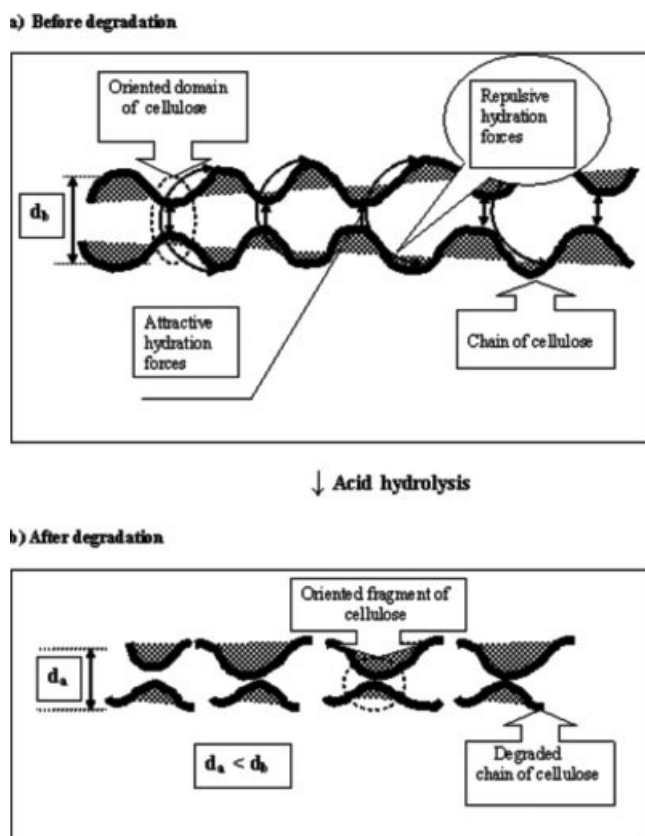
Figure 3 Schematic representation the shrinkage mechanism of cellulose chains during its degradation.

hydrolysis with and without application of external tension during cellulose oxidation process).

While the usual acid hydrolysis of native cellulose takes place predominantly in accessible amorphous domains, i.e., more topochemically, the degradation of native cellulose during its oxidation is faster and more intense (values of the exponent coefficient n are higher than 1) and this one also takes place in orientated crystalline domains of cellulose but not so intensive. Moreover, by application of external tension the acid hydrolysis is more extensive resulting in more homogeneous but more degraded cellulose material. Interestingly, depression of usual shrinkage of oxidized cotton gauze by application of external tension has been observed.

Respecting facts that, at the soaked state, water molecules are present in both amorphous and highly ordered crystalline domains of native cellulose (bounding cellulose chains mutually by hydration bonds[8]), it is possible to explain this behavior by mechanism schematically represented in Figure 3. Considering dominating effect of repulsive hydration forces in less ordered amorphous domains and of attracting hydration forces in more ordered predominantly crystalline domains of cellulose, by pulling on the individual cellulose chains, i.e., by the action of

external tension, an accessibility of reactants is approximately equalized in both of them. Therefore, as a result of action of oriented external tension the reactivity of native cellulose is more homogeneous and less topochemical. Because of more homogeneous reaction caused by application of external tension, an internal strain is eliminated significantly because the cellulose chains are also interrupted within oriented crystalline domains of cellulose.

Kinetics of oxidation

The increasing content of carboxyl groups during selective oxidation of native cellulose was observed indicating a presence of the oxidative reaction. Provided that there is an excess of oxidized ingredients in the water and the mechanism of the reaction does not change during the oxidation process, the reaction is of first order. Thus the following well known mathematical description is obtained:

$$-\frac{d[C_{el}OH]}{dt} = \frac{d[C_{el}OOH]}{dt} = k_{COOH} \cdot [C_{el}OH],$$

where $[C_{el}OH]$ and $[C_{el}OOH]$ is cellulose and PAGA concentration, respectively. If $[C_{el}OOH] \equiv [COOH] \equiv z$, then for the first order kinetics

$$dz/dt = k_{COOH} \cdot (z_0 - z), \qquad (8)$$

because

if $t = 0$, $[C_{el}OOH] \equiv [COOH] \equiv z = 0$, and
$$[C_{el}OH] = z_0;$$

if $t = t$, $[C_{el}OH] = (z_0 - z),$

where in limit $t \to \infty$, $[C_{el}OOH] \equiv [COOH] \equiv z \Rightarrow z_0$.
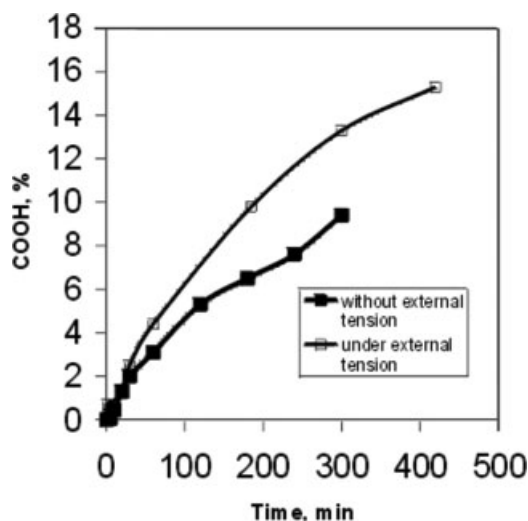
Figure 4 Kinetic of native cellulose oxidation.

TABLE II
Verification of Cellulose Oxidation Kinetic

Sample	Cotton gauze without external tension	Cotton gauze under external tension
s	0.30178	0.30546
$r_{x,y}$	0.99646	0.99921
Z_0 (%)	11.6	19.04
k_{COOH} (min^{-1})	0.00493	0.00402

$r_{x,y}$ and s are the correlation coefficient and standard deviancy coefficient of estimation, respectively.

Thus, a value of z_0 is the full concentration of methylol groups being potentially oxidized to carboxyl groups during selective oxidation of cellulose.

By integration of (8), the eq. (9)—available for experimental data verification—is obtained.

$$z = z_0 \cdot (1 - e^{-k_{COOH} \cdot t}). \qquad (9)$$

Some typical data needed for kinetic verification are presented in Figure 4 and the results received are collected in the Table II. By comparison with acid hydrolyzes, it is clear that the oxidation process of native cellulose is more homogeneous and this phenomenon is further improved by the application of external tension on oxidized cellulose. However, although the oxidation reaction under application of external tension is more homogeneous and intense, the reaction rate is lower.

These results signalize that the oxidation process of native cellulose takes place predominantly in homogeneous poorly organized amorphous parts of cellulose substrate. By the application of external tension, the process is partly extended into less accessible oriented parts of cellulose. These findings fully comply with observations of Zimnitski et al.[25] confirming that the oxidation of native cellulose takes place mainly in amorphous localities and on the surface of crystallites.

Relationship between DP and oxidation

As Figure 1 indicates, these parallel reactions occur during cellulose oxidation in acid water environment:

- selective oxidation,
- acid hydrolysis,

followed by destruction of monomer products of these reactions. The relationship between the degree of depolymerization and state of the cellulose oxidation at comparable conditions is possible to obtain explicitly in form of eq. (10) by mathematical connection of the eqs. (9) and (5)

$$z = B \cdot \left[1 - \exp(-C(1 + 3Ax).(1 - Ax)/x^2) \right], \qquad (10)$$

where $x \equiv DP$; $B = z_0$; $C = k_{COOH}/2k$; $A \equiv y_0 = 1/DP_0$, because

$$-\frac{dz}{dx} = \frac{dz/dt}{-dx/dt} = \frac{k_{COOH} \cdot (z_0 - z).(1 - a.x)^n}{K.x^{n+2}}, \qquad (11)$$

and $dy/dt = -1/x^2 \cdot dx/dt = K.x^n/(1 - a.x)^n$, where $y = 1/x$.

The usable eq. (10) is obtained by integration of eq. (11) provided that $n = 1$ and $K = k$ (simple DP-peeling off model) at the following boundary condition:

$$z \equiv [COOH] = 0; \qquad x = x_0 \equiv DP_0$$

$$z = z; \qquad x = x \equiv DP.$$

The relationship between the concentration of carboxylic groups in cellulose and its DP is demonstrated in Figure 5. The verification of this relationship according to eq. (10) is presented in Table III. Again, as resulted from the Table III, the both processes, i.e., the oxidation and the depolymerization of cellulose, are more intense if the cellulose oxidation is conducted under applied of external tension. This can be supported by comparing of values z_0, e.g., $z_0 = 22\%$ COOH (w/w) in the cellulose oxidized by application of external tension (compare with theoretical value of $z_0 = 25.57\%$ COOH for DS 1).

More exactly, an influence of external tension on oxidation process of native cellulose is featured by comparison of theoretical values of DP and COOH groups content at defined conditions (see Table IV). Results in Table IV demonstrate a strong influence of external tension application on the reaction time, DP and content of carboxyl groups in cellulose
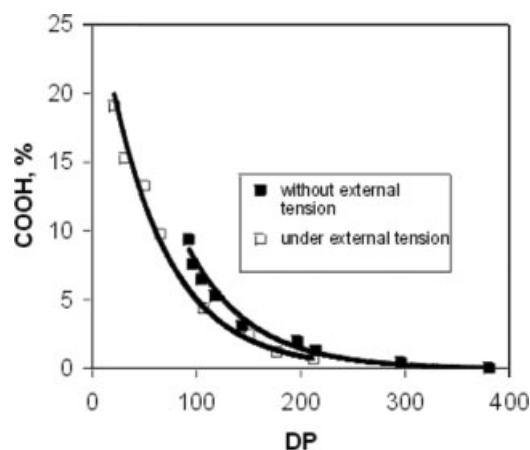
Figure 5 Relationship of COOH groups versus DP of native cellulose during its oxidation.

TABLE III
Verification of Relationship Between COOH Groups Content and DP of Native Cellulose During its Oxidation by Use of eq. (10)

Sample	Cotton gauze without external tension	Cotton gauze under external tension
$A \equiv y_0$	0.00043	0.00053
DP_0	2330	1870
$B \equiv z_0$, % COOH	14.6	22
$C = k_{COOH}/2k$	3559	913.2

increased by prolonged time of the oxidation. For instance, at low degree of oxidation (low content of COOH groups) the reaction time to receive PAGA with 5.2% COOH groups by cellulose oxidation under external tension influence is longer than the reaction at usual conditions of oxidation. On the other hand, at comparable conditions of cellulose oxidation and the relative low of PAGA-DP, it is possible—by application of external tension—to achieve higher content of carboxyl groups. The results in the Table IV also demonstrate the different sensitivity of DP and content of COOH groups to the reaction state of oxidation, e.g., at the high degree of oxidation the DP is more sensitive to the reaction state than the carboxyl group's content.

CONCLUSIONS

Selective oxidation of native cellulose is nonhomogeneous fully topochemical process during which, in addition to oxidation controlled by its supramolecular and hypermolecular structure, a depolymerization of cellulose occurs. Because of this fact, it is pos-

TABLE IV
Theoretical Calculated Values of DP and COOH Groups Content in Cellulose Oxidized by Two Modes of Preparation

DP	COOH (%)	Reaction time (min)
93	5.2	174
58	9.8	511
25	14.5	3380
15	14.6	10532
10	14.6	25886
60	5.2	270
40	9.8	1227
25	17.1	6985
15	21.6	45668
10	22	201521

The DP and COOH groups content were calculated by use of eq. (10) and the data in Table III. The reaction time was calculated by use of eq. (7) and the data in Table I.

sible to control all of these processes by nonchemical interventions, e.g., by use of an external mechanical tension with controlled orientation. In this case, the oxidation accompanied by degradation of cellulose chain is more homogeneous taking place not only within poorly organized amorphous parts of cellulose but also in less accessible oriented crystallites of cellulose.

While the kinetic of oxidation process is relative to simple first order reaction, it has been demonstrated that the acid hydrolysis of cellulose chains is more complicated topochemical process, which can be described by so called DP-peeling off models. According to these models, the depolymerization of cellulose chains is not fully random process but it is strongly influenced by its supramolecular structure.

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