Characterization of Oxidized Cellulose with Ultraviolet–Visible Spectroscopy

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ABSTRACT: This article describes some properties and behavior of oxidized cellulose evaluated with ultraviolet–visible spectroscopy. Newly defined analytical parameters are described. Mechanisms of poly(1,4-β;-D-anhydroglucuronic acid) degradation and destruction are formulated. The feasibility of using the same Staudinger–Mark–Houwink equation to calculate the degree of polymerization of cellulose and the degree of polymerization of oxidized cellulose is demonstrated. Utilization of ultraviolet–visible spectroscopy is shown for the optimization of oxidized cellulose production and aging. Advantages and limitations of this method are discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2045–2052, 2008

Key words: ageing; biomaterials; degree of polymerization (DP); molecular weight distribution/molar mass; UV–vis spectroscopy

INTRODUCTION

At present, two types of oxidized cellulose (OC) products are described. They are OC and oxidized regenerated cellulose (ORC). These types are prepared by the treatment of cellulose or regenerated cellulose with an oxidizing agent, such as nitrogen dioxide (the most usual),[1,2] HNO_3/H_2SO_4–$NaNO_2$ or HNO_3/H_3PO_4,[3,4] or others.[5] Partial oxidation of cellulose results in a biomaterial with controlled degradation characteristics. The various types of OCs and ORCs are used in medical devices such as absorbable hemostatic agents and absorbable adhesion barriers and furthermore in cosmetics, food production, and so forth. Detailed knowledge of nitroxide-mediated oxidation of cellulose, including its degradation and destruction, not only is important for OC preparation but also helps us to better understand and control the aging of OC and cellulose materials. Logically, it seems reasonable to suppose that these types of reactions are also evoked during the aging of cellulose in a natural atmosphere because oxides of nitrogen pollute the air. A major problem of oxidation is the difficulty of producing materials that should be homogeneous for chemical and physical properties. The oxidation of natural cellulose is a typical topochemical reaction. OCs are chemically heterogeneous compounds consisting of monoxidized and differently oxidized building units. The selective acidic oxidation of cellulose involves both a progressive stepwise reaction commencing with the oxidation of methylol groups of glucose units and direct hydrolytic cleavage of the glucosidic bonds (a cellulosic degradation process) followed by its destruction.[4] Thus, OC prepared by the oxidation of natural cellulose is a mixture of poly(1,4-β;-D-anhydroglucuronic acid) (PAGA) and other products initiating the destruction of PAGA that have different supramolecular structures in the oriented and amorphous part of the cell wall. PAGA is composed of many modified cellulosic molecules with different degrees of polymerization (DPs) characterized by their distribution. Furthermore, there is a different distribution of COOH groups around cellulosic chains. In reality, PAGA represents a lot of polymeric compounds on a glucose and glucuronic acid (GA) basis with different molecular weights and compositions. Maintaining control over the oxidation reaction determines the carboxylic group content measured by titration. OC is usually characterized by no less than 16 and no more than 24 wt % carboxylic acid groups; this corresponds to a 60–93 mol % conversion of the anhydroglucose units to anhydroglucuronic acid.[1]

Unfortunately, knowledge of the carboxylic acid content in OC and the DP value is insufficient for the determination of OC properties, as shown later.

Recent investigations have demonstrated that ultraviolet–visible (UV–vis) spectroscopy measurements are useful for the determination of hexenuronic acid and residual lignin in cadoxen solutions of pulps.[6,7] Moreover, other substances occasionally appearing in PAGA and indicating PAGA destruction can be observed through UV–vis spectroscopy of a cadoxen solution within a wavelength range of 350–450 nm.

This article describes a new method for analyzing OC in a cadoxen solution by UV–vis spectroscopy and gives new and more detailed characteristics of OC.

EXPERIMENTAL

As native cellulose, commercial cotton gauze for surgical utilization (VLT, Koclerov, Czech Republic) was used. DP of the gauze was determined by a viscosity method with cadoxen as a solvent. The DP value of the gauze was about 2400. For oxidized cotton gauze (OC) samples (Synthesia, Pardubice, Czech Republic), the common characteristics were a carboxyl content of 15–20 wt % and a DP value of 12–30. For cadoxen–cadmium ethylene diamine hydroxide $\{[Cd(en)_2](OH)_2\}$, the general characteristics were as follows: cadoxen was a clear and colorless solvent, was stable at low temperatures, and was capable of dissolving both cellulose and its derivates.[8]

In the first step, the concentration of carboxyl groups [x_{COOH} (%)] in OC and the value of DP were determined with common processes.

Carboxyl contents in OC

The determination of carboxyl contents in OC was performed with the classical acidimetric titration method.[4,9]

DP

The DP values of OC and cellulose were determined by a viscosity method in cadoxen solutions. The concentrations of cadoxen solutions were 4 g of OC/L of cadoxen and 2 g of cellulose/L of cadoxen.

The stability of cellulose and OC cadoxen solutions is the fundamental criterion for the determination of DP. The oxidative degradation of a cellulose solution in cadoxen is nearly negligible,[8] whereas the chemical processes of an OC solution in cadoxen continue.[2] Therefore, the DP value of OC must be determined under exactly equal conditions. The viscosity of OC cadoxen solutions was measured with an Ubbelohde no. Ia viscosimeter. The viscosity of the cellulose cadoxen solutions was measured with an Ubbelohde no. II viscosimeter. The time was measured with a ViscoClock (Schott, Mainz, Germany); its accuracy of measurement was ±0.01 s.

Calculation of DP

The viscosity-average DPs of cellulose and OC were calculated from their intrinsic viscosities in cadoxen solutions[10] with the Staudinger–Mark–Houwink equation:

$$DP = 148.3[\eta_{CAD}]^{1.105} \tag{1}$$

where η_{CAD} is the limit viscosity number of nitrous OC in a cadoxen solution.

An analogous approach for the calculation of DP of OC samples has been reported elsewhere.[4,11]

The correctness of using eq. (1) for the DP determination of OC was confirmed with the following theory and observation.

If we suppose equal viscosity behavior for mixtures of polymer molecules having different molecular weights but the same number of all monomer units, the same linear structure, and the same average molecular weight, which are proportionally added together according to the distribution of their molecules, and compare these with an OC-soluble polymer having the same number of all monomer units but different shares in individual polymer chains, then those can be mathematically written as follows:

$$M.c = \sum_i M_i \times c; \quad c = \sum_i c_i \tag{2}$$

where c and c_i are molar concentrations (moles of monomer units/volume of solvent) of polymers with average molecular weight M and molecular weight M_i, respectively. That is,

$$c = m/(M_{momomer} \times V); \quad c_i = m_i/(M_{momomer} \times V)$$

where m, m_i, and V denote the mass of the polymer in solution, the mass of the polymer with molecular weight M_i in solution, and the solvent volume, respectively. Then, by simple mathematical reorganization of eq. (2), eq. (3) can be obtained in the following form:

$$DP = \sum_i DP_i \times x_i; \quad \sum_i x_i = 1 \tag{3}$$

where $DP = M/M_{monomer}$ and $DP_i = M_i/M_{monomer}$ are the degrees of polymerization of an average polymer and a polymer with molecular weight M_i and mass concentration x_i (w/w), respectively. In the simplest case, the polymer solution consists of a binary mixture of polymers with a high molecular weight (characterized by DP_H) and with a low molecular weight (characterized by DP_L); then, eq. (3) can be rewritten as follows:

$$DP = DP_L \times x + DP_H \times (1 - x) \tag{4}$$

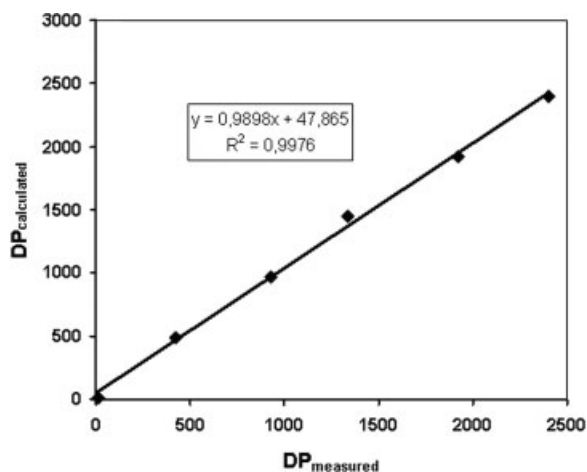where x is the polymer concentration (w/w) for a polymer of low DP_L.

Figure 1 $DP_{calculated}$ versus $DP_{measured}$.

Confirmation of the mass proportionality of DP in a mixture of polymers was demonstrated for a mixture composed of OC with $DP_L = 11.2$ and cellulose with $DP_H = 2400$ (Fig. 1). $DP_{calculated}$ was calculated with eq. (4) and the known compositions of the model mixtures.

Thus, eq. (4) describes the behavior of a mixture of OC and cellulose very well, as demonstrated in Figure 1. This implies also that the same Staudinger–Mark–Houwink equation can be used for calculating DP of cellulose and for calculating DP of OC.

New qualitative parameters of OC: Determination by UV–vis spectroscopy in cadoxen solutions

The principle of the determination of new quality parameters of OC is based on the reaction between low molecular fractions in OC and cadoxen under exactly described conditions. The presence of these low molecular fractions in OC leads to further chemical processes in OC cadoxen solutions, as shown later. The processes of the reaction of OC with cadoxen depend on the quality of OC, which is determined by conditions during its production.

UV–vis spectroscopy

First, samples of cadoxen solutions of OC or cellulose were prepared. These were made under the same conditions: the concentration of the cellulose or OC in cadoxen was exactly 1.5 g of cellulose/L of cadoxen or 3 g of OC/L of cadoxen, respectively. The time of addition of cadoxen to each sample for the measurement of its spectra was kept at 150 min exactly. The temperature was kept at 20 ± 0.1°C.

Second, UV–vis spectra of cellulose or OC cadoxen solutions were recorded on a Helios-Beta spectrophotometer (Thermo Spectronic, Cambridge, England) with carrousel in the range of 200–500 nm against cadoxen with 1-cm-thick quartz cells. The bandwidth was 2 nm.

Curves of UV–vis absorption spectra are shown later in Figures 6–9.

Five measurements were performed per test point, and the average value was reported for the verification of spectral data from each OC sample.

RESULTS AND DISCUSSION

Different types of OC and cellulose spectra (shown later in Fig. 6) indicate that the oxidation of cellulose leads to the creation of low molecular fractions of PAGA, which includes GA, glucose, and other components able to react with cadoxen (discussed later). Obviously, this is due to a keto–enol tautomeric transformation[2] of monosaccharides and oligosaccharides and their derivates in the basic cadoxen medium. On the contrary, this behavior was not indicated in the case of cellulose cadoxen solutions.

The new qualitative parameters have been described with the help of UV–vis spectra in cadoxen solutions:

- Characterization of the polydispersity in OC samples with the help of parameter P_{DP}.
- Content of free GA in OC [x_{GA} (mmol of GA/g of OC)].
- Degree of substitution of carboxylic groups in OC and share of COOH groups in PAGA [x_{DS} (%)].
- Content of destabilizing components in OC [$x_{GA–PAGA}$ (mmol of GA–PAGA/g of OC)].

Characterization of polydispersity in OC samples with the help of parameter P_{DP}

If we know the concentration of the monomers in the OC sample, that is, GA and glucose, then the distribution of DP in a sample can be characterized with the help of eq. (4) because $DP_L = 1$ and DP_H represents the polymer chain with the highest molecular weight. P_{DP} was defined to describe the polydispersity of the DP distribution in the OC sample as follows:

$$P_{DP} = (DP_H - DP)/(DP) \qquad (5)$$

where DP is the polymerization degree of an OC sample measured by the viscose cadoxen method. DP_H is calculated with eq. (4) that is,

$$DP_H = (DP - x_m)/(1 - x_m); \quad x_m(0;1)$$

where x_m (w/w) is the mass concentration of free GA and glucose in the sample. If OC is composed only of PAGA, GA, and glucose, the determination with the help of UV–vis spectra is simple (discussed later).

If $P_{DP} = 0$, then the DP distribution in the sample is monodisperse. With increasing P_{DP} values, the DP distribution becomes more polydisperse.

TABLE I
Characteristic UV Absorption Coefficients of Glucose
and GA in Cadoxen Solutions

	ε (L mol^{-1} g^{-1})	
	Wavelength = 328 nm	Wavelength = 272 nm
Glucose (M = 180)	45	7
GA (M = 194)	126	111

The time of reaction between OC and cadoxen was 150 min. The reaction temperature was 20°C.

Content of free glucuronic acid in the OC-x_{GA}

Optimal absorption wavelengths for GA and glucose were identified with the traditional method. The selective wavelength for GA is 272 nm, and the mass absorption coefficient at 272 nm is 0.57 L/(g cm). An acceptable wavelength for glucose is 328 nm. This one is less selective because it depends also on further low molecular components (predominantly GA). The absorption coefficients obtained for GA and glucose are summarized in Table I.

Degree of substitution of carboxylic groups in OC and share of COOH groups in PAGA

The degree of substitution of PAGA (DS$_{PAGA}$) is given by the molar ratio of the number of carboxyl groups in PAGA ($n_{COOH,PAGA}$) to the number of all anhydroglucopyranosic units in PAGA (n_{AG}):

$$DS_{PAGA} = n_{COOH,PAGA}/n_{AG}$$

where

$$n_{COOH,PAGA} = (x_{COOH}/45 - x_{GA}/194) \times m_{OC};$$
$$n_{AG} = (1 - x_{GA}) \times m_{OC}/178$$

$$x_{COOH}(w/w) = m_{COOH}/m_{OC}; \quad x_{GA}(w/w) = m_{GA}/m_{OC}$$

$$DS_{PAGA} = (3.955 \times x_{COOH} - 0.91752 \times x_{GA})/(1 - x_{GA}) \quad (6)$$

m_{OC} is the mass of the OC sample and m$_{COOH}$ is the mass of carboxyl groups in OC sample. x_{COOH} and x_{GA} in a sample of OC were measured by a titrimetric method and by UV–vis spectrophotometrical measurements, respectively.

If $x_{GA} \neq 0$ and $x_{COOH} \leq 0.23195 \times x_{GA}$, then DS$_{PAGA}$ is zero, and DS$_{PAGA}$ = 1 if x_{COOH} = 0.2582.

Furthermore, the degree of PAGA substitution (DS$_m$) is defined as follows:

$$DS_m = 1 \times x_{GA} + (1 - x_{GA}) \times DS_{PAGA} \quad (7)$$

Additionally, ratio X_{DS} describes the share of COOH groups in PAGA:

$$X_{DS} = (DS_{PAGA}/DS_m) \times 100(\%) \quad (8)$$

According to this ratio, if DS$_m$ = DS$_{PAGA}$ or x_{GA} = 0, then X_{DS} = 100%; that is, the amount of free GA in the sample of OC is zero, and then all COOH groups are contained only in PAGA. Controversially, if DS$_{PAGA}$ = 0, that is, x_{COOH} < 0.23195 × x_{GA}, then X_{DS} = 0%, and the sample of OC is composed of cellulose and GA only.

Content of destabilizing components of OC-$x_{GA–PAGA}$

It is useful to define a single parameter that can be used to estimate the self-destructive behavior of OC.

The characteristic UV spectrum of OC cadoxen solutions appears not only at wavelengths of 250–350 nm but occasionally within a wavelength range of 350–450 nm, especially with a maximum at 396 nm. It appears only under the condition of OC containing components initiating its destabilization and destruction (shown later in Figs. 6–9).

As documented in Figure 2, unstable substances (GA–PAGA) starting PAGA destruction are formed by a reaction between PAGA and free GA contained in the OC sample. It is reasonable to believe that this reaction is equimolecular.

The dependence of the light absorbance at a wavelength of 396 nm versus the GA concentration (Fig. 2) was approximated to a zero value to prove this hypothesis.

Supposing a mutual equimolecular reaction between GA and PAGA, then the destabilizing components in OC (designated GA–PAGA) have the characteristic light absorption wavelength of 396 nm.
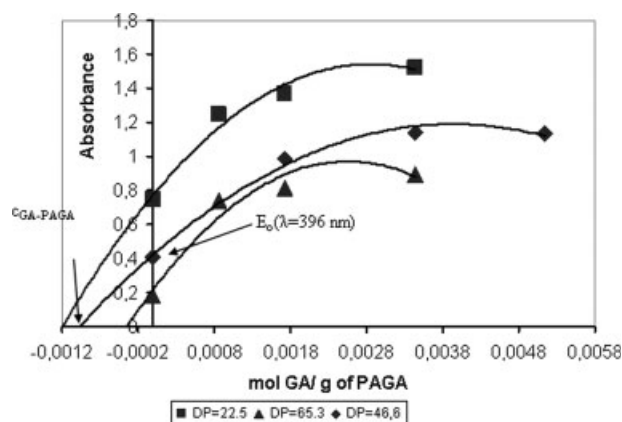

Figure 2 Influence of GA addition on the formation of the GA–PAGA substance. The concentration of OC was 3 g/L of cadoxen. The measurement conditions were as follows: a delayed time of 150 min, a temperature of 20°C, and a wavelength of 396 nm.
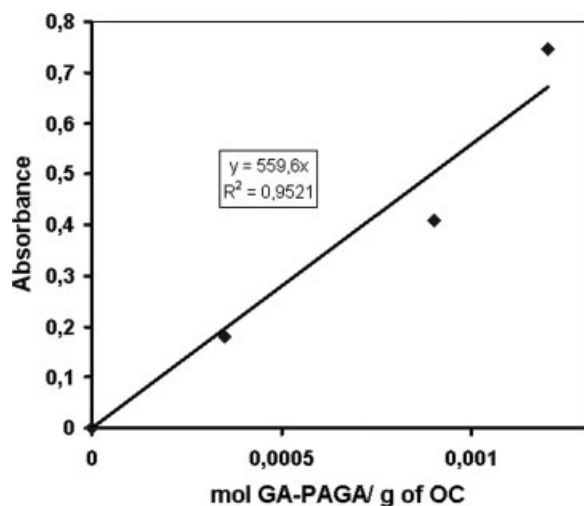
Figure 3 Calibration dependence of equimolecular substance GA–PAGA (for the measurement conditions, see Fig. 2). ε_m (wavelength = 396 nm) was 559.6 g/mol cm.

A plot of E_o (absorbance of OC cadoxen solution at zero GA addition) at a wavelength of 396 nm versus $c_{GA–PAGA}$ (approximated concentration of GA-PAGA in OC sample, see Fig. 2) must be linear with zero intercept. This behavior is confirmed by calibration dependence (see Fig. 3). The mass absorption coefficient (ε_m) at a wavelength of 396 nm (559.6 g/mol cm) or concentration absorption coefficient (ε) at a wavelength of 396 nm (186.5 L/mol of GA–PAGA cm) was calculated on the basis of the mass of OC or on the basis of the volume of the cadoxen solution, respectively.

According to these findings, it is possible to extend the interpretation of PAGA destruction. Obviously, the GA–PAGA substance represents an intermediate followed by its final destruction. The substance or kind of substance (GA–PAGA) has not been identified yet. However, as documented in Figure 4, the creation of GA–PAGA is initiated as soon as the GA concentration in OC achieves the critical concentration of GA ($x_{GAcritic}$) in a sample of 1.4 mmol of GA/g of OC.

A hypothetical mechanism of degradation and destruction of PAGA has been formulated, as shown in Figure 5. During PAGA degradation in a water medium, GA is formulated first, and this is followed by further acceleration of this process due to the strong acidic behavior of GA.

Cellulose in the nonoriented amorphous part of the cellulose matter probably reacts first, and this is followed step by step by a reaction in a deeper and deeper part of the oriented crystalline part of the cellulose matter. Moreover, in the case of suitable reaction conditions, GA initiates the creation of the GA–PAGA intermediate as a predecessor of total PAGA destruction. The suitable reaction conditions are represented by the formation of glucuronic end groups

of PAGA [Fig. 5(a)] reacting further with free GA to form the substance GA–PAGA. GA–PAGA is probably formulated in two forms, that is, the formation of glycosidic and ester O bonds in heptacyclic end structures of PAGA–GA and diester O bonds in decacyclic end structures of PAGA–GA. The stability of these formations is low, and the reactions continue further in the following steps: decacyclic end structures of PAGA–GA are split off into diester decacyclic structures, and this is followed by acid hydrolysis to form two molecules of GA and a remaining shorter PAGA molecule. The heptacyclic end structures of PAGA–GA are split off into a heptacyclic glucuronic ester (HCGE) structure and a shorter PAGA molecule, and this is followed by the destruction of HCGE into low molecular organic compounds in the second step of the destruction reaction [Fig. 5(b)]. As is typical for all of the processes, the dehydration of PAGA takes place.

The absorbance maximum at about 236 nm is not included in the evaluation because cadoxen itself has strong absorption near this value of the wavelength band.[6,7]

Practical utilization of research findings

Optimization of the reaction time in the process of OC preparation

Figure 6 shows UV–vis spectra of the OC cadoxen solutions. Three OC samples (A–C) were prepared through the oxidation of cellulose for different oxidation times. Curve A (oxidation time = 45 h) has maxima at about 300 nm and at 396 nm. With the shortening of the oxidation time (24 h), the maximum for
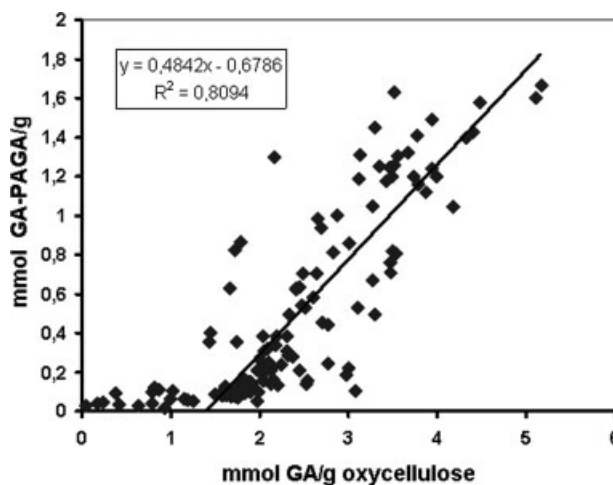

Figure 4 Concentration of destabilizing components in oxycellulose (mmol of GA–PAGA/g of oxycellulose) versus the concentration of GA in oxycellulose (mmol of GA/g of oxycellulose): determination of $x_{GAcritic}$ in OC. The regression line was calculated with all data when the GA concentration was greater than 1.3 mmol of GA/g of oxycellulose.
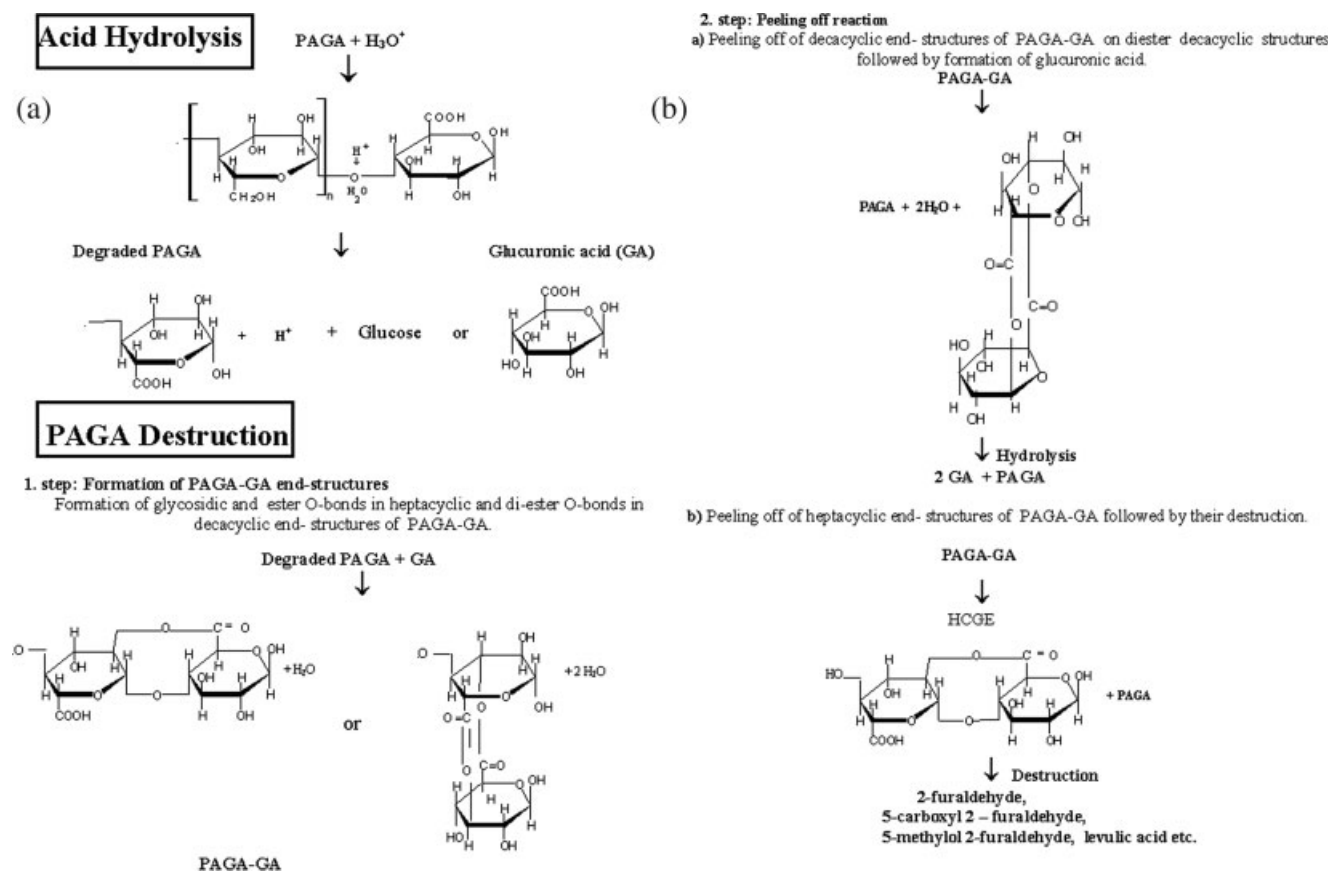
Figure 5 (a) Schematic representation of PAGA degradation followed by its destruction and (b) continuation of the schematic representation of PAGA degradation followed by its destruction.

curve B drops. For curve C (oxidation time = 17 h), neither a maximum at 300 nm nor a maximum at 396 nm was recorded. The data of the spectral absorbance together with the data for the carboxyl group content and DP values were used for the determination of new qualitative parameters. The overview of the determined parameters is presented in Table II.

The results in Table II demonstrate the influence of the time of oxidation of OC on its quality. Although the oxidation time changes new qualitative parameters of OC dramatically, the content of carboxylic acid groups and the DP values of OC are nonsensitive to this one. Therefore, the content of carboxylic acid groups and the DP values are insufficient for the determination of OC properties.

With the shorter oxidation time,

- P_{DP} considerably decreases; that is, OC gets more homogeneous.
- X_{DS} increases; that is, more COOH groups are bound to PAGA molecules.
- x_{GA} decreases; that is, OC destruction is minor.
- $x_{GA-PAGA}$ decreases dramatically. As shown in Table II and Figures 7–9, the decrease in this parameter for OC leads to longer stability during its storage.

Aging of OC during its storage at 40°C

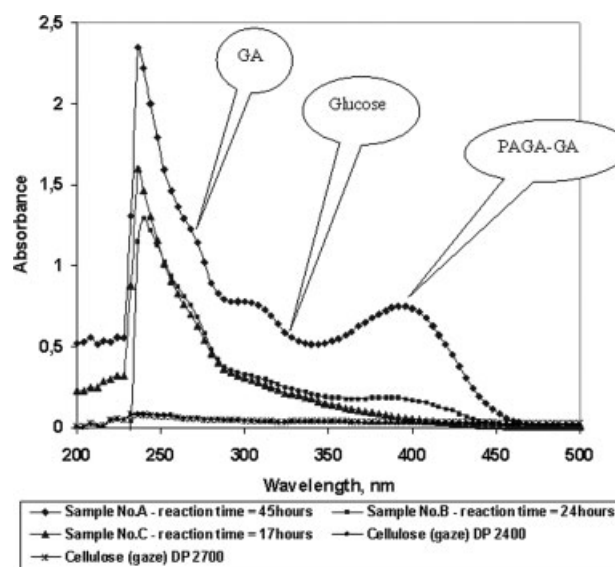OC samples A–C were put into an incubator at 40°C. As shown in Figures 7–9 and Table II, changes in

Figure 6 UV–vis spectra of cadoxen solutions of OC samples (different times of cellulose oxidation) versus UV–vis spectra of cellulose (raw material).

TABLE II
Qualitative Parameters of the OC Samples Prepared with Different Oxidation Times and Their Changes During Storage at 40°C

| OC sample	Time of oxidation (h)	Time of measurement	Storage at 40°C	Appearance of sample	Color of sample	DP	P_{DP}	x_{COOH} (%)	X_{DS} (%)	x_{GA} (mmol of GA/ g of OC)	$x_{GA-PAGA}$ (mmol of GA–PAGA/ g of OC)
A	45	After preparation		Elastic gauze	White	22.5	2.0	17.7	30.6	3.5	1.2
A			2 months	Powder	Yellow		—		—	5.5	2.1
B	24	After preparation		Elastic gauze	White	27.3	0.6	17	66.9	2.6	0.4
B			2 months	Loss of elasticity, fragile	Slightly yellow		3.7		—	4.1	1.5
B			3 months	Powder	Yellow		4.5		—	4.2	1.6
C	17	After preparation		Elastic gauze	White	20.4	0.5	17.7	78.7	1.9	0.1
C			2 months	Elastic gauze	White		1.4		49	3.1	0.6
C			3 months	Elastic gauze	Slightly yellow		1.4		50.9	3.1	0.7
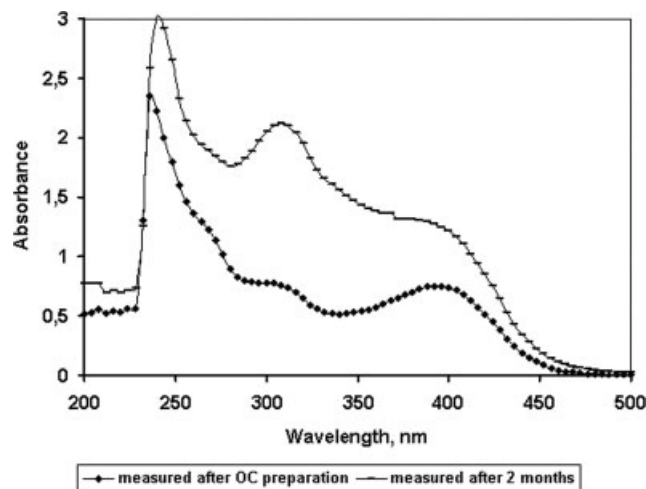
Figure 7 Sample A: change in the absorbance during storage at 40°C. The OC concentration was 3 g/L of cadoxen, and the time of cellulose oxidation was 45 h.

the OC properties during aging were most significant in sample A, which had the highest content of destabilizing components.

CONCLUSIONS

In this study, a new method based on UV–vis spectroscopy in the range of 200–500 nm was developed. It gave us the opportunity to determine new analytical parameters of OC. The new analytical parameters—P_{DP}, x_{GA} (mmol of GA/g of OC), X_{DS} (%), and
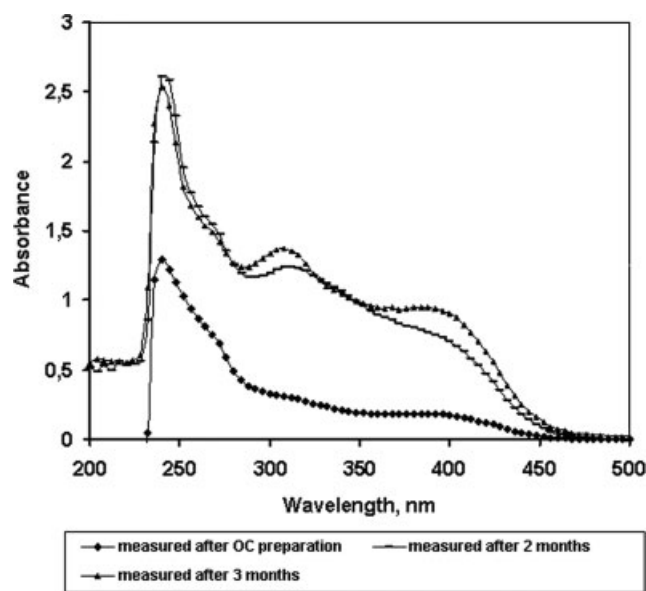

Figure 8 Sample B: change in the absorbance during storage at 40°C. The OC concentration was 3 g/L of cadoxen, and the time of cellulose oxidation was 24 h.
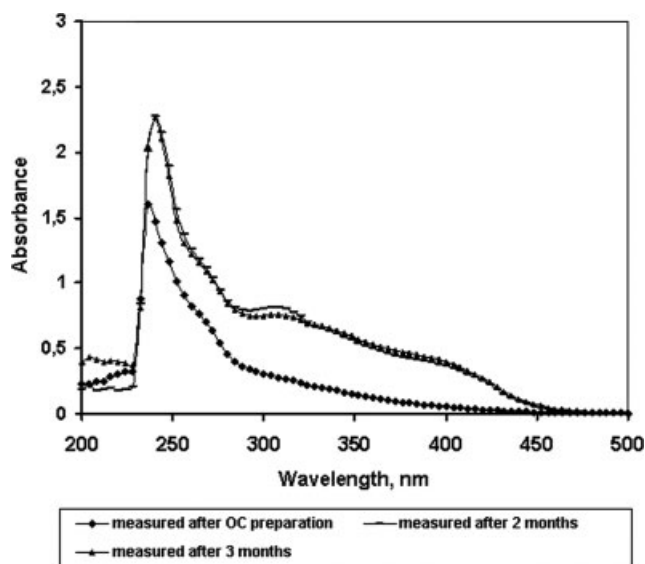
Figure 9 Sample C: change in the absorbance during storage at 40°C. The OC concentration was 3 g/L of cadoxen, and the time of cellulose oxidation was 17 h.

$x_{GA-PAGA}$ (mmol of GA–PAGA/g of OC)—allowed us to study and describe a hypothetical mechanism of degradation and destruction of PAGA during the oxidation of cellulose and its further degradation in a water medium.

Furthermore, the possibility of using the same Staudinger–Mark–Houwink equation for the DP calculation of cellulose and for the DP calculation of OC was proved. The mass proportionality of DP in a mixture of polymers of OC was shown. According to this finding, the characterization of the polydispersity of OC was elucidated with the help of the so-called P_{DP} parameter.

OC represents a lot of polymeric compounds with a glucose and GA basis with different molecular weights and different compositions.

A characteristic absorption wavelength for GA in cadoxen was determined. The equimolecular character of the reaction between unstable substances (GA–PAGA) starting the PAGA destruction and free GA in the OC sample was proved.

UV–vis spectroscopy is a potentially useful method for process optimization in OC production and for the study of processes taking place during cellulose aging. It can help producers to prepare OC with advisable properties.

NOMENCLATURE

c, c_i	molar concentrations (moles of monomer units/volume of solvent)
DP	degree of polymerization
DP_H	degree of polymerization of a polymer with a high molecular weight
DP_i	degree of polymerization of a polymer with molecular weight and mass concentration M_i x_i
DP_L	degree of polymerization of a polymer with a low molecular weight
DS_m	degree of PAGA substitution
DS_{PAGA}	degree of substitution of PAGA
ε	concentration absorption coefficient [L/(mol g)]
ε_m	mass absorption coefficient [L/(g cm)]
η_{CAD}	limit viscosity number
GA	glucuronic acid
HCGE	heptacyclic glucuronic ester
m, m_i	masses
M, M_i	molecular weights
m_{OC}	mass of carboxyl groups in OC sample
$n_{COOH,PAGA}$	number of carboxyl groups in PAGA
n_{AG}	number of all anhydroglucopyranosic units in PAGA
OC	oxidized cellulose
ORC	oxidized regenerated cellulose
PAGA	poly(1,4-β;-D>-anhydroglucuronic acid)
P_{DP}	number characterizing the polydispersity in OC samples
UV–vis	ultraviolet–visible
V	solvent volume
x, x_i, x_m	mass concentrations (w/w)
x_{COOH}	concentration of carboxyl groups (w/w)
X_{DS}	share of COOH groups in PAGA (%)
x_{GA}	content of free glucuronic acid in OC (w/w)
$x_{GA-PAGA}$	content of destabilizing components in OC (mmol of GA–PAGA/g of OC)
$x_{GAcritic}$	critical concentration of GA

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