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Oxidized cellulose with different carboxyl content: Structure and properties before and after beating

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Abstract

Our recent studies concentrated in investigating influence of beating oxidized cellulose, with different carboxyl content, on changing their basic properties (degree of polymerization, WRV - water resistant value and X-ray diffraction). Cellulose samples of oxidized cellulose were beaten by toroidal beating machine.

Cellulose consists of both amorphous and crystalline regions. Cellulose consists of linear chains of poly[β -1,4-D-anhydroglucopyranose] ($C_{6n}H_{10n+2}O_{5n+1}$ (n = degree of polymerization of glucose)), which crystallize through hydrogen bonding between the chains and has cellobiose as repeat unit. Oxidized cellulose is preparing by oxidation of cellulose in the C6 position of the glucopyranose units to carboxylic group (-COOH) and polyanhydroglukuronic acid (PAGA) is arised. An other option is oxidation with sodium hypochlorite with catalytic amounts of sodium bromide and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) under various conditions.

Beating and refining or mechanical treatment of fibers in water is an important step in using pulps for papermaking. It is an energy intensive process. The purpose of the treatment is to modify fiber properties to obtain the most desirable paper machine runnability and product properties. End of beating pulps was characterized by position, when all beaten pulps under mixture passed through of riddle (about sizes mesh of 50).

During beating of samples about different ratio of oxidation it was found, that samples with higher contents of COOH groups in starting pulp are characterized by a significantly lower specific beating energy consumption needed to achieving the same sizes of particles. X-ray analyse shows that for non-beated oxidized cellulose was perceptible high share amorphous contents compared with beaten oxidized cellulose.

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Keywords: oxycellulose, amorphous and crystalline regions, beating, X-ray diffraction, degree of polymerization

1. Introduction

Oxidized cellulose containing carboxyl groups is a very interesting material. It is used for biomedical applications (adhesion barriers, sutures, absorbable haemostats or scaffolds for tissue engineering),

because it is degradable in human body [1] and also has haemostatic and antibacterial properties. It is prepared and used mostly in its traditional fibrous form with carboxyl group content of $\geq 14\%$ (w/w) [2].

Refining and beating processes modify cellulose material properties by imposing cyclic deformation on fibers in water medium [3]. Pulp swelling during beating or refining is a real hydration process, taking place, in water medium under a common mechanical action of the beating elements of the beater or refiner. Hydration and mechanical action plays decisive role in pulp refining processes and finally in properties of pulp fibers. Both the hydration and the mechanical action are mutually influenced during refining. All refining and beating processes have two following aspects (the mechanical one and the hypermolecular-chemical one) and should be evaluated from these points of views, as well.

Nitrogen dioxide is one of the most selective oxidants that convert primary hydroxyl cellulose groups into carboxyls. Oxidized cellulose can be prepared in reaction of cellulose with liquid or gaseous nitrogen dioxide or in solution with different organic solvents [4]. An other option to obtain oxidized cellulose is catalytic and selective oxidation of primary hydroxyl groups of carbohydrates using water-soluble and stable nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) [5].

Pure cellulose exists in several crystalline polymorphs with different packing arrangements [6]. The determination of the cellulose structures is difficult to achieve, with X-ray reflections observed at low diffraction angles. However, this observed data applicable for the determination of unit cells for polymorphs of cellulose (I α , I β , II, III, IV). The structure of materials in small dimensions is imaged by diffraction patterns of single crystals, fibers or powders (Debye-Scherrer method). This diffraction patterns can be used for identification of crystalline structures of all kinds.

Cellulose crystallinity is defined as the mass fraction of crystalline domains in cellulose materials. This mass fraction can vary significantly in diverse materials. Crystallinity has an important effect on the physical, mechanical, and chemical properties of cellulose. For example, with increasing crystallinity, tensile strength, dimensional stability, and density increase, while properties such as chemical reactivity and swelling decrease. X-ray powder diffraction is a method to study the sample crystallinity due to the diffraction peaks from cellulose crystals. We used one method to assess the crystalline part of a cellulose diffraction pattern in order to determine the sample crystallinity: Segal method, based on the intensity measured at two points in the diffractogram [7].

In this paper, we determine crystallinity of oxidized cellulose with different carboxyl content by X-ray diffraction during beating process. By using Debye-Scherrer method we comparing changing in polymorphs structure and finally we used degree of polymerization and WRV value to describe basic properties.

2. Materials and methods

2.1. Materials

In this study were used these types of samples of oxidized cellulose: OC-1(carboxyl content 15.13%), OC-2 (carboxyl content 18.92%), TEMPO oxidized cellulose (carboxyl content 3.49%) and cellulose cotton linter (carboxyl content less than 0.01%). All of these samples were from Synthesia Semtín, Pardubice, Czech Republic. Cadoxen and other reagents and solvents obtained from commercial sources were p.a. grade, and used without further purification.

2.2. Beating and sample preparation

The experiments were carried out in laboratory conditions only, in a laboratory toroidal beating machine. Samples were beaten in two different ways. In the first beating process were used 30 l of water

and the consistency of pulp slurries, temperature and pH varied in the range of 2.2-5%, 20-30°C and 2,6-5,5. In the second beating were used 3 l of distilled water, consistency of samples, temperature and pH were in the range 2,2-14,5%, 22-32°C and 2,4-5,6.

2.3. Degree of polymerization

The degree of polymerization of all samples was determined by viscosity method using Ubbelohde capillary viscometer size 2 and cadmium oxid-ethylenediamine (CADOXEN) solution as the solvent, according to the equation $DP = 193,5 [\eta]^{1.064}$, where $[\eta]$ is the intrinsic viscosity. The test is based on measuring the time dependence and on volume of fluid flow through the capillary viscometer at a considering temperature. All samples of oxidized cellulose (0,1g a.d.) were suspended in CADOXEN (50mL).

2.4. X-ray diffraction method (XCR)

To determine the crystallinity of the oxidized cellulose the powder was dispersed onto a stub and place within the chamber of a powder X-ray diffractometr. The sample was then scanned from $2\theta = 5-50$ in steps of 0,025. The crystallinity of the samples was determined by integration of the crystalline reflections, and expressed as percentage ratio of the integrated intensities of the sample.

Crystalline allomorphs of cellulose were determined by resolution of wide-angle X-ray diffraction curves and compared with Debye-Scherrer pattern in Figure 1.

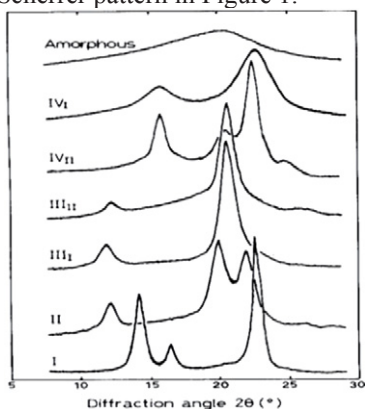


Fig. 1 Intensity traces of Debye-Scherrer patterns versus diffraction angles of various polymorphs of cellulose

2.5. Determination of crystallinity

Crystallinity of oxidized cellulose in samples was calculated from diffraction intensity data using Segal's method. This method is simple to determine the degree of crystallinity. The X-ray apparent crystallinity (%) of oxidized cellulose is calculated from the height ratio between the intensity of the crystalline peak and the total intensity after the subtraction of the background signal (non-crystalline) measured without cellulose according to following equation:

$$x_{CR} = 100 \cdot \frac{I_{200} - I_{non-cr}}{I_{200}} [\%] \quad (1)$$

The sample crystallinity, x_{CR} , has frequently been determined by means of Eq. 1 using the height of the 200 peak (I_{200} , $2\theta = 22.7^\circ$) and the minimum between the 200 and 110 peaks (I_{AM} , $2\theta = 18^\circ$). I_{200} represents both crystalline and amorphous material while I_{AM} represents amorphous material only. In the Figure is shown valley between these peaks.

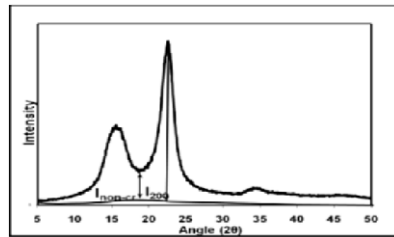


Fig. 2 X-ray diffraction spectra of cellulose I sample illustrating the peak height method.

3. Results and discussion

Samples of oxidized cellulose with different carboxyl content were beaten in a laboratory toroidal beating machine. It was found, that during beating of oxidized cellulose, samples with higher contents of COOH groups in starting pulp are characterised by a significantly lower specific beating energy consumption needed to achieving the same sizes of particles. In Figure 3 is beating in different condition than in Figure 4. Thus, the tenacity of pulp is decreased with intensity of oxidation which is characterized by content of COOH groups.

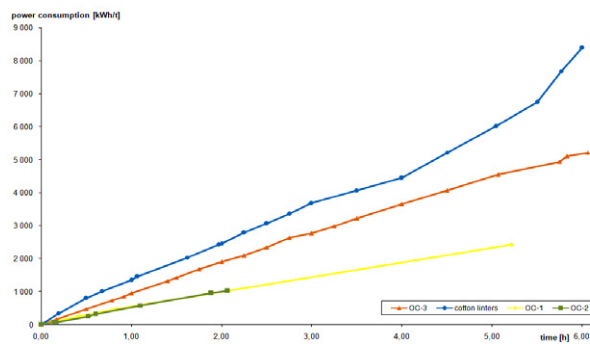


Fig. 3 Time dependence of beating process on power consumption - First beating of oxidized cellulose

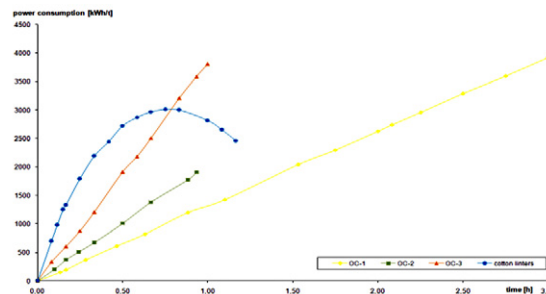


Fig. 4 Time dependence of beating process on power consumption - Second beating of oxidized cellulose

An X-ray pattern of an unknown substance Figs. 5 – 6 is visually compared with patterns of known structures with Fig. 1 and the unknown material can be identified upon agreement with the known pattern. A diffractometer scan of the diffraction pattern for samples during beating is shown in Figure 5. X-ray analyse shows that for non-beated oxidized cellulose was perceptible high share amorphous contents compared with beated oxidize cellulose in Table 1, where crystallinity of oxidized cellulose is increases during beating process.

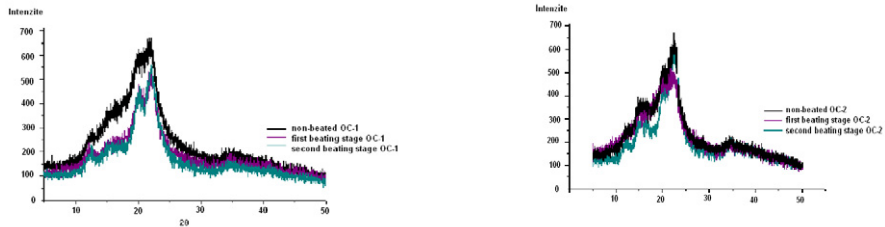


Fig. 5 XRD patterns of oxidized cellulose OC-1 and OC-2 - First and Second beating process. Changes in contents of crystallinity

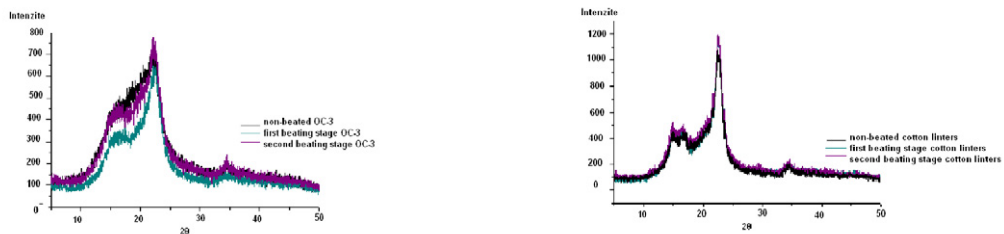


Fig. 6 XRD patterns of oxidized cellulose OC-3 and cotton linters - First and Second beating process. Changes in contents of crystallinity

However, as follows from Fig. 5 – 6 a separation of fines, hydrocolloids and dissolved substances has no influence upon structure of crystalline cellulose polymorphs because during beatings are evolved into surrounding water predominantly non-oriented amorphous parts of cellulose. As expected, the supermolecular structure of native cellulose forming cell-wall of linters is practically unchanged during both modes of beating processes. Moreover, a separation of fines, hydrocolloids and dissolved substances does not influence as well these supermolecular characteristics of oxycellulose again. Combination X-ray diffraction patterns of oxidized cellulose with Debye-Scherrer pattern was found that during beating cellulose I can be transformed to cellulose II.

Table 1. Changes in the degree of crystallinity x_{CR} (%) before and after beating by Segal method

	Non-beated sample (x_{CR})	First beating sample (x_{CR})	Second beating sample (x_{CR})
OC-1	33,69	55,75	46,81
OC-2	40,63	52,71	24,10
OC-3	26,09	45,26	37,87
Cotton linters	57,18	59,08	55,75

Conclusion

The received results reveal that supermolecular structure of cellulose is changed by chemical and mechanical treatment. The oxidative-hydrolysis process taking place during oxycellulose preparation has a qualitative influence upon crystalline domains of cellulose. Primary cellulose I is changed to more amphoteric polymorph cellulose II being change further by beating to polymorphs II in the case of intensively oxidized cellulose (OC-1, OC-2, OC-3). For native cellulose is typical only quantitative change of this supermolecular structure due to intensive beating. Intensively fibrillation beating leads to increase of amount the crystalline domains in cellulose.

All these changes are evoked because a peculiar character of water molecules forming a weaker hydration bonding system of cellulose in wet state of cellulose as well as. The supermolecular complex structure of wet cellulose, i.e. formed by weak hydration bonding system among cellulosic chains, is establishing from the hydrogen bonding system of cellulose in dry state. It is primary influenced by chemical composition of hydrophilic cellulose and secondary by mechanical action, e.g. by beating.

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