

**RESEARCH ARTICLE****STRUCTURE AND PROPERTIES OF OXYCELLULOSES BEFORE AND AFTER BEATING USING X-RAY DIFFRACITON****Michaela Filipi and Miloslav Milichovský**

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**ABSTRACT**

Oxidized celluloses belong to a very interesting class of cellulose derivatives with unique chemical and mechanical influence on supermolecular structure of cellulose significantly different from those of unmodified cellulose. Oxidative-hydrolysis process taking place during oxy cellulose preparation has a qualitative influence upon crystalline domains of cellulose. Primary cellulose I is changed during oxy cellulose preparation to more amphoteric polymorph cellulose II being change further by beating to polymorphs II and IV<sub>II</sub> in the case of intensively oxidized cellulose (15 % and 19 % of COOH groups) and to polymorph IV<sub>I</sub> for carefully oxidation of bleached linters (3.5 % of COOH groups). In contrast to oxy cellulose, intensively fibrillation beating of native cellulose leads only to increase of amount the crystalline domains in cellulose.

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**INTRODUCTION**

Cellulose consists of linear chains of poly [-1,4-D-anhydroglucopyranose], which crystallize through hydrogen bonding between the chains and has cellobiose as repeat unit(Hejlová *et al.* 2013). Cellulose consists of both amorphous and crystalline regions(Hejlová *et al.* 2013). Amorphous and crystalline parts are of course playing their key role in supermolecular structure of cellulose(Thygesen *et al.* 2005). It is well known an influence of acid hydrolysis upon increase of crystalline parts of cellulose (Filipi *et al.* 2014). Accessible amorphous and non-accessible crystalline parts of cellulose are indicated by peeling off model of kinetic of acid hydrolysis taking place during oxidative-hydrolysis process of oxy cellulose preparation (Zugenmaier 2008). Whilst 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 and this one also takes place in orientated crystalline domains of cellulose but not so intensive (Filipi *et al.* 2014). Moreover, by application of external mechanical tension the acid hydrolysis is more extensive resulting in more homogeneous but more degraded cellulose material.

Beating of fibres in water is important step in using pulp for papermaking. 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 consumption needed to achieving the same sizes of particles (Hejlová *et al.* 2013). X-ray analyses show that for non-beated oxidized cellulose was perceptible high share amorphous contents compared with beated oxy celluloses (Hejlová *et al.* 2013). Certain pulps will develop some strength by simply agitating at high speeds with a stirrer, but most pulps require a more vigorous action (Casey 1952).

**Beating**

The term "beating" is used in the paper industry to describe the operation of mechanically treating of pulp fibres. Refining usually refers to a fibre separation and fibres cutting, whereas beating action may include these two effects, and also a fibrillating or bruising effect on the fibre. Sometimes, however, beating is referred to as refining in a general way, as it is one step in the refining of the pulp for paper (Casey 1952).

Mechanical beating process created a partial skin fibrillation, while grinding turned fibre from micro to nanoscale through nanofibrillation mechanism (Afraa *et al.* 2013). The partially fibrillated and nano fibrillated fibres had significant effects on paper density, tear strength, tensile strength and water drainage time (Afraa *et al.* 2013). The effect of nanofibrillation on paper properties was quantitatively higher than that of mechanical

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beating (Afraa *et al.* 2013). Mechanical beating and nanofibrillation were both found to be promising fibre structural modifications (Afraa *et al.* 2013). Beating is probably the most fundamentally important process in papermaking. Paper made from unbeaten stock is low in strength, fluffy, porous, and unfit for most uses, whereas paper made from beaten stock is strong, dense, and hard in texture. Well-beaten fibres can be readily formed into a uniform sheet of paper of quite high density, whereas unbeaten fibres cannot. The old maxim, "Paper is made in the beater," is still as basically true today as it was over two hundred years ago. In fact, the original Hollander beater has undergone very few improvements since its development in the eighteenth century (Casey 1952).

The aim of this study was to better understand to supermolecular structural changes of cellulose during chemical and mechanical treatments. Especially, does it change the supermolecular structure of cellulose during its beating?

## MATERIALS AND METHODS

### MATERIALS

Hydrogen peroxide bleached cotton linter pulp (Alpha cellulose content 97 – 98 %, P. TEMMING AG, Germany) made from 100% second cut cotton linters was used as the raw material for an acid process of N<sub>2</sub>O<sub>4</sub>-mediated cellulose oxidation. The resulting H-form of oxy cellulose in fibrous form was used in all beating experiments (Havelka *et al.* 2010). Oxidized cotton linter (OC) developing samples OKCEL HL 242/05 ..... (SynthesiaPardubice, Czech Republic), common characteristic of OC: carboxyl content 15-20wt. % were used.

### X-ray diffraction method

To determine the crystallinity of the oxy celluloses the powder was disperse onto a stub and place within the chamber of a powder X-ray diffractometer. The sample was scanned from 2 =5-50 in steps of 0.025. The crystallinity of the samples was determinate by integration of the crystalline reflections and expressed as percentage ratio of the integrated intensities of samples (Hejlová *et al.* 2013). Crystalline allomorphs of cellulose were determined by resolution of wide-angle X-ray diffraction curves and compared with Debeye-Scherrer pattern. Powder X-ray diffraction data (Cu K $\alpha$ ,  $\lambda$  = 1.5418 Å) were collected on a D8 Advance diffractometer (Bruker AXS, Germany) with Bragg-Brentano - goniometer (radius 217.5 mm) equipped with a secondary beam curved graphite monochromator and Na(Tl)I scintillation detector. The generator was operated at 40 kV and 30 mA. The scan was performed at room temperature from 5 to 50° (2) in 0.02° step with a counting time of 5 s per step.

For determination of the sample crystallinity two methods were used: according to Segal and Rietveld. The Segal method (Segal *et al.* 1959), based on the intensity measured at two points in the diffracogram. The sample crystallinity,  $x_{CR}$ , has frequently been determined by means of Eq. 1 using the height of the 200 peak ( $I_{200}$ , 2 = 22.7°) and the minimum between the 200 and 110 peaks ( $I_{AM}$ , 2 = 18°).  $I_{200}$  represents both

crystalline and amorphous material while  $I_{AM}$  represents amorphous material only.

$$x_{CR} = \frac{I_{200} - I_{AM}}{I_{200}} \quad (1)$$

The expression that the amorphous material diffracts with the same intensity at 18° and 22.7°, and that the crystalline cellulose does not contribute to the intensity at 18° (Isogai 1994).

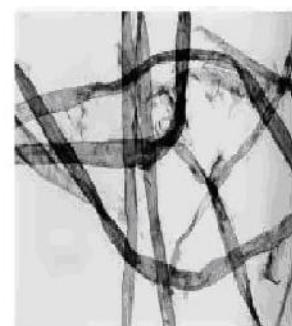
Crystalline allomorphs of cellulose were identified by the resolution of wide-angle X-ray diffraction curves. The diffraction patterns can be used for identification of crystalline structure of all kinds (Debye-Scherrer Method) (Zugenmaier 2008). They are predominantly used and are very helpful in identifying biological material such as cell walls and in establishing their source as cellulose. For this purpose, standards of cellulose X-ray patterns of various structures are necessary to identify unknown material.

### Beating on toroidal beating machine MSO

The experiments were carried out in laboratory conditions only, in a laboratory toroidal beating machine MSO. Oxidized cellulose or linter pulp was added to tap water and the fibrous slurry was intensively stirred to achieve its good defibrillation (see Figure 1) finished by beating (see Figure 2). Pulp was added to tap water and the fibrous slurry was intensively stirred. The slurry had to be stirred till no large clusters were present in the mixture. Two different conditions for beating of cellulose samples were used. First beating process of samples proceed in these conditions: pulp charge at 5% consistency in dependence on dry matter (3 kg of oxidized cellulose, 0.7 kg of cotton linter) with starting volume of tap water 30 litres, temperature of pulp slurry was around 30 °C. During this beating a change of the pH value, time and power consumption was observed. At beginning the pulp was beaten by use of fibre shortening mode. After 30 minutes it was turn off and the mode of beating was changed on fibre fibrillation mode. In this mode of beating a fibre slurry was concentrated through mesh riddle screen (50 meshes).



**Graph 1** Non-beaten only defibrillated fibres



**Graph 2** Beated fibres

For second beating process the following conditions were used: pulp charge at 10% consistency in dependence on dry matter of used pulp and machine ability (usually 0.5 kg of oxidized cellulose and 0.1 kg of cotton linter) with starting volume of

distilled water 3 litters, temperature of pulp slurry was around 20 °C. In this second beating process the fibre slurry was not concentrated through mesh screen. End of beaten of pulps was characterized by position when all beaten pulps under stirring passed through the riddle screen (mesh of 50).

## RESULTS

### X-ray diffraction analysis

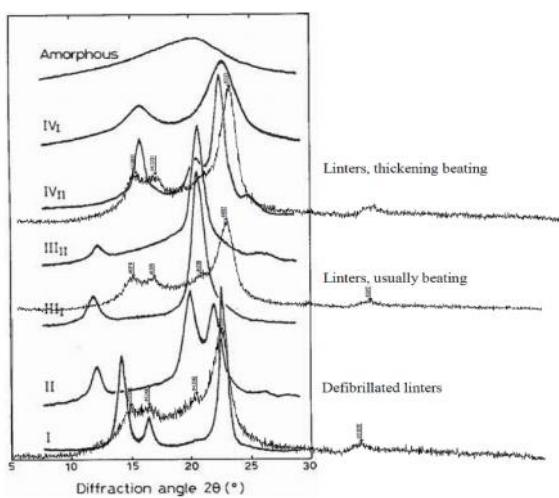
In order to elucidate an influence of fines, hydrocolloids and dissolved substances insurrounding solution during beating the experiments were carried out by use of two process modes:

1. Mode - beating accompanied by continually thickening of pulp slurry resulted in partly separation of fines, hydrocolloids and dissolved substances;
2. Mode - usually beating without thickening and separation.

### Chemical and mechanical influence on supermolecular structure of cellulose

Debye-Scherrer patterns of isotropically oriented samples as shown in Figures 3 - 6 represent a simple method of characterizing crystalline cellulose polymorphs (Isogai 1989, 1994). A fingerprint procedure suffices for identifying a certain polymorph. An X-ray pattern of an unknown substance is visually compared with patterns of known structures as shown in Figures 3 - 6 and the unknown material can be identified upon agreement with the known pattern.

Logically, as follows from Figures 5 and 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, beating and a separation of fines, hydrocolloids and dissolved substances does not influence as well these supermolecular characteristics of cellulose (see Graph 3).



**Graph 3** Intensity traced of Debye-Scherrer patterns versus diffraction angles of various polymorphs of cellulose: native cellulose I, regenerated or mercerized cellulose II, ammonia-treated cellulose of original cellulose I or II resulting in cellulose III<sub>II</sub> and heat-treated cellulose IV<sub>I</sub> and cellulose IV<sub>II</sub> (Isogai 1994). The influence of different beating mode on native cellulose represented by bleached linters is presented

However, oxidative-hydrolysis process taking place during oxy cellulose preparation (Milichovsky *et al.* 2008, 1990, 2010, Jaganathana *et al.* 2008) is changing the supermolecular structure of native cellulose from a crystalline cellulose polymorph I to a more amphoteric polymorph II being change by beating to polymorphs II and IV<sub>II</sub> in the case of intensively oxidized cellulose (15 % and 19 % of COOH groups) and to polymorph IV<sub>I</sub> for carefully oxidation of bleached linters (3.5 % of COOH groups) as documented in Figures 4 – 6, respectively.

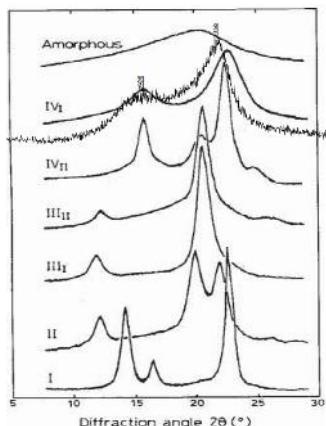
Although a quality of supermolecular structure of cellulose is not changed by beating the quantity of crystalline portion of cellulose in both sorts of cellulose is changed as documented by Figure 7. This behaviour is not influenced only by separation of fines, hydrocolloids and dissolved substances during thickening mode of beating but it has more sophisticated reason in effective influence of mechanical action in connection with cooperative water activity on supermolecular structure of cellulose and oxy cellulose. An exception exists for the intensively oxidized oxy cellulose (19% of COOH groups) due to obviously high eroded and consequently dissolvable crystalline portion of this form of oxy cellulose<sup>[13]</sup>. Crystalline part of oxy cellulose with 15% and 19% COOH characterized by X-ray diffraction analysis are 11.73% and 28.22% respectively.

Beating and refining or mechanical treatment of fibres 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 fibre properties to obtain the most desirable paper machine runnability and product properties. During beating and refining, fibres randomly and repeatedly undergo tensile, compressive, shear and bending forces. During the beating process, fibres are subjected to a mechanical action, and in the presence of water they swell. Carbohydrates and lignins in the swollen fibres can be leached from the cell wall and transferred to the surrounding solution. In the case of oxy cellulose samples with 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. Thus, the tenacity of pulp is decreased with intensity of oxidation, which is characterized by content of COOH groups.

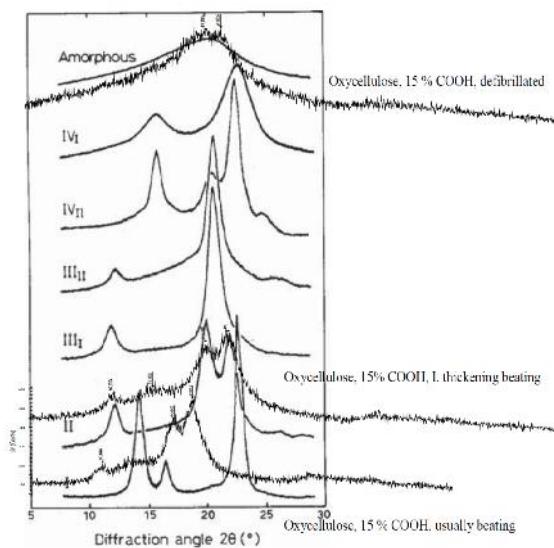
### Mechanism of cellulose crystalline state increase during fibrillation pulp beating

The mechanism of cellulose crystalline state increase during fibrillation form of pulp beating is possible to explain by use the SCHL (Structural Changes in Hydration Layers) concept (Milichovsky 2008) of hydration attractive – repulsive forces formation acting among hydrated nano-sites of both the

oriented crystalline and the non-oriented amorphous parts of cellulose in wet pulp state. If we assume a rush mechanical action during pulp beating in water, the plasticised cellulosic fibres are kneaded evoking so a mutually friction of micro fibrils particularly in amorphous structural micro-regions of cellulose. With respect to this fact, interstitial mutually movement of hydrated cellulosic chains, micro fibrils, fibrils etc. is evoked accompanied by formation of new hydration bonding abilities among them. The all process results then in decrease of inner energy connected with an increase of oriented part of cellulose (more details see on Graph 8). As schematically documented in the Figure 8, due to intensively oriented mechanically action during pulp beating a part of amorphous cellulose fraction is mutually shifted followed by more attractive hydration bonds formation which resulted in increase of oriented the crystalline domain of cellulose.

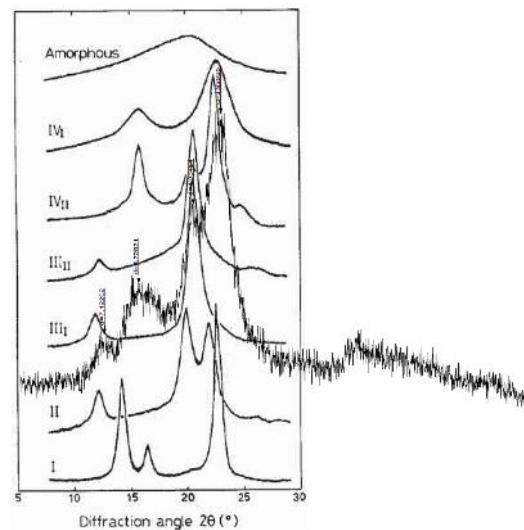


**Graph 4** Intensity traced of Debye-Scherrer patterns versus diffraction angles of various polymorphs of cellulose: native cellulose I, regenerated or mercerized cellulose II, ammonia-treated cellulose of original cellulose I or II resulting in cellulose III<sub>II</sub> and heat-treated cellulose IV<sub>I</sub> and cellulose IV<sub>II</sub> (Isogai 1989, 1994). The influence of thickening mode of beating on native oxycellulose prepared by selective carefully oxidation of bleached linters (3.5 % of COOH groups, thickening beating) is presented.

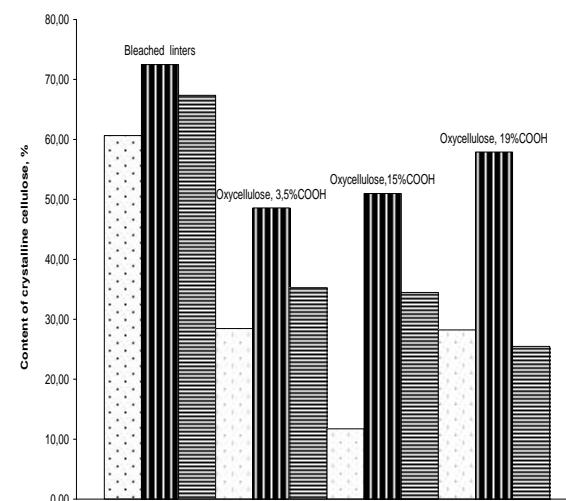


**Graph 5** X-ray patterns of oxycellulose with 15% COOH group content only defibrillated and beated at two different beating modes:

- I. Mode - beating accompanied by continually thickening of pulp slurry
- II. Mode - usually beating without thickening.



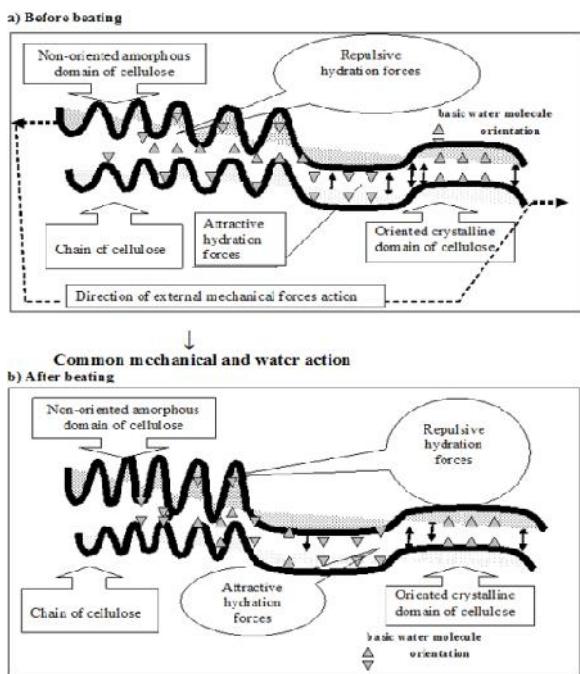
**Graph 6** Intensity traced of Debye-Scherrer patterns versus diffraction angles of various polymorphs of cellulose: native cellulose I, regenerated or mercerized cellulose II, ammonia-treated cellulose of original cellulose I or II resulting in cellulose III<sub>II</sub> and heat-treated cellulose IV<sub>I</sub> and cellulose IV<sub>II</sub> (Isogai 1989, 1994). The influence of thickening mode of beating on native oxycellulose prepared by selective carefully oxidation of bleached linters (19 % of COOH groups, thickening beating) is presented.



**Graph 7** Comparison of crystalline amount of cellulose in linters and oxycellulose (3.5 - 19 % of COOH groups) only defibrillated -

or beated by two process modes:

- I. Mode - beating accompanied by continually thickening of pulp slurry -
- II. Mode - usually beating without thickening -



**Graph 8**Schematic representation of interstitial movement of hydrated cellulosic chains during beating accompanied by formation of new hydration bonding abilities among them.

## DISCUSSION

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 and IV<sub>II</sub> in the case of intensively oxidized cellulose (15 % and 19 % of COOH groups) and to polymorph IV<sub>I</sub> for carefully oxidation of bleached linters (3.5 % of COOH groups). For native cellulose is typical only quantitative change of its super molecular 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 super molecular are 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 (Filipi *et al.* 2014).

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