



Research Article

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Chemical and Mechanical Influence on Super molecular Structure of Cellulose

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Abstract

The both chemical and mechanical influences on super molecular structure of cellulose represented by oxidative-hydrolysis process of oxycellulose preparation and beating of bleached linters, were studied by the use of X-ray computed microtomography methods. In order to elucidate a role of fines, hydrocolloids and dissolved substances in this context, the beating experiments were conducted with and without separation of the ones. The samples of paper sheets were prepared by usually drainage papermaking methods and by drying the pulp slurries at Petri dishes as well as. The received results suggest an increase of crystalline portion of cellulose during beating of native cellulose followed by deep changes in their qualities in case of oxycellulose.

Keywords: cellulose, oxycellulose, X- Ray microtomography

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1. Introduction

The unique properties and recent universal focus on natural material resources put also group of cellulose and cellulose derivatives into the position of intensive scientific effort and consequently to the attention of industrial companies [1-3]. Knowledge of macrostructure of the cellulose chains, i.e. super molecular and hyper molecular structure of cellulose, accompanied by changes during its chemical or mechanical treatment is important not only for technical or biomedical applications, but also predominantly, as a novel approach to better understanding and control of aging of cellulose materials, e.g. paper and paper products. Amorphous and crystalline parts of course play their key role in super molecular structure of cellulose [4].

It is well known the influence of acid hydrolysis on the increase of crystalline parts of cellulose. 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 oxycellulose preparation [5]. While the usual acid hydrolysis of native cellulose takes place, predominantly in accessible amorphous domains, i.e. more top

chemically, the degradation of native cellulose during its oxidation is faster and more intense but this one also takes place in orientated crystalline domains of cellulose but not so intensively. Moreover, by application of external mechanical tension the acid hydrolysis is more extensive resulting in more homogeneous but more degraded cellulose material. Cellulose fibres must be subjected to mechanical treatment before they can be turned into paper. This treatment may be applied in a number of different ways, but it ordinarily includes a bruising, rubbing, or crushing action on the fibres. Certain pulps will develop some strength by simply agitating at high speeds with a stirrer, but most pulps require a more vigorous action [6].

2. Experimental

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_2O_4 -mediated cellulose oxidation and for beating experiments. The resulting H-form of oxycellulose in fibrous form was used in all beating experiments [7 - 8]. Oxidized bleached cotton linter (OC) developing samples OKCEL HL 242/05, OKCEL HL 4/08 (Synthesia Pardubice, Czech Republic), common characteristic of OC: carboxyl content 15-20 wt%, were used [9].

Methods

Topography - Micro tomography beamline

X-Ray computed micro tomography (μ CT) consists from recording a number of projections from an object, with different angle of views, and reconstructing from these projections a 3D image with the help of an adopted algorithm. The applications are based, as far as absorption imaging is concerned, on the very broad choice available in the photon energy (typically between 6 and 120 keV), which makes it possible to improve the contrast, on the improved spatial resolution (on the order of the μ m), and on the quantitative data evaluation allowed by the monochromatic and parallel character of the beam. The very small source size provides, in an instrumentally simple way, phase images that reveal phenomena that are difficult to evidence by other means. [10, 11].

Beamline ID19 and microtomography

ID19 is a multi-purpose long (145 m) screening beam for radiography (absorption and phase contrast imaging) microtomography, and diffraction imaging (topography, analyzer-based imaging) experiments [11]. The beamline is installed on a low-beta section of the storage ring in ESRF, Grenoble, France. Synchrotron X-ray is provided by the deviation of electrons through periodic arrays of magnets. On ID19, this deviation is ensured by one of the three insertion devices: two adulators and one wiggler. They consist of a succession of magnets whose sizes and periodicity govern the characteristics (size and brilliancy) of the provided beam.

This device forces the electrons to oscillate along their way. The created beam is the superposition of all the beams created by each magnet. Wiggler created a beam whose energy spectrum is continuous and whose intensity depends on the numbers of magnets. The magnets in adulators are smaller than the ones in wiggler. The inversion of the magnetic field is consequently more frequent. Beams created by these oscillations can interact. The resulting spectrum is not continuous anymore and present maximum for some energies. The choice of the source depends on the experiment requirements [10, 11]. This device has a small source size (30 μ m vertically x 120 μ m horizontally). Three insertion devices are located in the ID19 straight section (two undulators and one wiggler) the choice of one of them as source being a function of the experiment requirements. Long beamline coupled with the small source size allows us:

- a. Exploiting the coherence properties of the beam
- b. Having either a wide and homogeneous beam when needed, or a focus spot below 100 nm when required [10 - 11].

Experimental setups

- a. Various setups designed for the different imaging techniques are permanently installed in the experimental hutch of ID19. They are:
- b. A microtomograph designed to perform absorption microtomography and, by varying the sample-to-detector distance, phase microtomography
- c. A "horizontal" diffractometer, designed for experiments requiring white beam and/or bulky sample environment (furnaces, cryostats, magnets ...)
- d. A "vertical" diffractometer that includes the possibility of using an analyzer crystal, for very accurate monochromatic beam imaging and diffraction [10].

During most of the experiments carried out on paper samples, the undulator is set at energy of 20.5 keV as this device present a maximum of brilliancy for this energy. The beam is monochromatised by a multilayer. To meet reconstruction, beamline parameters are optimised. The sample is a place of a highly precision rotation-translation

stage that aligns the three main components: beam, sample and detector accurately. A scintillator converts the transmitted beam into visible light which is recorded by a camera. This 2048x2048 pixels detector has a large dynamic range, low noise and a short read-out time. It plays a crucial role in the acquisition time and data quality.

Sample preparation

Small pieces are extracted from the sheet of interest. To cut the sample, gloves were worn to hold the paper sheet and use a pair of scissors. The gloves limit the moisture transfer from hands to paper, which could modify paper structure [11]. The scissors were preferred to the blade razors as the induced modifications cannot be seen on reconstructed data. Square of about 1.6x1.6 mm are extracted [11]. They also prevent the structure from strain. One may recall here that microtomography techniques are said to be non-destructive [11]. The studied sample is set on a capillary, which is fixed on the rotation stage of the microtomograph during data acquisition. The used technique to hold the sample on the capillary must avoid glue penetration and prevent the sample from moving. Several protocols were tested. The one presented hereafter gives the best results [11].

Beamline optimisation for paper samples

The beamline parameters are optimised for celluloid materials. The parameters that influence the image quality in term of signal to noise ratio are: the number of projections and the energy that are linked to the quality of reconstruction, on one hand and the exposure time that concerns the detector optimisation, on the other hand. First of all, according to the detector sizes (2048 pixels x 2048 pixels) [11] and to the Shannon theorem needed to reconstruct the data, 1500 projections are required to get the best possible results in term of signal to noise ratio evaluated by the noise standard deviation fibre [11].

The number of counts of the detector, the coefficient of absorption of fibres μ_{fibre} and the different standard deviation of "grey levels" evaluated in both fibre $\text{std}_{\text{fibre}}$ and pore std_{air} phases are reported. These last three magnitudes are evaluated on many different areas of the reconstructed slice and averaged. However, these two values are close. The coefficient of absorption and the standard deviation of the fibre grey levels have the same order of magnitude. The standard deviation in the fibre phase is a little bit larger than the one in pores as it is the combination of the noise of data acquisition and the in homogeneity inside of fibres. These two results are independent of the energy [11].

Beating on toroidal beating machine MSO

Pulp was added to tap water and the fibrous slurry was intensively stirred. The slurry had to be stirred till no large clusters were presented in the mixture. Oxycellulose or linters 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.

Condition of beating: temperature around 30°C,

Starting volume of water 30 l

Pulp charge at 5% consistency

First we need to prepare fibres to usable form, it means that we put some cellulose into water and defibrillation is followed in laboratory defibrillator finished by beating on toroidal beating machine MSO. There a fibre shortening, concentrating (removing of water) is taking place and the last step is fibrillation (cutting of fibres to fibrils). End of beaten pulps was characterized by position, when all beaten pulps under mixture passed through of riddle (about sizes mesh of 50).

3. Results and Discussion

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 lignin in the swollen fibres can be leached from the cell wall and transferred to the surrounding solution. In the case of oxycellulose 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.

Microtomography analysis

In plain original slices of two paper grades (on cellulosic and only oxycellulose basis) and their corresponding histograms following of microtomography measurements are presented in Figs. 1 and 2. Logically, the histogram of printing paper composed of calcium carbonate filler and bleached wood pulp has typical bimodal character and the histogram of paper composed of pure oxidised cellulose is typically uni-modal but thorough evaluation of this histogram suggests more complicated super molecular state of oxycellulose.

Gauss probability functions $f_i(x) = a_i \cdot \exp(-(\mu_i - x)^2 / 2 \cdot \sigma_i^2)$ were used for histogram data verification where μ_i and σ_i are the mean and the dispersion values of this probability function, respectively. The histogram of pure oxidised cellulose is also composed of two Gauss theoretical probability functions (compare Figs. 3a, 3b) with both different mean values ($\mu_1 = 116$ and $\mu_2 = 127$) and dispersions ($\sigma_1 = 24$ and $\sigma_2 = 50$). In reality the matter of oxidised cellulose is not homogenous involving two parts of cellulosic super molecular structures – the oriented crystalline part and the non-oriented amorphous part of cellulose. Obviously, a more compact crystalline part is characteristic with higher X-ray absorption, i.e. high grey value and less chemical reactivity. Due to typical topochemical reactions during the cellulose oxidation preparation [5] the probability function $f_2(x)$ is so broadly distributed across the grey values. The high value of F_2/F_1 (0.633) suggests a relative high amount of crystalline parts in oxycellulose concluding that the oxidation of cellulose has resulted in an increase of crystalline parts of cellulose matter. Crystalline part of oxycelluloses with 15% and 19% COOH characterized by X-ray diffraction analysis are 11.73% and 28.22%, respectively [12].

The general shape of the histogram does not depend on the X-ray energy but does not correspond to the expectations. Specifically, as paper can be considered in a first approach as a two phase material (a pore phase and a solid phase), we can easily imagine that the histogram of the grey levels of such a material would be bimodal and would have two separated distributions but only in non-regularly distributed systems. However, if paper is consisted of three sorts of particles of different density the probability of regular distribution of these ones rapidly decreases. But, the amount of verified data is also important. As the amount of data increases the histogram is more unimodal with a smaller dispersion and vice versa. We have experienced that optimal data collection which resulted in a maximal distinction of these micro-objects has to be around 10^6 items. This comes from the fact that paper is mainly constituted of light chemical elements that do not evoke distinct changes in the coefficient of absorption in the range of energies traditionally used on this beam. Therefore the characteristics of the grey level distributions do not depend on the energy in the particular case of paper samples.

In order to ensure maximal objectivity of the data evaluation we have compared only data objects with the same amount of pixels. In contradiction to filler particle (chemical precipitated CaCO_3) fibre cross profile measurements (see Figs. 4a-4d) demonstrate a complicated profile of fibre wall because complicated well-known fibre wall morphology. It seems that due to erosive hydrolyse-oxidative process during oxycellulose preparation [5] the width of cellulosic fibre has decreased and the fibre cross profile gained a more regular form. As directly documented in the Figs. 4a-4d, in comparison to natural fibres, the fibres of oxycellulose are slender and they are seemed as pieces of melting ice in water.

Beating influence upon structure of cellulose

As expected, the lateral size of beated cellulosic fibres was significantly smaller than fibres only gently defibrillated in a defibrillator (see Figs. 4a-4d). This observation indicates that the beating of fibres in toroidal beating machine MSO is typical a fibrillation process. Paper prepared from these fibres, i.e. by dewatering fibrous slurry followed by its drying, is distinguished by a wide histogram of micro-matter distribution characterised by X-ray absorption (see Fig. 5). Histogram of paper prepared from gently defibrillated fibres is less homogenous – the histogram is typical bimodal – relatively to paper prepared from beated fibres. This observation suggests that the paper matter is being composed of different three sorts (really two sorts) of cellulosic matter – one sort is characteristic with less X-ray absorbability ($\mu_1 = 97$), second one with higher X-ray absorbability ($\mu_2 = 158$) and the small amount of third one is characteristic with high dispersion of numerical pixel distribution ($\sigma_3 = 160$).

For the paper prepared from the beaten cellulosic fibres is characteristic practically an uni-modal histogram but with a broad dispersion. However, analysing this histogram using the Gauss probability functions it has been demonstrated that in reality the histogram curve is also bimodal composed of two similar probabilities functions with different mean values ($\mu_1 = 97$ and $\mu_2 = 155$). Obviously, the results confirm the well-known existence of two structural forms of cellulose: crystalline oriented part ($\mu_2 = 155-158$) and amorphous non-oriented part of cellulose ($\mu_1 = 97$). Aside from the fact that a lot of fine parts of cellulose fibres – especially so called crill – are separated from pulp slurry during paper preparation, i.e. during sheet dewatering, it is interesting to have a closer look at the areas in the fibre that may have a different level of supermolecular matter organisation.

Homogeneity difference between paper and paper sheet prepared only by drying of pulp slurry

At first look, the sheet prepared merely by drying of pulp slurry (see Figs. 6a, 6b) is more homogeneity (compare the values of dispersion, or standard deviation, StdDev in histograms; paper (see Figs. 5a, 5b) gently defibrillated or beated StdDev = 46,29 or 45,77, sheet (see Figs. 6a, 6b) gently defibrillated or beated StdDev = 20,73 or 16,64, respectively) than the paper sheet prepared only by dewatering of pulp slurry because mostly separation of fine particles. Additionally, as results from histograms of gently defibrillated and beated linters prepared by drying at

Petri dishes (see Fig. 6a, 6b), the histograms of gently defibrillated fibres and beaten fibres are in contradiction to results of paper prepared from the same fibres (see Figs. 5a, 5b) more closely and have unimodal and bimodal character, respectively. The sheet prepared from gently defibrillated fibres is more compact with small dispersion of X-ray absorbabilities, i.e. the cellulosic matter quality (σ_1 approximately 20). On the other hand, histogram of the sheet prepared from wet beaten fibres has bimodal character composed of two close Gauss probability functions ($\sigma_1 = 11$ and $\sigma_2 = 12$) and overweighing character of probability function $f_2(x)$ ($F_2/F_1 = 0,664$), i.e. crystalline oriented parts of cellulose. The results prove that intensively fibrillation beating of cellulose is connected with increase of crystalline state of cellulose.

Mechanism of cellulose crystalline state increase during fibrillation pulp beating

The interesting cellulose behaviour during its beating can be explained by use the SCHL (Structural Changes in Hydration Layers) concept [13-14] of hydration attractive – repulsive forces acting among hydrated nano-sites of both of 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 a mutually friction of microfibrils particularly in amorphous structural submicro-regions of cellulose. With respect to this fact, interstitial mutual movement of hydrated cellulosic chains, microfibrils, fibrils etc. is evoked accompanied by the formation of new hydration bonding abilities among them. The whole process results in a decrease of inner energy connected with an increase of oriented part of cellulose.

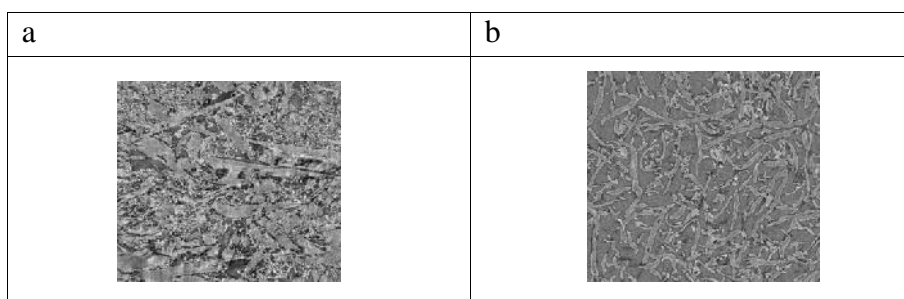


Figure 1: Different features of fibres on cellulosic and oxycellulosic basis in paper, Synchrotron X-ray microtomography on ID19 multi-purpose beamline, ESRF, Grenoble 320x320 μm .

- a) Printing Paper, OP Olšany, Polar bright, 50 g/m^2
- b) Paper from OKCEL HP 247/05 , 6,1% COOH, 105 g/m^2

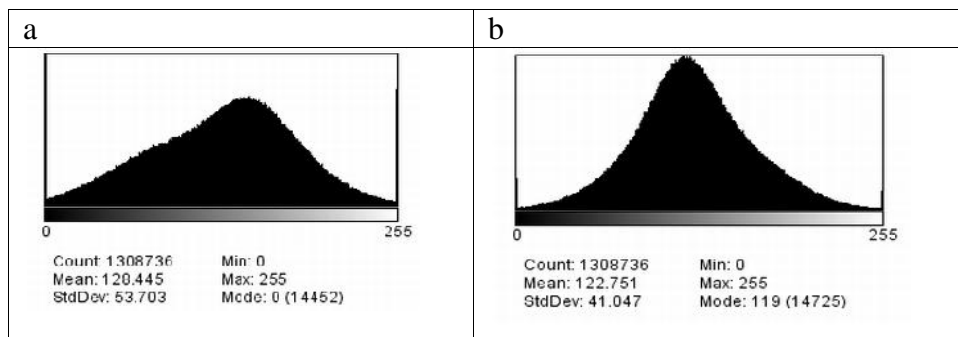


Figure 2: In-plane original slices of two paper grades (on cellulosic and oxycellulosic basis) and their corresponding histograms, Synchrotron X-ray microtomography on ID19 multi-purpose beamline, ESRF, Grenoble 320x320 μm .

- a) Printing Paper, OP Olšany, Polar bright, 50 g/m^2
- b) Paper from OKCEL HP 247/05, 6,1% COOH, 105 g/m^2

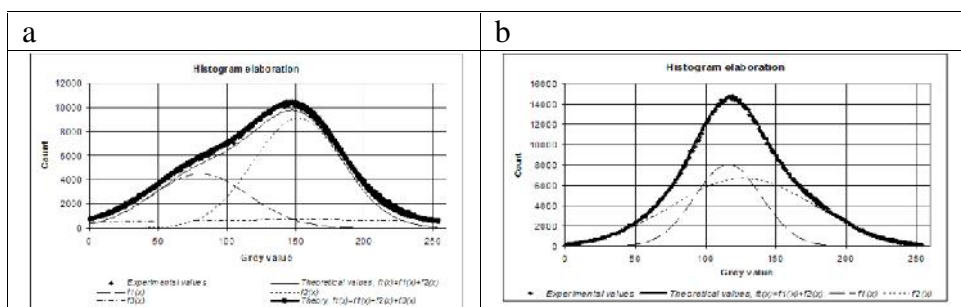


Figure 3: Histogram of gray values verified by use of Gauss probability function.

- a) Printing paper, OP Olšany, 50 g/m², filled with chemical precipitated CaCO₃. f₁(x): Mean = 81; Dispersion = 35; f₂(x) : Mean = 152; Dispersion = 32,5; f₃(x): Mean = 152; Dispersion = 160. F₁/F_t = 0,305; F₂/F_t = 0,579; F₃/F_t = 0,116 if $\int_1^{255} f_i(x)dx = F_i$ and $\sum F_i = F_t$.
- b) Paper from oxidized cellulose fibres OKCEL HP 247/05, 6,1 % COOH, 105 g/m² f₁(x): Mean = 116; Dispersion = 24; f₂(x) : Mean = 127; Dispersion = 50. F₁/F_t = 0,367; F₂/F_t = 0,633, if $\int_1^{255} f_i(x)dx = F_i$ and $\sum F_i = F_t$.

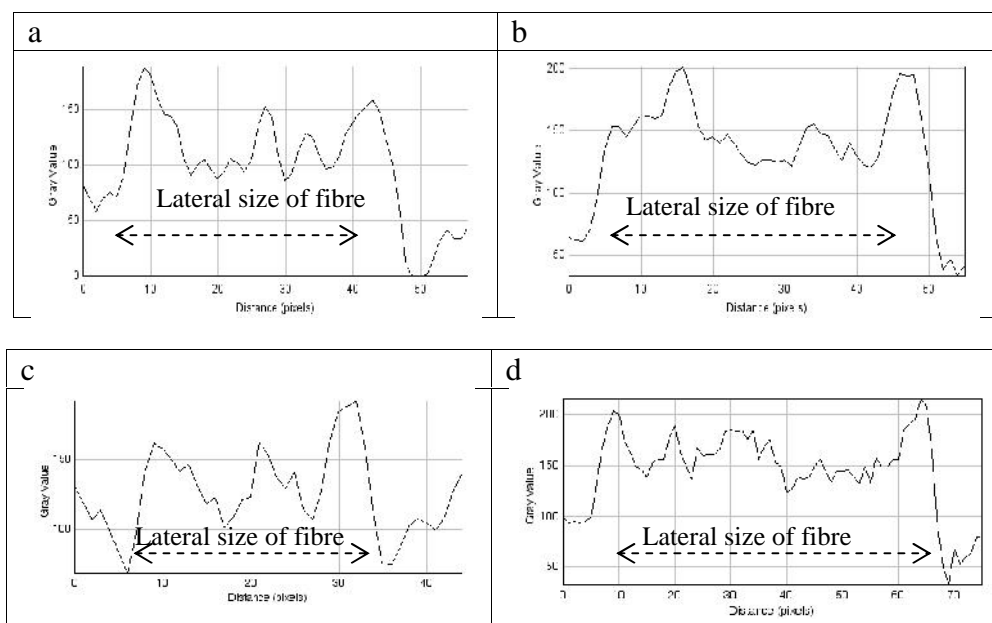


Figure 4: Fibre cross profile measured as gray value vs. distance. Synchrotron X-ray microtomography on ID19 multi-purpose beamline, ESRF, Grenoble

- a) Only defibrillated linters
 b) Beated linters
 c) Oxidized cellulose fibre. OC paper from OKCEL HP 247/05, Synthesia Pardubice-Semtin, CZ 6,1% COOH, 105 g/m²
 d) Bleached pulp fibre. Printing paper Polarbright, 50 g/m², OP Olšany, CZ, 1 pixel = 0,28 um

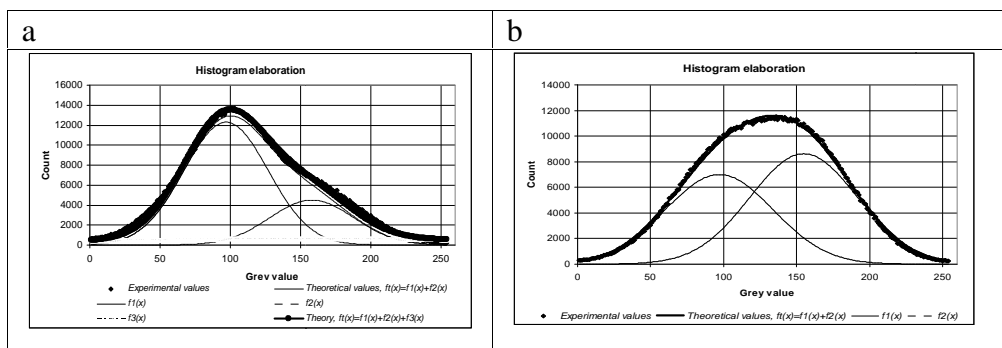


Figure 5: Histogram of gray values verified by use of Gauss probability function. Bleached linters.

- a) A paper was prepared by dewatering of pulp slurry composed only of defibrillated linters. Slice 132/256. StdDev = 46, 29. Results of verification: f₁(x): Mean = 97; Dispersion = 30; f₂(x) : Mean = 158; Dispersion = 30; Background f₃(x) : Mean = 152; Dispersion = 160 . F₁/F_t = 0,655; F₂/F_t = 0,240; F₃/F_t = 0,105 if $\int_1^{255} f_i(x)dx = F_i$ and $\sum F_i = F_t$.

- b) A paper was prepared by dewatering of pulp slurry composed only of beaten linters. Sample 100628/CZ/Linters /B. Slice 239/256. StdDev = 45, 77. Results of verification: $f_1(x)$: Mean=97; Dispersion =37; $f_2(x)$: Mean=155; Dispersion = 37. $F_1/F_t = 0,448$; $F_2/F_t = 0,552$ if $\int_1^{255} f_i(x)dx = F_i$ and $\sum F_i = F_t$.

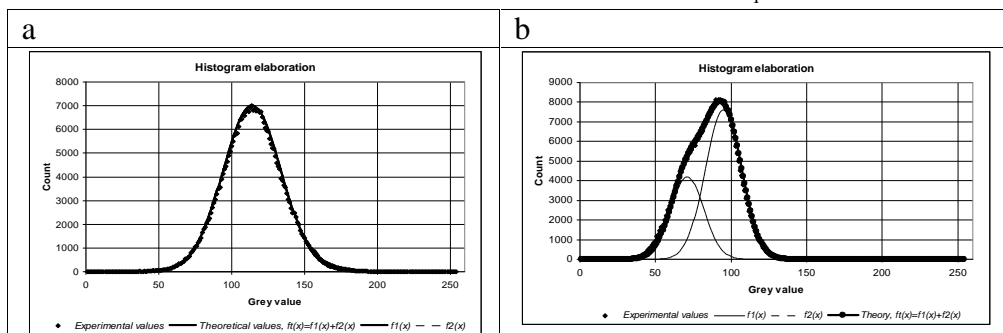


Figure 6: Histogram of gray values verified by use of Gauss probability function. Bleached linters.

- a) A sheet was prepared only from defibrillated linters by drying at Petri dish. Sample 100628/CZ/5A. Slice 2/256. StdDev = 20,73. Results of verification: $f_1(x)$: Mean = 114; Dispersion = 20; $f_2(x)$: Mean = 0; Dispersion = 30; $F_1/F_t = 1$; $F_2/F_t = 0$ if $\int_1^{255} f_i(x)dx = F_i$ and $\sum F_i = F_t$
- b) A sheet was prepared only from beaten linters by drying at Petri dish. Sample 100628/CZ/5B. Slice 2/256. StdDev = 16, 64. Results of verification: $f_1(x)$: Mean = 71; Dispersion = 11; $f_2(x)$: Mean = 95; Dispersion = 12; $F_1/F_t = 0,336$; $F_2/F_t = 0,664$ if $\int_1^{255} f_i(x)dx = F_i$ and $\sum F_i = F_t$.

4. Conclusion

The received results reveal that super molecular structure of cellulose is changed by chemical and mechanical treatment. The oxidative-hydrolysis process taking place during oxycellulose preparation has a qualitative influence on crystalline domains of cellulose. Only quantitative changes of this super molecular structure are typical to native cellulose due to intensive beating. Intensive fibrillation beating leads to an increase of the amount of the crystalline domains in cellulose. All these changes are evoked because of a peculiar character of water molecules forming a weaker hydration bonding system of cellulose in wet state of cellulose. The super molecular complex structure of wet cellulose, i.e. formed by weaken hydration bonding system among cellulosic chains, establishes 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. As shown, the chemical changes are accompanied predominantly by qualitatively super molecular structural changes. The rush mechanical action is influenced particularly the quantity of crystalline portion of cellulose obviously by virtually mutual movement of cellulosic chains, microfibrils, fibrils etc.

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6. Competing Interests

All authors declared that there are no conflicts of interest to report regarding this work.

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