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MODIFICATION OF CELLULOSE PERMOLECULAR STRUCTURE IN THE PROCESS OF BEATING

Beating of fibrous materials in water environment is one of the most important processes in the technology of manufacturing both paper and cardboard. The degree of beating determines basic properties of the received kinds of paper and cardboard.

The work dwells upon the permolecular structure of cellulose and its change in the process of beating. The methods applied here are ones: infrared spectroscopy, X-ray structure analysis, electronic microscopy and nuclear-magnetic resonance.

All samples of the chosen materials with a degree of beating equal to 14, 19, 24 and 32⁰SR are investigated. With the purpose of preventing recrystallization of the ground cellulose drying cellulose was engaged with toluol with subsequent drying at 293⁰K. The conditions of engaging were picked up experimentally.

With the help of X-ray structure analysis the basic parameters of an elementary cell of cellulose were determined and the "index crystallinity" for each kind of cellulose of a various degree is calculated.

The received spectra have confirmed, that in process of beating the quantity of liquid-like phase increases and the quantity of crystal phase decreases which is, probably, connected with infringement of regulations in the arrangement of circuits in fibre cellular construction.

For analysis of permolecular structure of cellulose and its change during beating in a water environment and solvents the method IR – spectroscopy was used. The purpose of spectroscopic researches – definition of detail structure of crystalline areas in cellulose and its change during dissolution in different solvents.

As object of research for obtaining the information about influencing processes of beating and dissolution on change of permolecular structure the unbleached bisulphite pulp was selected.

In activity samples of pulp with degree of beating 14, 19, 24 and 32⁰ShR were studied. Inclusion conducted by toluene with the subsequent drying at the temperature of 293⁰K. For obtaining IR-spectra of cellulose samples of weight 0,003 (+1%) g pelleted in KBr were taken. The IR-spectra were obtained on the device Specord – 75IR.

With the purpose of determination of change of permolecular structure of cellulose spectra of samples with different degree of beating were compared. IR-spectra of cellulose with different degree of beating are shown in a fig. 1.

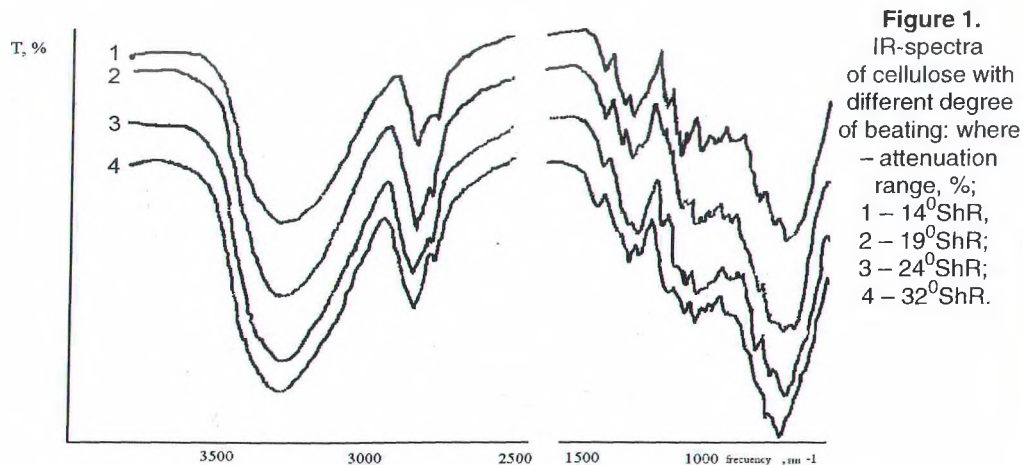


Figure 1.
IR-spectra
of cellulose with
different degree
of beating: where
– attenuation
range, %;
1 – 14⁰ShR,
2 – 19⁰ShR;
3 – 24⁰ShR;
4 – 32⁰ShR.

The greatest concern from the point of view of analysis of structure and definition of degree of crystallinity of cellulose is introduced by an intensive band in the field of 2800–3000 cm^{-1} referred accordingly to stretching vibrations of groups CH_2 , and CH . It is known, that the intensity of bands of CH_2 -groups considerably surpasses intensity of bands of CH -groups. As a result of a strong interaction of these groups with neighboring building blocks, as a rule, it is difficult to section frequencies of stretching vibrations CH_2 - and CH -groups, which one can be varied depending on object in enough broad limits [1].

Band 1639 cm^{-1} in a spectrum of pulp rather legibly shows, it relates to stretching vibrations $\text{H}\ddot{\text{O}}$ and is expedient for using for measurement of quantity of moisture in a sample. Is remarkable, that in all samples of cellulose after inclusion the moisture content practically is identical that allows to make a quantitative assessment of change of intermolecular hydrogen bindings.

Spectra of reviewed samples of cellulose with different degree of beating are characterized by broad intensive bands in the field of frequencies of stretching vibrations of OH – groups, live in a hydrogen binding, – 3250–3550 cm^{-1} [1]. The analysis of these spectra, allows us to draw a conclusion, that during beating of pulp with subsequent it include quantity of bound OH – groups decreases.

Definition of an «index of a crystallinity» of cellulose was conducted with two methods: O’Konnor and Nelson [2], and Putiev and Tashpulatov [3].

The method of O’Konnor and Nelson allows to find out degree of crystallinity by ratio of absorption at 1372 cm^{-1} (deformation oscillations of CH -groups) to absorption at 2900 cm^{-1} (stretching vibrations of CH -groups). The choice of the first band is based on the supposition that the deformation oscillations of groups CH do not depend on presence of water and monotonically change at change of an order strength. The band 2900 cm^{-1} depends slightly on degree of crystallinity and in consequence can be used as internal standard, which is taking into account the distinctions in conditions of sample preparing. Analyzing the data it has been received that the degree of crystallinity of cellulose changes from 67% (degree of beating 14⁰ShR) up to 62% (degree of beating 32⁰ShR).

Putiev and Tashpulatov method is based on estimation of crystallinity degree of permolecular order of cellulose by usage of ratio of bands 1430 and 894 cm^{-1} intensities in infrared spectra of these compounds. The band 894 cm^{-1} is used for measurement of crystallinity degree of cellulose and is caused by deformation oscillations of CH -groups. The areas of a band 1430 cm^{-1} in a spectrum should be related to segment shears oscillations of CH -groups that enables to assess of crystallinity degree of cellulose. In the field of 1300–1400 cm^{-1} in a spectrum of cellulose the frequencies of diffraction oscillations of CH -groups lie, which are present at spectra of all structural modifications of cellulose.

The data analysis with the help of this method has shown that the crystallinity degree of cellulose at beating changes from 69% (degree of beating 14⁰ShR) up to 63% (degree of beating 32⁰ShR).

The analysis of the obtained spectra gives the basis to suppose that by a physical destruction of pulp (beating) the intermolecular bonds of its crystalline area are slacken and the part of them, probably, is disintegrated due to violation of orderliness in arrangement of chains. It means that quantity of an amorphous part of cellulose is increased at the expense of its crystalline part. It is possible to draw such conclusion by compare of absorption bands of IR-spectra corresponding to stretching vibrations of CH -groups which are responsible for amorphous and crystalline parts of cellulose.

The beating can be considered as the process of «expansion» of a fiber structure by combined effect of beating machines and liquid in which the beating takes place. At some approximation the beating of a fiber can be considered as the primary stage of its dissolution. Thus there is an opportunity to execute indirect, precise measurement of a structural state of a fiber during beating at the presence of water (a poor solvent of pulp) by measurement of fiber solubility before beating in a liquid, whose dissolving capacity for cellulose fibers can be varied and which one is capable to solve cellulose fibers completely.

When fibers contact to a liquid at the primary stages there is an infiltration of a liquid into interfibrillar space and, further, in crystalline areas increasing their volume and forming with pulp compounds of restricted swelling capacity.

The swelling capacity is determined from a degree of a resizing of a sample and depends on that a completely dry sample or particulate swelled sample is used as the standard for comparing. If the bone-dry sample is applied as the standard, it is possible to consider almost any liquid, which is capable to wet cellulose as medium in which one the pulp swells more than in water. Therefore it is expedient to compare a swelling of cellulose in aqueous solutions on standard samples swelled in water instead of to a bone-dry samples.

At research of a swelling of natural pulp change of fiber width was measured. Measurements of cellulose fiber width conducted on large number of samples allow to characterize quantitatively process of a swelling in water and in a strong solvent – EWNN complex (FeTNa).

The degree of swelling (R) was calculated by the formula:

$$R = S/S_0$$

where:

S – width of a cellulose fiber after swelling, mm;

S_0 – width of an initial cellulose fiber, mm [4].

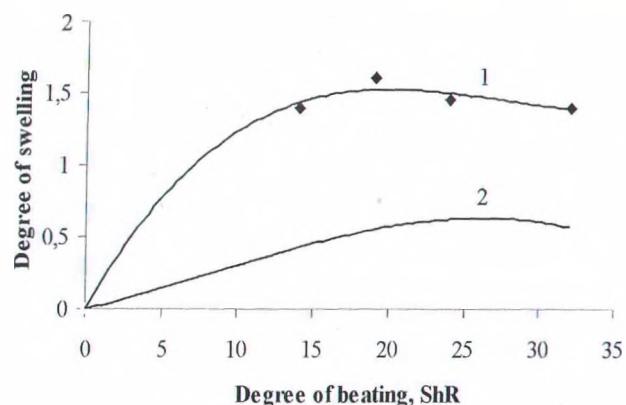


Figure 2.
Swelling of cellulose fibers:
where 1 – in EWNN,
2 – in water

Swelling of cellulose fibers in water and solution EWNN is shown in a fig. 2.

The reduced outcomes of activity demonstrate that width of a dry cellulose fiber is increased by 23% at immersing it in water. Fiber width increases very much considerable in solution EWNN then in water. At further increase of degree of beating (and, therefore, and dwell-time of cellulose fibers in solvents) the fast increase of fiber diameter is watched up to achievement of its maximum value which one makes 62 % at degree of beating 22⁰ShR. The maximum swelling grows is a result of destruction of a primary wall of a fiber. The data of X-ray crystallographic analysis shows that infibrillar swelling of natural cellulose occurs.

X-ray structure analysis was conducted on the apparatus Dron-3. After X-ray structure analysis and the decryption of the obtained roentgenogram interplanar spacing intervals of investigated samples have been compared with the only agreed card No 03 - 0289 (from more than 300 thousand). The looking up of eligible cards implemented with accuracy of concurrence of a line ($\pm 2\theta$) equal 0.2.

The roentgenograms swelled in water or other solvent and initial cellulose differ among themselves. This difference means that there was an intracrystalline swelling which one for natural pulp it is possible to call infibrillar as was marked earlier.

At dissolution of beaten cellulose the preparations are formed on roentgenograms of which there are no any traces of crystallinity. Though it cannot be considered neither completely crystalline nor completely amorphous. It is possible to suppose that this material possessing an intermediate order strength consists of chains arranged on a surface of crystallites with cross section 29-65Å [5].

At the analysis of X-ray it is possible also to draw a conclusion that when beating of pulp in a water environment there is decreasing degree of crystallinity but there is no transition of cellulose I in cellulose II. At the subsequent dissolution of cellulose fibers in EWNN the contents of an amorphous part is increased up to 67% (degree of beating 32⁰ShR, time of dissolution 25 min, temperature of dissolution 293⁰K). The tendency of dissolution of cellulose fibers grows in process of beating. Basing on correlation between dissolution ability and kinds of cellulose fibers it is possible to make attempt to classify fibers by their ability to beating. That will allow the industrial enterprises to

estimate correctly cellulose fiber fitness to processing and use in a composition of a paper and cardboard.

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