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INTERPRETATION OF THE PHYSICAL STRUCTURE OF CELLULOSE FROM THE ESR SPECTRUM OF A GAMMA-IRRADIATED PREPARATION

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A method is proposed for determining the crystallinity index of cellulose by an ESR method the principle of which is based on the identification in the recorded spectrum of a signal from radicals of the alkoxyl type stabilized in crystalline sections of the preparation. The radicals are generated by irradiating the cellulose with γ-radiation in vacuum with a dose of 10-100 kGr. The crystallinity index of the cellulose is calculated from the equation $CI = I_1/I_2 - 1$.

The crystallinity of the structure in cellulose preparations can be evaluated from physical and physicochemical indices of the samples (density, heat of wetting, sorption and water-retaining capacity, etc.) [1-3] from the depth of acid hydrolysis [4] and deuterium exchange [4, 5]; and from the results of IR spectroscopy [6] and x-ray diffractometry [7, 8]. The possibility has recently appeared of analyzing the structure of cellulose by using the ESR method to determine ordered and unordered sections [9] and the degree of crystallinity [10, 11]. Of course, the information obtained in each of these cases differs, but, on the whole, it is possible to characterize the physical structure of cellulose from these results.

We have studied the interrelationship between the crystal structure of cellulose preparations and the ESR spectra of these samples obtained on γ-irradiation.

Figure 1 shows the ESR spectra of the initial cellulose and mechanically ground cellulose after γ-irradiation. It can be seen that, as a result of mechanical grinding, the ESR spectrum of irradiated cellulose changes — namely, with an increase in grinding time it acquires a symmetrical form. An analogous change in the ESR spectrum is observed when native irradiated cellulose is stored [12]. This is connected with the formation and transformation of radicals of the alkoxyl type in the γ-irradiated cellulose.

It has been established previously that in cellulose irradiated at 77 K radicals of the alkoxyl type are formed in both the crystalline and the amorphous sections of the polymer [13]. With a rise to 300 K in the temperature of samples irradiated at 77 K, or even in cellulose irradiated at 300 K, the alkoxyl radicals remain stable only in the crystalline sections of the material. With time, these radicals as well undergo change and after storage for 165 days no ESR signal from alkoxyl radicals is recorded. The total change for an alkoxyl radical stabilized in an amorphous or a crystalline section of cellulose is its transformation with the opening of the pyranose ring at the $C_{(1)}-C_{(2)}$ bond.

The ESR spectrum of cellulose irradiated at 300 K consists of a superposition of three individual signals: a triplet with $\Delta H_s = 2.5$ mT, a doublet with $\Delta H_s = 1.2$ mT, and a singlet with $\Delta H_i = 0.8$ mT. The identification of radicals on the basis of the observed signals has been achieved in [12] and [13]. Here we may merely note that as a result of the transformation of the radical $R\dot{O}_{(2)}$ the intensity of the doublet with $\Delta H_s = 1.2$ mT due to an $-O\dot{C}H-O-$ radical in the ESR spectrum increases.

In the light of the given facts the tendency of the ESR spectrum of γ-irradiated mechanically ground cellulose to acquire a symmetrical shape can be explained by the fact that with an increase in the time of grinding a decrystallization of the cellulose occurs, and the transformation of the alkoxyl radical into an $-O\dot{C}H-O-$ radical leads to a corresponding change in the ESR spectrum.

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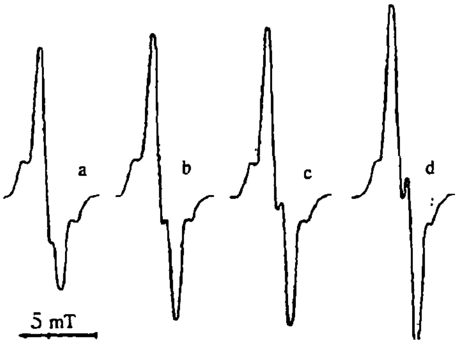

Fig. 1. ESR spectra of the initial cellulose γ-irradiated at 300 K (*a*) and of cellulose mechanically ground for 2 (*b*), 5 (*c*), and 10 (*d*) min. Radiation dose 10 kGr.

What has ben said above may be represented clearly by calculated ESR spectra: the presence of a singlet with $\Delta H_i = 0.8$ mT leads to an asymmetric spectrum (Fig. 2*a*) and its absence to a symmetrical spectrum (Fig. 2*b*).

The position of the singlet with $\Delta H_i = 0.8$ mT from alkoxyl radicals in the I_1 region of the ESR spectrum of the γ-irradiated sample makes the I_1 line sensitive to the crystal structure of cellulose (Fig. 3).

The mutual antibatic relationship of the intensities of the lines I_1 and I_2 permit the line I_2 to be considered as sensitive to the amorphous structure of cellulose. The essence of the analysis performed consists in the measurement of the intensities of the I_1 and I_2 lines in the ESR spectrum obtained. Then the ratio I_1/I_2 is calculated and, from this, the crystallinity index (CI) by means of the equation

$$CI = I_1/I_2 - 1, \tag{1}$$

where 1 is the value of the ratio I_1/I_2 corresponding to the maximum possible amorphization of the cellulose structure. Unity is included in Eq. (1) on the basis of the following considerations. The equation for determining the CI of cellulose from the ESR spectrum of the γ-irradiated material may be represented in general as

$$CI = (I_1/I_2)x - (I_1/I_2)_0, \tag{2}$$

where the subscripts x and 0 respectively denote the indices of the sample under investigation and a sample the ESR spectrum of which does not include the singlet with $\Delta H_i = 0.8$ mT. In the second case the ESR spectrum is a superimposition of a triplet with $\Delta H_s = 2.5$ MT and a doublet with $\Delta H_s = 1.2$ mT, the value of the ratio I_1/I_2 being 1.15. The deviation of the ratio I_1/I_2 from 1.0 is due to an unsymmetrical superposition of the two signals (see Fig. 2*b*). For simplicity, we assume that $(I_1/I_2)_0 = 1.0$, and the equation for determining the CI therefore has the form (1).

Table 1 gives the values of the CI for cellulose samples *a*, b, c, and d, determined from the characteristics of Fig. 1. It can be seen that the CI of the cellulose decreases with an increase in the time of mechanical grinding.

According to a proposed CI scale, cellulose preparations with a high crystallinity will have CI values above 3.0, and preparations with a low crystallinity will have values close to 0. Other preparations will have intermediate values of the CI.

It is desirable to determine the CI of cellulose within the radiation dose interval of 10-100 kGr.

EXPERIMENTAL

In the experiments we used cellulose obtained from cotton lint. The mechanical grinding of the cellulose was done on a laboratory electrovibromill. Samples (20-30 mg) of the preparations obtained were placed in sealed bulbs of Luch glass and were degassed in a high-vacuum apparatus to a residual pressure of $1.33 \cdot 10^{-2}$ Pa. Irradiation was carried out at 300 K with a Co^{60} γ-source at a dose rate of 2 Gr/s. ESR spectra were recorded on a RÉ-1301 radiospectrometer at 300 K.

TABLE 1. Dependence of the CI of Cellulose γ-Irradiated at 300 K with a Dose of 10 kGr on the Time of Mechanical Grinding

Cellulose sample	Time of mechanical grinding, min	CI
a	0	3.06
b	2	0.86
c	5	0.47
d	10	0.21

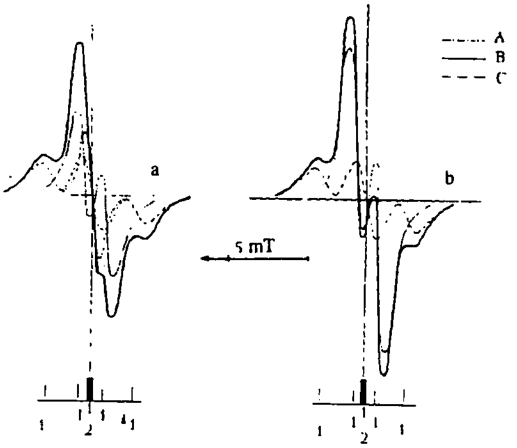

Fig. 2. Calculated ESR spectra of cellulose γ-irradiated at 300 K: *a*) spectrum obtained by the superimposition of a triplet with ΔH_s = 2.5 mT (*C*), a doublet with ΔH_s = 1.2 mT (*B*), and a singlet with ΔH_i = 0.8 mT (*A*); *b*) spectrum obtained by the superimposition of a triplet with ΔH_s = 2.5 mT (*C*) and a doublet with ΔH_s = 1.2 mT (*B*).

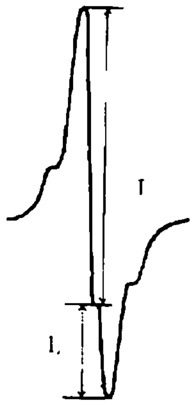

Fig. 3. ESR spectrum of cellulose irradiated at 300 K: I_1) intensity of the line sensitive to the crystal structure of cellulose; I_2) intensity of the line sensitive to the amorphous structure of cellulose.

The calculated ESR spectra were constructed by the graphical summation of the individual signals in accordance with their g-factors. As the individual signals we used the theoretically calculated ESR spectra, with the Lorentzian shape of the individual lines [14] and the experimental ESR spectrum of paramagnetic lignin (singlet with ΔH_i = 0.8 mT).

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