Infrared Spectroscopy Study of Powder Celluloses Modified by Lewis Acids

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SYNOPSIS

It is shown that modified powder celluloses distinguish from microcrystal cellulose produced by a hydrolytic method by the presence of the modification of cellulose II and by a low index of crystallinity. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In our earlier works[1,2] we showed certain structural peculiarities of powder cellulose (PC) under investigation in comparison with microcrystalline cellulose (MCC) that forms as a result of hydrolytic destruction.

To obtain additional independent data to judge the structure of the objects under investigation, the infrared spectroscopy method was used in this work.

EXPERIMENTAL

The samples modified by Lewis acids (LA) were prepared in the following way: a weighed amount of cellulose was soaked in an ethanolic solution of LA with concentration 0.2 M per I M anhydroglucose link of a polymer, then pressed out until mass increased 3 times. Then it was heat treated at 80–100°C for 30–60 min. The product was washed by active stirring until the reaction was neutral.[2]

The spectra were recorded by a two-ray infrared spectrometer "Specord-75-IR" with a prism-diffraction monochromator: working region 4000–400 cm^{-1}, slotted programme 3, strengthening 1, writing speed 150 cm^{-1}/min, scale of wave numbers 7.5/15/mm/100 cm^{-1}.

For obtaining more precise results 3 or 4 samples were recorded, then the statistical data were averaged. During the calculating and processing the results of quantitative analysis, the baseline was drawn tangentially to the spectral curve in the regions of the least absorbance. To show the crystallinity index of samples we used the ratio of the optical density of bands D_{1430}/D_{900} and D_{1375}/D_{2900},[3] modification cellulose II.[3,4]

To determine the presence of cellulose II by a method of internal standard a tangent line was drawn to the scattering curve in the interval of values $2\Theta = 9$–$19°$, separating (reweaving) the amorphous background. After that we determined the X-ray scattering intensity from crystal regions at $2\Theta = 12, 15$, and $16°$. For quantitative estimation of cellulose II content in samples we used the formula

$$K = \frac{I_{12} \cdot 100}{I_{12} + 0.5(I_{15} + I_{16})}, \%$$

where I_{12}, I_{15}, and I_{16} are intensities of peaks of X-ray scattering from crystal regions, at $2\Theta = 12, 15$, and $16°$, that were obtained after the separation of the amorphous background.[5]

RESULTS AND DISCUSSION

Before discussing the obtained results it should be noted that when the degree of crystallinity changes and when cellulose I changes structurally into cellulose II, material changes of the intensity of maximums and contours of absorption bands in the region of bending vibrations of CH_2 groups (1430, 1375, and 1325 cm^{-1}) and of conformational conversions (900 cm^{-1}) can be observed in the spectra.[3–6]

Table I   Comparative Characteristics of Powder Celluloses

	Infrared Spectroscopy Data		
Sample	$\dfrac{D_{1375}}{D_{1325}}$	$\dfrac{D_{1430}}{D_{900}}$	$\dfrac{D_{1375}}{D_{2900}}$
PC–SnCl$_4$	1.03	2.47	0.91
PC–TiCl$_4$	1.05	2.74	1.02
PC–BF$_3\cdot$O (C$_2$H$_5$)$_2$	1.03	2.76	1.02
PC–SbCl$_5$	0.98	2.88	0.97
PC–AlCl$_3$	1.05	2.96	1.02
MCC	1.02	2.71	1.23
Initial cellulose	1.00	2.10	1.09

It is considered that ratios of optical densities in the maximum of bands at 1375 and 2900 cm^{-1} or at 1430 and 900 cm^{-1} may serve as a characteristic of the degree of crystallinity of cellulose,[3] and the ratios of intensities of a pair of bands at 1375 and 1325 cm^{-1} may be a measure of the content of structural modification of cellulose II.[4] However, in spite of a discussion of long standing, there is no unanimous opinion presently about the correspondence between the ratios of absorption bands and the degree of crystallinity and the content of structural cellulose modifications.

Quantitative analysis (Table I) carried out by means of infrared spectroscopy shows that the index of crystallinity of the powders under investigation
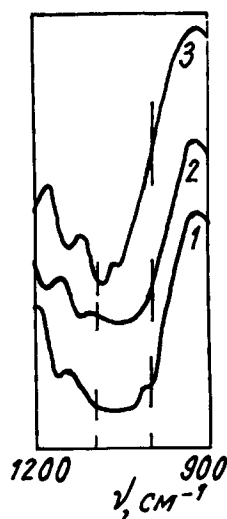
Figure 1   Infrared spectra of different cellulose samples: (1) cotton fibre; (2) MCC, (3) PC–TiCl$_4$.
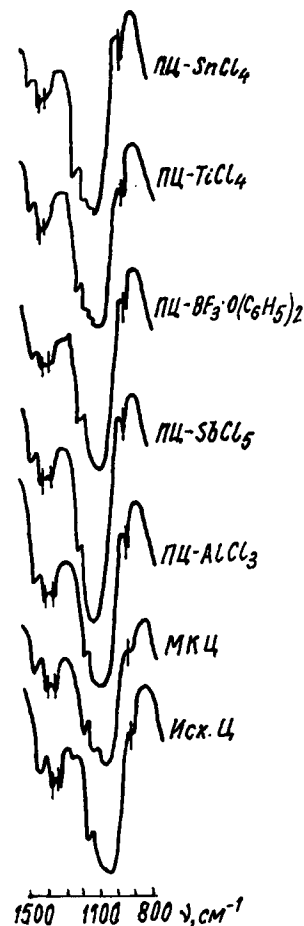
Figure 2   Infrared spectra of starting cotton cellulose and destructed celluloses.

calculated according to the ratio of the optical densities of two bands at 1375 and 2900 cm^{-1} is somewhat lower than that of the starting cellulose and is considerably higher than that of MCC. This fact testifies to the remarkable amorphization of the regulated part of modified powders. Apparently it occurs as a result of the penetration of LA molecules into the polymer lattice. The central atoms of LA are supposed to combine coordinately with oxygen atoms of the carbohydrate chain. That seems to be confirmed by the infrared spectroscopy data (Fig. 1). For example, absorption bands in the 1100–1000 cm^{-1} region that can be attributed to the formation of the C—O—Ti bond, were found in infrared spectra of cellulose samples destructed in the presence of TiCl$_4$.[7]

Analysis of intensities of absorption bands at 1375 and 1325 cm^{-1} as well as at 1430 and 900 cm^{-1}, whose ratios are considered to be a measure of the content of cellulose II structural modification, demonstrates the presence of this modification in the destroyed
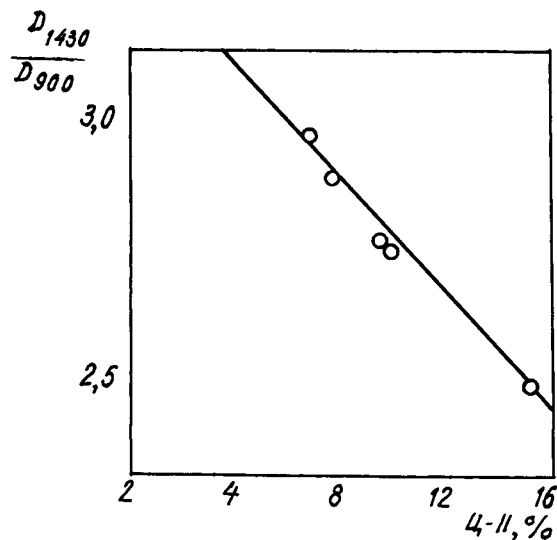
Figure 3 The relation between the ratio of intensities of bands at 1430 and 900 cm^{-1} and the content of cellulose II modification according to roentgenographic data.

samples (Fig. 2). Moreover, quite a satisfactory correlation may be observed between spectroscopic and X-ray diffraction data (Fig. 3).

It should be noted that the question of the cellulose II structure is still open in spite of a great number of crystallographic studies. In one of our recently published[8] works on this problem, the authors considered the most probable models of cellulose chain arrangement and came to a conclusion that all these models actually characterize an integral structure with a system of labile hydrogen

bonds. Under the influence of heat this system of H-bonds can easily reform by means of transfer of H-atoms from one center to another. It may be presumed that LA molecules can also introduce themselves into the crystal structure and promote the transition of one cellulose modification into another.

Infrared spectroscopy data confirm the fact of the presence of cellulose II modification in the cellulose modified by Lewis acids and a comparatively low index of their crystallinity.

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