The relationship between dielectric and optical properties of cellulose micro/nanoparticles with their spatial structure

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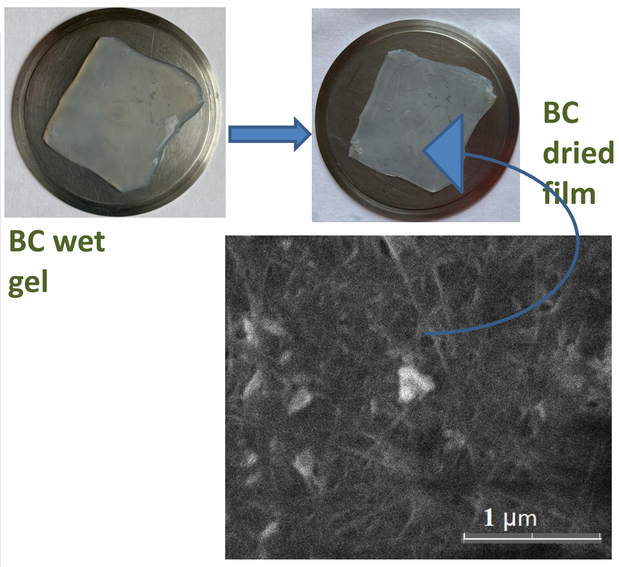
Introduction

Cellulose is the basis of many materials of industrial use, in particular, such as dielectrics in electrical products. It is known, that cellulose can be obtained from plant raw materials, and it can also be a product of the vital activity of bacteria. Therefore, the study of the relationship between a cellulose dielectric and optical properties and the ways of its production is relevant

The aim of our work is to establish the differences in the structure and physical properties of plant and bacterial cellulose

Samples

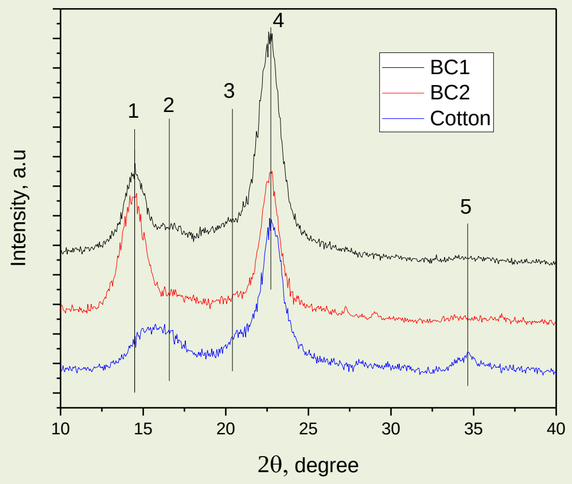
The Cotton linters Sigma-Aldrich cellulose powder and two types of bacterial cellulose (BC) synthesized with use of the *Gluconacetobacter (BC1)* or *Komagataeibacter xylinus (BC2)* bacteria were used for the study.
Bacterial cellulose *BC1* was grown at +30°C for 4-7 days in HS medium (2% glucose, 0.5% peptone, 0.5% yeast extract, 0.27% Na_2HPO_4, 0.115% citric acid) with the addition of 1% of ethanol. Nutrient solution for bacteria in the synthesis of *BC2* was a mixture of distilled water (1.25 l), filtered black tea (87.5 g) and sugar (8.75 g); the cultivation was carried out at +15°C for 30 days in an environment with pH 4. After that, both types of bacterial cellulose were washed and cleaned from the remains of the nutrient medium in dH_2O and in a solution of 0.1 M NaOH and dried under room conditions on substrates



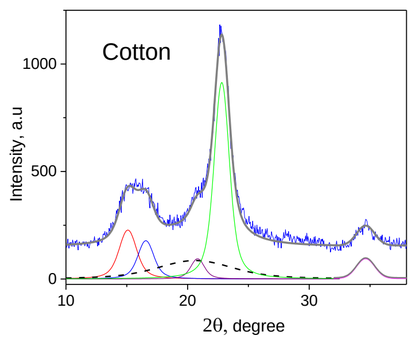
X-ray diffraction analysis

Measurements were performed using DRON-4M ($\lambda_{CuK\alpha}$=0.15418 nm).

Crystallinity degree of cellulose was estimated by the method of peak deconvolution. Size of the crystallites was obtained with Scherrer's formula.



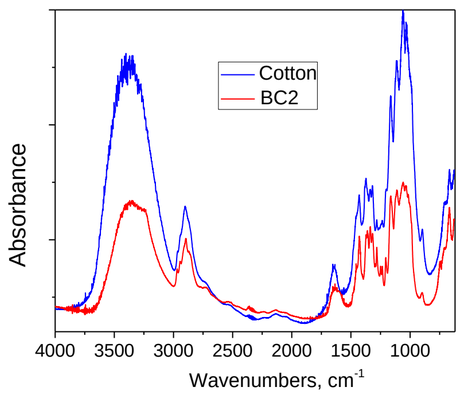
Peaks [1] : 1 - $(100)_{I\alpha}$ and $(1^-10)_{I\beta}$;
2 - $(010)_{I\alpha}$ and $(110)_{I\beta}$; 3 - $(10^-2)_{I\alpha}$ and $(102)_{I\beta}$,;
4 - $(110)_{I\alpha}$ and $(200)_{I\beta}$, 5 – $(11^-4)_{I\alpha}$ and $(004)_{I\beta}$

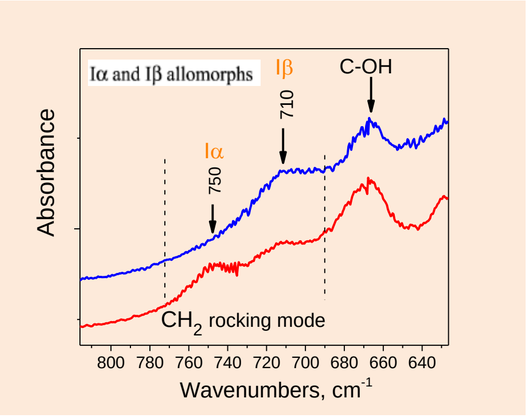


Crystallinity degree (CI) and crystal lateral size (D_{200}) of cellulose microfibrils from different origins

Cellulose	*CI (%)*	*D_{200}, nm*
BC1	*75*	*5.7*
BC2	*84*	*6.5*
Cotton	*76*	*6.0*

Infrared spectroscopy (FT-IR)





FT-IR spectra of cotton and bacterial cellulose at room temperature

Iα fraction was estimated by

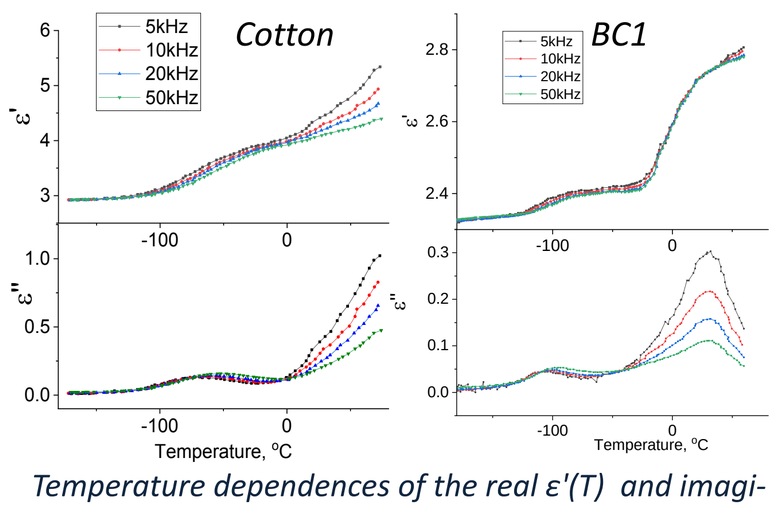
$$f_\alpha^{IR} = \frac{A_\alpha}{A_\alpha + A_\beta}$$

with A_β and A_α , being the integrated absorbance at about 710 and 750 cm^{-1}.

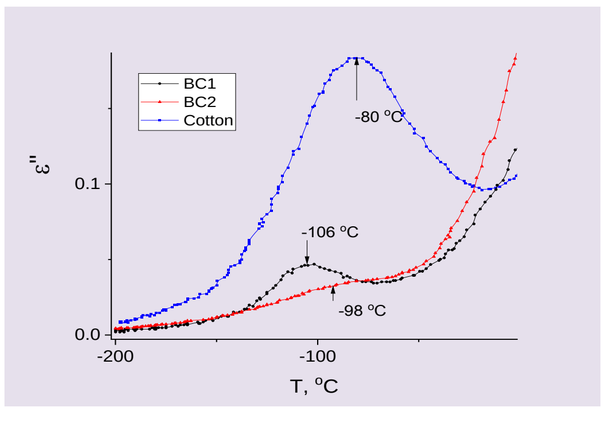
Relative percentage of allomorphs Iα and Iβ for celluloses from different origin

Cellulose	*Iα (%)*	*Iβ (%)*
BC1	*36*	*64*
BC2	*62*	*38*
Cotton	*0*	*100*

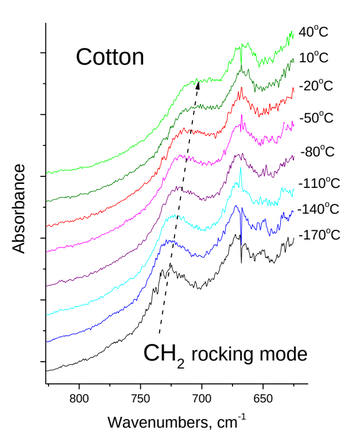
Temperature dependences of complex permittivity and IR spectra

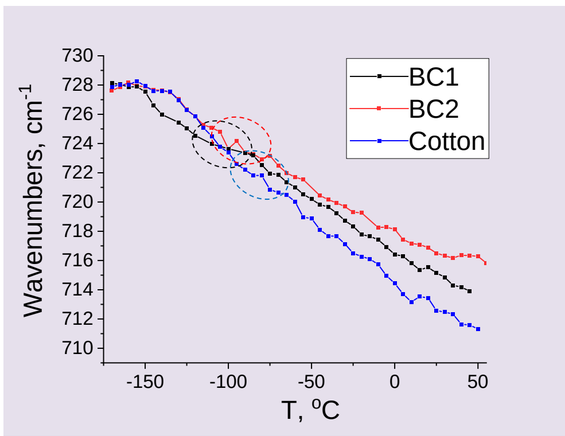


Temperature dependences of the real ε'(T) and imaginary ε''(T) part of dielectric permittivity at different field frequencies for cotton and bacterial cellulose



Temperature dependences of the imaginary part of dielectric permittivity at 10 kHz for different celluloses

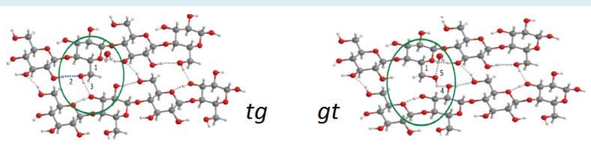




Temperature dependences of the position of the band assigned to CH_2 oscillations in FT-IR spectra

- Temperature dependences of the ε''(T) for cotton and bacterial celluloses indicate a maximum that shifts to a higher temperature when the frequency increases. Similarly, the inflection on the dependences of the real component of the ε'(T) shifts. This can be explained by relaxation processes occurring in all celluloses. Dielectric relaxation for bacterial cellulose is observed at lower temperatures than for plant cellulose.
- The region of nonlinear changes in the dependence of the position of the band of CH_2 oscillations in the IR spectra on temperature correlates with the temperature region of the dielectric relaxation of cellulose. Therefore, dielectric relaxation in celluloses is related to the movement of methylol groups.
- A model was applied [2], according to which dielectric relaxation occurs in the surface layers of cellulose crystallites, which are surrounded by a hydrate shell.

*The relaxation is associated with the reorientation of the surface methylol groups of the cellulose molecule by changing their conformations from **tg** to **gt**.*



A two-level model of identical relaxers was used to calculate the parameters of the relaxation process [2]

- ✓ Calculations showed that the activation energy for bacterial cellulose has the same order as for cotton cellulose, which indicates the same nature of dielectric relaxation in all samples.
- ✓ Also, the entropy of activation increases for bacterial cellulose compared to cotton cellulose. This is due to differences in the structure of the hydration shell around the crystals of these celluloses.
- ✓ The concentration of relaxers is larger in cotton cellulose than in bacterial cellulose, which indicates a different structure of the surface of cellulose nanoparticles and a different fractal dimension of the spatial structure of these celluloses at the micro level.

[1] A.D. French, *Cellulose.* V.21., P.885, (2014).
[2] O. M. Alekseev et al., *Cellulose Chem. Technol*. V. 53 (1–2), P. 15 (2019).