Modulation of structure and optical properties
micro-fibrils of plants by means of electrical,
deformation and optical treatments

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Abstract. Variations of structure and optical properties of micro-fibrils of plants induced by
optical, electrical, deformation and water treatments were studied in situ by means of optical
polarization microscopy. Bundles of dry fibrils pulled out from nettle, maple and spruce were
used for the experiments. Strong enhancement of the optical anisotropy in all of the fibrils has
been found just after their wetting with water. Appearance of this anisotropy is attributed to
orientation ordering of cellulose molecules in the neighbor layers of the walls of the fibrils. This
ordering is explained by penetration of water molecules into the interfaces between cellulose
layers and amorphous lignin polymers bound with cellulose molecules in the dry state of the
fibrils. Relatively week electrical fields applied to the fibrils removes this anisotropy by pushing
out the molecules of water from these interfaces. Evaporation of water returns the fibrils to
optically isotropic state as well. The changes of the anisotropy of the fibrils are followed with
their deformations. These deformations induce internal electrical fields. Hence the interactions
of the fibrils with water, electrical and deformation fields result in self-consistent propagation
electromechanical waves along the plants vessels. These waves are capable to transport
feeding nutrients. Irradiation of wood components immersed in water by ultraviolet light
induces dissolving of lignin and produces pure cellulose fibers. This phenomenon provides the
development of new ecologically safety technology of production of cellulose.

1. Introduction
The actuality of studies of substances based on cellulose polymers is growing quickly. On
the one hand, severe ecological problems connected with difficulties of utilization of synthetic
polymers [1] used in various packages, crockeries, etc. require substitution of synthetics with
cellulose as the most abundant, economic and safety natural polymer [2]. On the other hand
recent scientific results demonstrate promising prospects of applications of cellulose containing
materials (either in natural or in nano-crystalline state) for bio-medicine, alternative energetics,
electronic and optical devices [3–5]. E.g., nanocrystals of cellulose are used for targeted
delivery of drugs [3]. Whereas branches and green leaves of plants with high content of cellulose
molecules produce comparatively high electric potentials during interactions with wind and
solar radiation [4]. Suspensions of cellulose nanocomponents form nematic and cholesteric liquid
crystals [5–10]. It should be emphasized that the methods of industrial extraction of cellulose
from plants are energy consuming and harmful for ecology [11]. This paper presents several
results useful for more effective applications of cellulose as well as for better understanding of mechanisms of feeding of plants with active participation of cellulose molecules [4].

Promising materials are described in the papers [9, 12–14], relaxation processes in such materials are of particular interest [8,15–18] and surface effects [19–21].

2. Experimental results and discussion

The bundles of plant fibrils were pulled out with thin tweezers from dry stems of nettle or branches of maple and spruce. The transverse diameters of the bundles varied from 30 to 300 micrometers whereas their lengths were from 10 to 20 millimeters. These samples were fixed at aluminum electrodes placed at the glass slide of the optical polarization microscope. The distance between the electrodes varied from 2 to 2.5 millimeters. The thicknesses of the electrodes and corresponding heights of the sample above the glass slide were about 1 millimeter. The behavior of the samples was recorded in situ with the optical microscope and a video camera. The dimensions of the field of observation were varied from 1.5 0.15 millimeter by changing of the microscope objectives.

The optical anisotropy as well as the optical transparency were the main optical parameters, which were used for comparison of structural and optical characteristics of the bundles of the fibrils subjected to various treatments. Four kinds of the treatments were used: several versions of the contacts of the bundles with water, application of permanent electrical field (the strength up to 100 v/cm), optical irradiation with blue laser (the wavelength 450 nm) and ultraviolet light, mechanical deformation by ball rolling along the fibrils.

It should be emphasized optical and deformation treatments of the bundles immersed into water resulted in separation of cellulose from lignin molecules, which deteriorate the optical transparency of the fibrils. This effect was observed more clearly, when pieces of sawdust made from dry maple or spruce were subjected to optical irradiation. These pieces are thicker essentially than the bundles of the fibrils and at the initial state they are non-transparent for the visible light. But after several tens of minutes of irradiation they became transparent (Fig. 1).

Figure 1. Optical microscopy of sawdust made from dry branch of maple before (left) and after (right) irradiation with ultraviolet light

This phenomenon is attributed mainly to optical activation of dissolving of lignin molecules by water. These molecules are attached to the fibrils of cellulose in the initial state of the bundles preventing the propagation of the light through them. The activation of their solubility in water is explained with the photoionization of these molecules by the light photons. This ionization enhances the attraction of these substances to water because its molecules have strong static dipole moments. The intensive deformation of fibrils of cellulose immersed into water is capable to break interatomic bonds in the molecules resulting in their ionization as well with subsequent
dissolving of the ionized molecules by water. When water surrounding the bundles during the irradiation evaporated solid optically anisotropic micro-pieces with rhombic or rectangular geometries were formed at the dry glass. We attribute these pieces to single crystals of vanillin and phenol formed from lignin remnants dissolved by water. So the creation of these crystals confirms our version about the activation of lignin dissolving by ultraviolet irradiation. When the bundles of wood fibrils immersed into water are subjected to deformation by ball rolling removal of lignin from the fibrils proceeds as well increasing the transparency of the bundles.

The immersion of the bundles of the fibrils into water without their irradiation does not induce essential dissolving of wood components. But nevertheless water induces severe enhancement of the optical anisotropy of the bundles (Fig. 2). The process of observations was as follows. The bundle of the fibrils attached to the aluminum electrodes at the glass slide was covered with layer of water by it pouring onto the glass. This process was registered microscopically by the video-camera. The angle of the axis of the parallel fibrils composing the bundle and the directions of transmission of the polarizers in the microscope was 45°. This angle corresponds to the most sensitive registration of the optical anisotropy of the fibrils (the stronger the anisotropy the higher the brightness of the light transmitted through the sample placed between two polarizers with mutually perpendicular directions of the light transmission). Just after the pouring of water the enhancement of the bundle image occurred (in 1 – 2 seconds).

![Figure 2. Optical microscopy (in crossed polarizers) of a bundle of nettle fibrils in dry state (left) and after immersion into water (right)](image)

Then the bright intensity of the transmitted light remained stable until the moment when the level of water surface reducing monotonously due to evaporation approached the upper edge of the bundle. Starting from this moment the dramatic changes in the structure of the bundle of fibrils began (Fig. 3).

At the top photo the whole bundle is immersed into water and its brightness between the crossed polarizers and corresponding anisotropy is high due to strong optical anisotropy. The second photo corresponds to the moment when the level of water decreasing due to natural evaporation became lower than the top edge of the bundle. Dark regions corresponding to lower anisotropy appeared. The third photo demonstrates the abrupt change of the distribution of the transparency and the anisotropy in 2 seconds after the moment when the water surface has been separated from the bottom edge of the bundle. Then the growth of dark regions became monotonous. The bottom photo corresponds to 10 minutes after the beginning of the process.

When the permanent voltage (20 – 25 volts) was applied to the aluminum electrodes supporting the bundle the gradual decrease of the light transmission started in spite of the fact that the immersion of the bundle into water remained full. The general process of the decrease of the intensity reminded the process of water evaporation presented at Fig. 3. But the developing of the system of dark zones was proceeding two times faster.

The additional experiments with the increase and decrease of the light transmittance described above showed that these phenomena are observed when the entrance and the exit
Figure 3. The process of decrease of transparency of a bundle of the nettle fibrils during gradual lowering of water level from the top to the bottom edge of the bundle (time goes from the top to the bottom photo). The total duration of the process is 10 minutes. The upper photo corresponds to the total immersion, whereas at the bottom water does not touch the bundle at all. The interval between the photos 2 and 3 (from the top) is 2 seconds and corresponds to the moment when the surface of water has been separated from the bottom edge of the bundle.

Polarizers have mutually perpendicular directions of the transmittance (“crossed” polarizers). When these directions are parallel or the polarizers are removed at all these phenomena are not observed. Hence the total transparency of the bundles is not changed. Due to these facts the variations of the transmittance of the bundles between the crossed polarizers are attributed to the processes of modifications of orientation ordering (or vice versa disordering) of cellulose molecules induced by contacts with water or application of electrical fields. The analogous phenomena have been described earlier concerning liquid crystallization of pure cellulose nanocrystals [11]. In the natural state of the bundles the cellulose micro-fibrils are connected with the polymers of lignin. The molecules of cellulose compose the layers of the walls of the vessels (Fig. 4).

These molecules of cellulose in neighbor layers of the wall are separated by amorphous lignin. The attachment to lignin prevents orientation ordering of cellulose. But we suppose
Figure 4. The scheme of cellulose distribution within the wall of a plant vessel [5]

that when the contact with water is arranged its molecules penetrate between the cellulose polymers and their lignin neighbors. Due to the interruption of the bonds with lignin the orientation ordering of the cellulose in neighbor layers of the walls of plants vessels occurs resulting in severe enhancement of the optical anisotropy. This assumption is supported by our earlier experiments on the treatment of the oak wood with ultrasonic irradiation [22]. X-Ray diffraction measurements of the structure of the wood before and after the ultrasonic treatment showed that this irradiation resulted in significant increase of the content of the crystallized cellulose. We ascribed this increase to breaking of the bonds between cellulose and amorphous lignin which prevented cellulose from crystallization. On the other hand the attraction of water molecules by the bundles of cellulose fibrils is confirmed by dripping a limited portion of water onto one of the edges of the bundle. In this case the lateral surface in the center of the bundle remained dry. But the gradual increase of the optical anisotropy in this region was observed nevertheless. This means that the molecules of water inducing this anisotropy are penetrating into the bundle using internal channels.

The decrease of the anisotropy induced by application of the electrical field can be explained by the inverse removal of the water molecules from the interfaces between the cellulose molecules and lignin. The nature of this removal is connected with the necessity to minimize the electrostatic energy. The bound molecules of water in the interfaces have the dielectric permittivity much lower than the permittivity of the same molecules being free. Hence the ability of the bound molecules of water to reduce the electrostatic energy is much lower. So due to the necessity to decrease the electrostatic energy the electrical field is pushing out the molecules of water from the interfaces. This removal of water recovers the bonds between cellulose and lignin and destroys its orientation ordering decreasing the optical anisotropy induced earlier by water.

The correlated local changes in orientation of cellulose molecules confirmed by variations of the optical anisotropy of the fibrils described above induce corresponding local stresses. These stresses produce in their turn local electrical fields due to piezoelectricity of cellulose [4]. These electrical fields should modify local content of water molecules between cellulose and lignin. The modifications of the interfaces between cellulose and lignin should in their turn induce changes in orientation of the layers and in corresponding optical anisotropy, etc. Hence we should conclude that the temporal and spatial distributions of all of these factors are mutually interacting. These interactions are confirmed by correlated deformations of external geometry and internal anisotropy of the bundle of nettle fibrils immersed into water when the ends of the bundle were not fixed (Fig. 5).

The local variations of the optical anisotropy of the plant fibrils (the increase induced by contacts with water and the decrease induced by the electrical field) correlated with the changes if external geometry of the sample confirm the possibility of generation of electromechanical waves travelling along the wood micro-capillaries due to active interaction of cellulose molecules in the walls of the capillaries with water molecules and with electrical field. The generation
Figure 5. The correlated variations of local distributions of the optical anisotropy and the external geometry of the bundle of nettle fibrils immersed into water of electromechanical waves is a typical phenomenon for piezoelectric materials \cite{23}. The propagation of these waves is followed with the local particularities of the electrostatic field which are capable to transport the nutritive substances along the vessels of plants as we have assumed earlier \cite{4}.

3. Conclusion
The experimental results presented in this paper provide several ecological and economic improvements for applications of micro-fibrils of plants as follows:

The treatment of wood components immersed into water by optical irradiation results in separation of cellulose fibers from lignin. This fact provides the development of ecologically safe technology for preparation of pure cellulose instead of harmful procedures of chemical hydrolysis of wood. Application of solar radiation for the process of cellulose separation by ultraviolet irradiation is capable to improve significantly economical and ecological characteristics of this technology.

Bundles of fibrils pulled out directly from stems and branches of plants demonstrate after their wetting high electro-optical activity resulting from severe modifications of orientation ordering of cellulose molecules induced by their interactions with water and electrical field. These phenomena provide the development of new kinds of devices for governing of optical flows by means of low electrical fields.

Active interactions of fibrils of plants with water, electrical and deformation fields presented in this paper confirm the possibility of effective transportation of plant nutrients by electromechanical waves propagating along their micro-capillaries.
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