Scanning electron diffraction reveals the nanoscale ordering of cellulose in a hierarchically structured hybrid material

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Background

Biopolymers are electron beam-sensitive materials with low scattering power, which poses a significant challenge for nanoscale characterization. One promising technique to overcome these issues is scanning electron diffraction (SED), utilizing the strong interaction between electrons and matter. In SED, the sample is raster scanned using a near-parallel electron probe while simultaneously capturing a diffraction pattern at each beam position. These patterns provide highly localized crystalline information from the sample, including strain, phase, and orientation, later characterized through post-acquisition data analysis.

Cellulose, with its unique properties and crystalline structure, has emerged as a promising resource for sustainable composite materials. Controlling its hierarchical organization is an essential consideration in cellulose utilization. The aligned orientation of the highly anisotropic cellulose nanofibers is vital to macroscale mechanical properties. Fundamental insights into the intrinsic arrangement of cellulose enhance its exploitation in composites with new and improved properties.

Methods

The wood-based composite material was sectioned using ultramicrotomy in two orthogonal directions, longitudinally and transversely, relative to the elongated wood cell structure. The microscope was configured with a convergence angle of 0.1 mrad, resulting in a probe diameter of less than 10 nm. SED data was acquired using a beam current of 2 pA with a dwell time of 5 ms to minimize beam damage. Cellulose orientation and degree of alignment in each beam position were determined through post-acquisition data processing. 360 virtual detectors were arranged in an annular pattern around the unscattered beam, with a radius corresponding to the scattering angle of the most prominent 200-reflection of cellulose to optimize the signal-to-noise ratio.

Results

In this study, we employed SED to unveil the hierarchical assembly of cellulose nanofibers in transparent wood, a composite material prepared by infiltrating wood with polymerized methyl methacrylate (PMMA)[1]. Our results reveal a well-ordered hierarchical arrangement of nanofibers in the secondary cell wall with a spatial resolution of 15 nm[2]. In the inner regions, the nanofibers are aligned parallel to the cell elongation, including the innermost part closest to the lumen. In the outer part, the nanofibers transition to a tangential orientation. Based on the quantitative SED data, we can conclude that this reorientation occurs smoothly over 1.5 µm. Despite the change in direction, cellulose nanofibers stay well-aligned. Uniform cellulose orientation in the inner part and a plateau in the outermost part support a layered cell wall structure.

Furthermore, wood cells sectioned longitudinally exhibit clockwise or counterclockwise nanofiber rotation towards the outer part. This rotation difference is caused by sectioning the cells at different depths and is consistent with a helical arrangement of nanofibers with a gradually changing pitch.

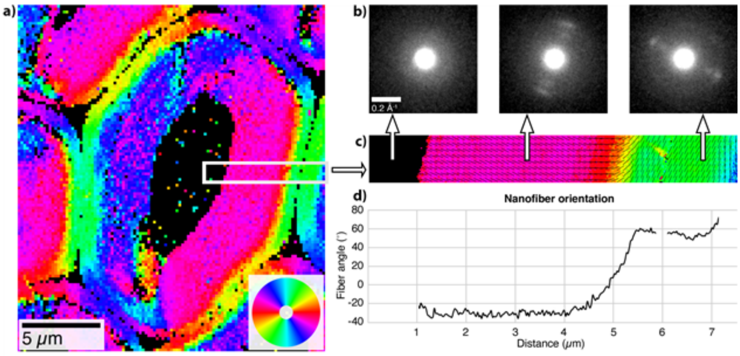
Peak width analysis of transversely sectioned transparent wood discloses a higher degree of nanofiber alignment in the outer part of the cell wall than in the inner part.

Preserving the anisotropic organization of cellulose in this new biocomposite retains the mechanical properties of wood.

Conclusions

This work demonstrates the potential of Scanning Electron Diffraction in characterizing biobased composite materials. Combining sensitive detectors and innovative data analysis enables the detection of very subtle signals from the sample. SED provides quantitative crystal information with exceptionally high spatial resolution from a relatively large field of view (20x20 µm).

Graphic:



Organization of cellulose nanofibers within transversely sectioned transparent wood in an entire fiber cell (a). Colors in the figure correspond to the nanofiber orientations according to the color wheel, with black indicating areas lacking cellulose. The enlarged view (c) reveals the aligned orientation of nanofiber within the secondary cell wall captured with a step size of 30 nm. Representative diffraction patterns (b) show the rotation and absence of Bragg's reflection in selected areas. The line scan (d) reveals the smooth oriental transition of nanofibers in c with a plateau in the outermost part of the cell wall, indicating a layer of uniformly oriented fibrils.

Keywords:

scanning electron diffraction, hierarchical structures

Reference:

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