Carbohydrates/Matrix Lignin in Mechanically Graded Bamboo Culms

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The mechanical performance of bamboo is highly dependent on its structural arrangement and the properties of biomacromolecules within the cell wall. Along the radius of bamboo culms, the concentration of xylan within the fiber sheath increased, while that of cellulose and lignin decreased gradually. At cellular level, although the consecutive broad layer (Bl) of fiber revealed a relatively uniform cellulose orientation and concentration, the outer Bl with higher lignification level has higher elastic modulus (19.59–20.31 GPa) than that of the inner Bl close to the lumen area (17.07–19.99 GPa). Comparatively, the cell corner displayed the highest lignification level, while its hardness and modulus were lower than that of fiber Bl, indicating the cellulose skeleton is the prerequisite of cell wall mechanics. The obtained cytological information is helpful to understand the origin of the anisotropic mechanical properties of bamboo.

multilayered bamboo fiber | topochemistry | microscopic imaging | gradient micromechanics

1. Introduction

In terms of tissue types, the bamboo culm consists of fibers, parenchyma and conducting elements (including the xylem vessels, sieve tubes, and companion cells). As the source of the superior mechanical properties of bamboo, the fibers’ density and quality vary significantly along and across the bamboo culm. For example, along the diametric direction, the longitudinal tensile modulus of elasticity for the outermost layer was 3–4 times as high as that of the innermost layer, while the longitudinal tensile strength ranged from 115.94 to 328.15 MPa from the outermost layer to the innermost layer [1].

Actually, much of the mechanical behavior of bamboo is governed by the properties of the cell wall, which, in turn, can be described in terms of the submicroscopic structure of the wall and the localization of cell wall components of cellulose, hemicelluloses, and lignin. Cellulose is the main structural fiber in the plant kingdom and has remarkable mechanical properties for a polymer: its Young’s modulus is roughly 130 GPa, and its tensile strength is close to and even more than 1 GPa [2]. The properties of hemicelluloses and lignin are similar to common engineering polymers. Lignin, for instance, has a modulus of roughly 3 GPa and a strength of about 50 MPa [3]. An important role of lignin in the wood cell wall is to function as a cross-linking matrix between moisture sensitive cellulose and hemicelluloses, thereby, lignin contributes to the mechanical rigidity [4]. The modulus of xylan varies from a value of 8 GPa at low moisture contents (0–10%) to 10 MPa at moisture contents near saturation (70%). Meanwhile, the incorporation of xylan in the cell wall, especially in the secondary wall, has a strength-enhancing effect on the joint strength individual fiber crossings [5]. The arrangement of the basic building blocks in bamboo cell walls and the variations in cellular structure give rise to a remarkably wide range of mechanical properties.

Unlike the typical three-layered structure of wood secondary wall, bamboo exhibits a polylamellate secondary wall with alternating broad and narrow lamellae that arise from the alternation in the orientation of cellulose microfibrils in a matrix of intertwined hemicelluloses and lignin. To date, macro- and micro-structural investigations have been reported comprehensively.

2. FT-IR Chemical Image of Bamboo Culm

The FT-IR spectra of the bamboo fiber sheaths extracted from Bg, Bt and By are shown in **Figure 1**a. FT-IR spectra indicated peak changes in fingerprint regions at various tissues and cell locations. The main differences in the absorption spectra are visible at wavenumbers 1730, 1508, 1369, 1240, 1158, and 896 cm^{-1}. The IR band at 1508 cm^{-1} corresponds to a C=C stretching the vibration of the aromatic rings of lignin. The carbohydrates peaks at 1730, 1369, and 1158 cm^{-1} are assigned, respectively, for unconjugated C=O in xylan, C-H deformation in cellulose and hemicelluloses, and C–O–C vibration in cellulose and hemicelluloses [6][7]. Moreover, the band at 1240 and 896 cm^{-1} is a diagnostic peak for cellulose by the C–O–C vibration and C–H deformation in cellulose, respectively [8][9]. The relative absorbance of characteristic FT-IR absorbance bands is plotted as a function of the fiber sheaths (**Figure 1**b).

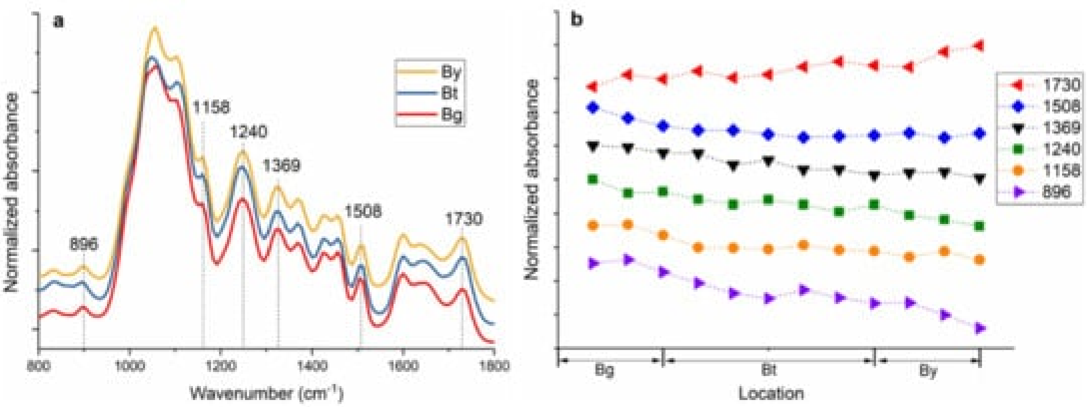

Figure 1. (**a**) FT-IR spectra of fiber sheath extracted from Bg to By; (**b**) Change in relative intensity of absorbance bands for fiber sheath from Bg to By.

Previously, the investigation of carbohydrate and lignin in the bamboo cell wall mainly focused on the total value of lignin in bamboo tissues, comprising all tissues, such as fibers, vessels and parenchyma, rather than specifying the lignin and values for individual cell types [10][11][12]. Actually, the extent of compositional variation was found to be influenced by the age of the culm, in certain ages by the position of the vascular bundle, and most strikingly, by the proportion of fibers within the vascular bundle and surrounding parenchyma.
Figure 2 shows the functional group chemical images of bamboo culm transverse sections. The red color represents high intensity and the blue color stands for little or no intensity. Thus, chemical images at bands near

1730, 1508, and 1240 cm^{-1} can show the relative concentrations of xylan, lignin, and cellulose, respectively. The chemical images indicated that the xylan (**Figure 2**a) and lignin (**Figure 2**b) mostly accumulated in the fiber sheath within the vascular bundles and appeared much less in the ground parenchymatic regions. This is to be expected, because the vascular bundles are believed to be the main mechanical support for the whole bamboo culm. Interestingly, for a single vascular bundle, there is also a heterogeneity in compositional distribution. High lignin and xylan concentration was visualized in the outermost part of the fiber sheath. Comparatively, cellulose showed a more homogeneous distribution pattern for the fiber sheaths within the vascular bundles (**Figure 2**c). It has been revealed that the average tensile modulus for the bamboo fiber is three times higher than that of the parenchyma [13]. Cellulose has been proved to be the main structural component and has remarkable mechanical properties. Thus, the higher concentration of cellulose in the fiber sheaths area may partly explain the superior modulus and strength properties compared with parenchyma cells.

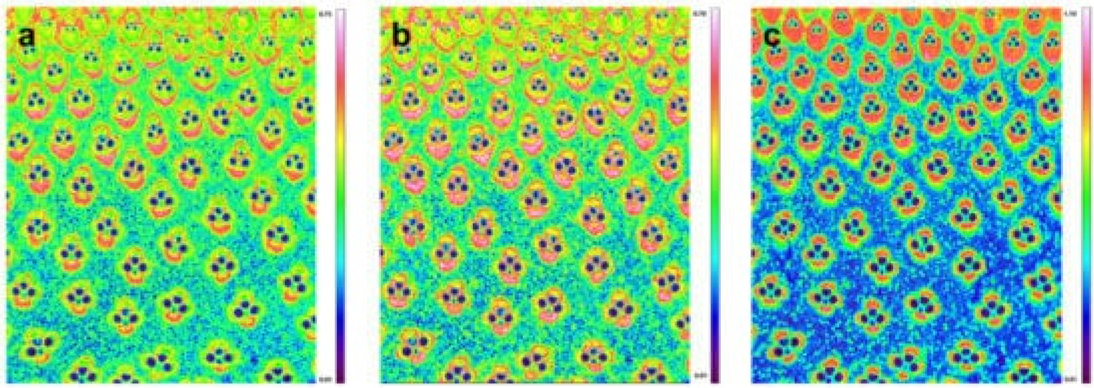

Figure 2. FT-IR images of the relative concentration and distribution of xylan (**a**), lignin (**b**), and cellulose (**c**).

3. Confocal Raman Chemical Image of Bamboo Fiber

To further explore the chemical constituent distribution of bamboo fiber at the cellular and sub-cellular level in situ, confocal Raman microscopy with high spatial resolution (<0.5 μm) was employed.

By integrating over the CH and CH_2 stretching vibrations (2800 cm^{-1} to 2918 cm^{-1}), high intensity and thus high carbohydrates concentration were observed especially in the secondary wall (SW) of fiber (**Figure 3**a–c). As shown in **Figure 3**d–f, lignin concentration was the highest in cell corner (CC) and compound middle lamella (CML). Within the SW, the lignin concentration decreased from the outer layer to the cell lumen, with relative higher concentration in the lumen edge as well as the interface between adjacent layers of the multilayered fiber.

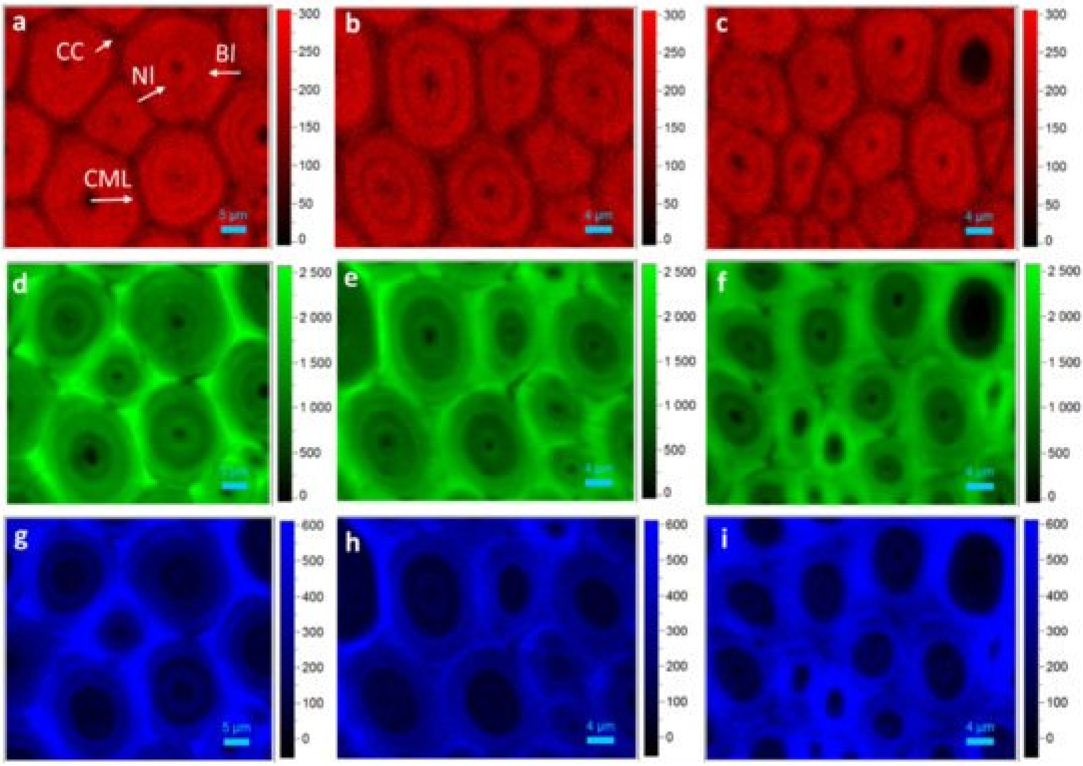

Figure 3. Raman images showing the distribution of fiber wall components from Bg (**a,d,g**), Bt (**b,e,h**) and By (**c,f,i**). (**a**–**c**) Carbohydrates, 2800–2918 cm^{-1}; (**d**–**f**) Lignin, 1540–1660 cm^{-1}; (**g**–**i**) HCA, 1120–1200 cm^{-1}.

4. The Variation in the Mechanical Properties of Fiber Cell Walls

As shown in **Figure 4**a–c, the mean value of indentation modulus and hardness of bamboo fiber within a single fiber wall, displayed an obvious difference. The outer layer of fiber SW in all the Bg, Bt and By areas has higher modulus (19.59–20.31 GPa) and hardness (428–445 MPa) than the inner layer of fiber close to the lumen area with modulus of 17.07–19.99 GPa and hardness of 410–440 MPa. Although previous studies suggested that the microfibril angle is negatively correlated with the elastic modulus of fiber cell wall [14][15], the Raman spectral analysis result revealed a relatively uniform cellulose orientation distribution in the multilayered fiber by extracting the cellulose orientation sensitive band around 1097 cm^{-1} (**Figure 4**d). This result is consistent with the earlier typical microfibril angle model of multilayer fiber by Parameswaran & Liese [16]. Thus, the variation in the modulus was mainly due to the variation in the cell wall lignification level and its composition. Similarly, in the spruce tracheid wall, the observed difference in the modulus of elasticity between developing and fully lignified cell walls is due to the filling of spaces with lignin and an increase in the packing density of the cell wall during lignification [17].

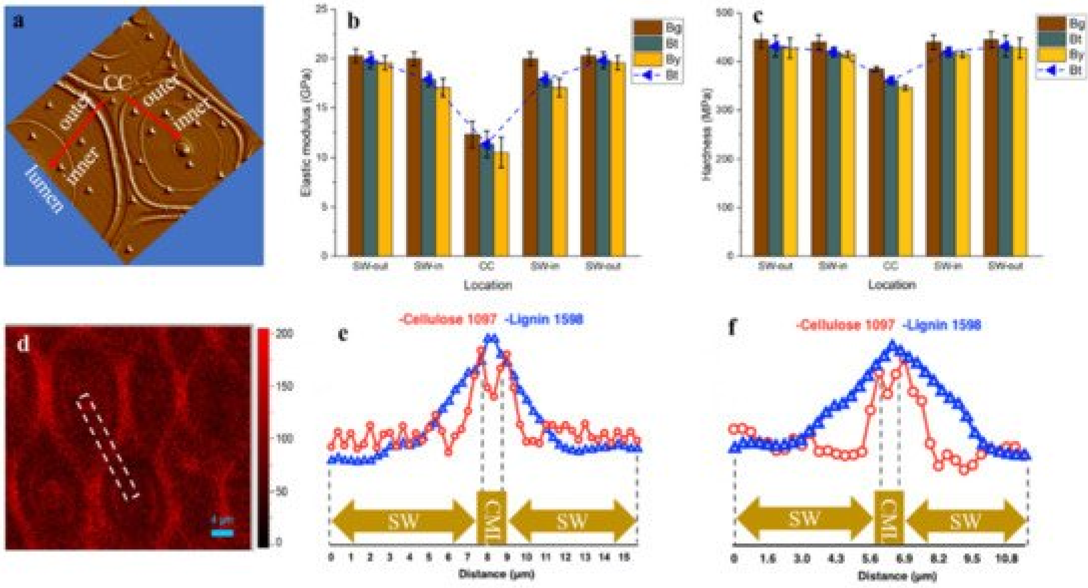

Figure 4. (**a**) The image obtained after indenting shows the actual position of indents; (**b,c**) The elastic modulus and hardness of bamboo fiber at different locations; (**d**) Raman image showing the cellulose microfibrils orientation distribution by integrating over 1097 cm^{-1}; (**e,f**) the Raman line scan of Bg (**e**) and Bt (**f**) fiber wall. The white dotted line indicates the typical region of the Raman spectra collected. SW-out: outer layer of fiber secondary wall; SW-in: inner layer of fiber secondary wall.

5. Conclusions

Combined microscopic techniques have been used to non-destructively investigate the compositional heterogeneity and variation in cell wall mechanics in moso bamboo. At the tissue level, the fiber sheath has a higher concentration of carbohydrates and lignin than the ground parenchyma cells from Bg to By. For the multilayer bamboo fiber, the Bl revealed a higher carbohydrates and lignin concentration than the Nl, and the outer Bl showed a higher lignification degree than the inner Bl, yet the consecutive Bl revealed a relatively uniform cellulose orientation and concentration. Furthermore, the Bg displayed the highest elastic modulus and hardness followed by Bt and then by By, and the elastic modulus and hardness decreased from the outer Bl to the inner Bl. Comparatively, the CC displayed the highest lignification level but the lowest hardness and modulus.

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