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Glass-Transition Temperature Profile Measured in a Wood Cell Wall Using Scanning Thermal Expansion Microscope (SThEM)

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Abstract This study aims to assess the *in situ* spatial distribution of glass-transition temperatures (T_g) of the main lignocellulosic biopolymers of plant cell walls. Studies are conducted using scanning thermal expansion microscopy to analyze the cross-section of the cell wall of poplar. The surface topography is mapped over a range of probe-tip temperatures to capture the change of thermal expansion on the sample surface versus temperature. For different temperature values chosen between 20 °C and 250 °C, several quantitative mappings were made to show the spatial variation of the thermal expansion. As the glass transition affects the thermal expansion coefficient and elastic modulus considerably, the same data line of each topography image was extracted to identify specific thermal events in their topographic evolution as a function of temperature. In particular, it is shown that the thermal expansion of the contact surface is not uniform across the cell wall and a profile of the glass-transition temperature could thus be evidenced and quantified corresponding to the mobility of lignocellulosic polymers having a role in the organization of the cell wall structures.

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1 Introduction

A scanning thermal microscope (SThM, μ-TA) is known to be a powerful tool for imaging topography with the characterization capabilities of microthermal analysis by combining the high spatial resolution of an atomic force microscope (AFM) and a thermal resistive probe [1]. In this study, a related technique called scanning thermal expansion microscopy (SThEM) developed by Hammiche et al. [2], was applied to analyze the cross-section of a wood cell wall, on an area of few square microns. The aim of this study was to assess the possibility of using SThEM to measure the local surface temperature profile across a wood cell wall, related to the glass transition of the constituent lignocellulosic biopolymers. The method consisted of employing a resistive thermal probe in the active mode to provide localized heating and consequently, localized phase transitions that can generate softening, thermal expansion of the sample surface, or melting at the apex of the tip. The ability to scan regions to map topographic and thermal changes of a surface makes the technique particularly attractive to study thermal transitions. The topographic images are of particular importance as such thermal events are strongly related to the thermal expansion coefficient and elastic modulus, more so than upon the thermal conductivity [3]. However, during a phase transition, changes in measured signals are partly due to the increase in contact area and the temperature of the sample material in immediate contact with the probe can be measured provided a suitable calibration of the probe-tip temperature is previously carried out [4–9].

2 Experimental Apparatus and Results

2.1 Description of the Cellular Wall of Vegetables

In wood tissue, the cell wall structure consists of several composite layers. Each individual cell has a primary wall and a stiff secondary wall. The primary wall is composed of a flexible network of cellulose microfibrils in an amorphous matrix hydrated by pectins and hemicelluloses. The primary wall is elastic and deformable to allow for the strain of cells. The secondary wall is a compact, stiff, and weakly hydrophobic structure constituted by 50 % cellulose and 25 % lignins. The secondary wall presents three successive layers, S_1, S_2, and S_3, distinguished by the orientation of their cellulose microfibrils, providing rigidity to the cell wall. The S_2 layer is the thickest and most important for mechanical stability. Between adjacent cells, a middle lamella layer (ML) attached to the primary cell wall (PI) ensures the adhesion of a cell to its neighbors. A key fact is that lignins are especially localized in the primary wall.

As hydrophobic compounds, the major role of lignins is to conduct water between fibers within the intermediate layer (ML).

2.2 Sample Preparation

The poplar sample is first cut into a small cube (5 mm side), then embedded in LR white resin. The LR white resin is a polyhydroxy-aromatic acrylic resin. Its hydrophilic character allows for good penetration in all the pores of the sample. Moreover, this resin exhibits low shrinkage after drying. After polymerization of the resin, the sample is sliced with a microtome to expose a very smooth surface.

2.3 Thermal Microscope

The experimental apparatus is a thermal microscope type μ-TA 2990 from TA Instruments combining an AFM platform with thermal control of a thermoresistive probe. The probe is a Wollaston-wire type. A current is applied to the wire causing Joule heating and allowing the wire to act as both a resistive heater and a resistive temperature detector (RTD). In the active, constant temperature mode of the probe used in this study, the power necessary to maintain a constant average probe resistance (constant temperature) is measured allowing for the study of the thermal flux dissipated in the sample. A temperature calibration of the tip was carried out prior to measurements.

2.4 Scanning Thermal Microthermal Expansion Analysis

In a first step, the thermal probe is implemented in the constant temperature mode at a given probe temperature. This mode allows mapping topographical and thermal images at the sample surface with a resolution of less than a micrometer at constant temperature. Figure 1 shows mappings of the poplar sample revealing the individual cell structures. Our investigation focused on a section of the double cell wall (interface of two cells) of poplar filled with LR white resin. Topographies and thermal images were measured at given probe temperatures varying from ambient to 180 °C by steps of 1 °C. Two sets of the images (8 μm $\times$ 8 μm) are displayed in Fig. 2 for temperatures of 30 °C, 75 °C, 110 °C, and 180 °C. The images of topographies show the influence of the heated probe on the state of the surface of the sample. Below 75 °C, the double wall is very evident. The heated zone under the probe first expands, deflecting the probe. Then the deformed surface displays a more complex viscoelastic behavior. For higher temperatures, an apparent spreading of the wall is observed. There is a reduction of the effective stiffness of the tip-surface contact and the biopolymers of the cell wall soften leading to plastic deformation under the pressing probe. At these temperatures, there are significant irreversible effects from the eventual peeling of the surface from the probe. Finally, if the polymer melts, the tip of the probe sinks into the material (not represented here).

The temperature evolution of topography for the same line of pixels for a series of images was studied to find a spatial profile of a glass transition. Let us note that around T_g, Young's modulus generally decreases three orders of magnitude for polymers, leading to a sudden volume expansion. That property will be used for the determination of the glass transition. Each pixel has been analyzed to find temperatures corresponding to the abrupt change of thermal expansion. Figure 3 presents the profile

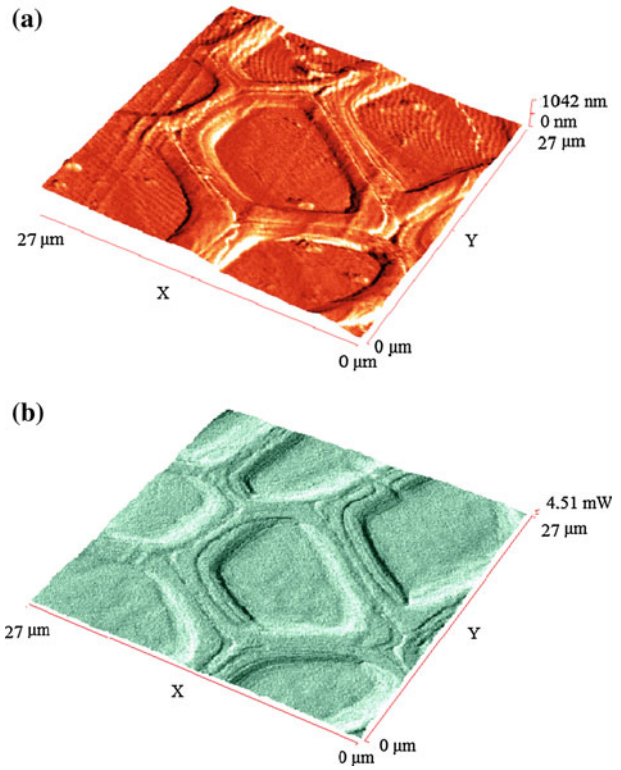

Fig. 1 (a) Topographic and (b) thermal images of a cross section of a poplar sample scanned at a constant temperature of 120 °C

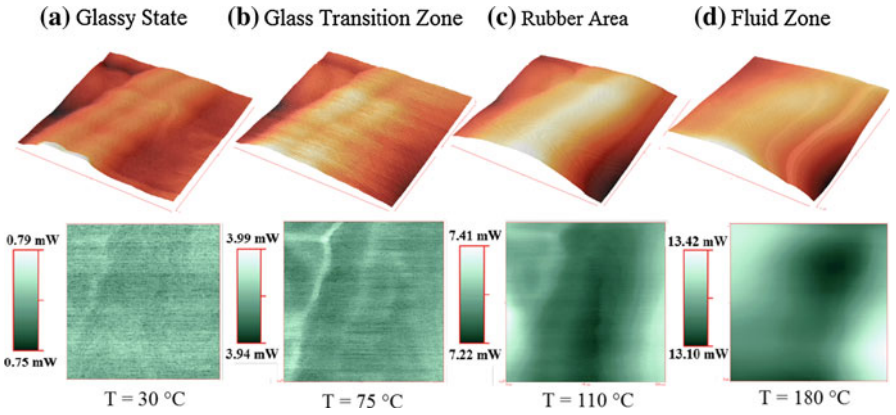

Fig. 2 Series of images acquired by SThM for corrected probe temperatures of (a) 30 °C, (b) 75 °C, (c) 110 °C, and (d) 180 °C. Scanned images (8 µm × 8 µm) represent the topography of the poplar sample (*top*) and the corresponding dissipated thermal flux (*bottom*)

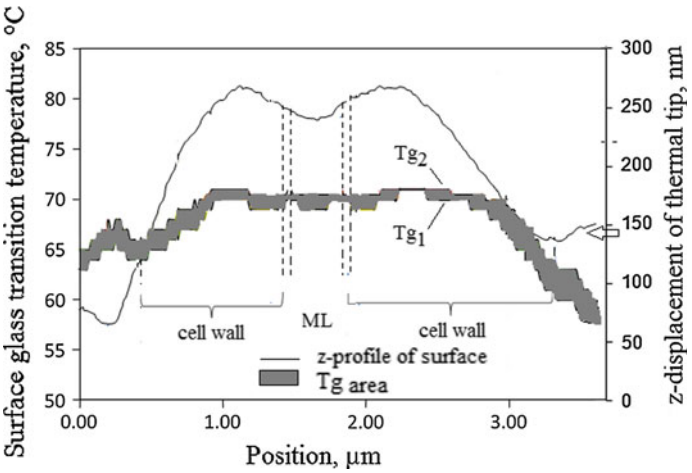

Fig. 3 Resultant profile of T_g as a function of position on the double cell wall of poplar. *Gray area* refers to the interval of uncertainty of the measured T_g. *Solid line* represents the topographic profile of the surface

of glass-transition temperatures found on the double cell superimposed with the topography measured at room temperature. The thickness of the T_g profile marked by T_{g1} and T_{g2} represents the onset and ending temperatures of the phenomena. As expected, the highest T_g values are obtained within the secondary zone, while the lowest values correspond to the primary layer and ML, identifiable in the topographic profile. The measured T_g values range from 68 °C to 72 °C and are relatively low compared to values obtained on similar materials in anhydrous conditions (In that case, T_g of lignin is above 140 °C). Comparatively low glass-transition temperatures, T_g, as were found here, have already been observed for various moisture contents in the wood of spruce [10]. According to that study, the phenomenon could be interpreted as a secondary transition of type β resulting from micro-Brownian motions of lignocellulosic polymers in the non-crystalline regions for a moisture content in the sample near 30 %. The migration of water in the wall is then at the origin of the plasticizing, lowering the glass-transition temperature of the analyzed composite. One should note the possible influence of LR white resin penetrating the sample [11]. Water migration into the internal border of the cell walls could result from resin contamination, explaining their increased plasticizement and, consequently, leading to the limiting diminished T_g value of 64 °C. The internal borders between layers of the secondary wall are not discernible due to the strong influence of the thermomechanical behavior of the resin interacting with the cell wall.

3 Conclusion

The thermal analysis of a cell wall of poplar having a thickness of a few microns was performed on a local scale by SThEM. The distribution of glass-transition temperatures on the surface of a cross-section of a cell wall was extracted despite the complexity of the thermal effects at the probe–sample interface. This study revealed

relatively low values of T_g ($\sim$65 °C to 70 °C) on a hydrous sample compared to those from anhydrous samples. This could be due to a secondary phase transition of the β type and to the contribution of the motions of the end of macromolecular chains close to the surface.

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