Proceedings of the 58th International Convention of Society of Wood Science and Technology
June 7-12, 2015 – Grand Teton National Park, Jackson, Wyoming, USA

Timber Physics from 1 μm to 10 m Session
Moderator: *Samuel Zelinka, US Forest Products Laboratory, USA*

Subcellular Electrical Measurements as a Function of Wood Moisture Content

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Abstract

Recent work has highlighted the importance of movement of chemicals and ions through the wood cell wall. Movement depends strongly on moisture content and is necessary for structural damage mechanisms such as fastener corrosion and wood decay. Here, we present the first measurements of electrical resistance at the subcellular level as a function of wood moisture content by using a 1 μm diameter probe. Measurements were taken with the probe contacting the S2 layer and the compound corner middle lamella of the cell wall within the latewood, and the compound corner middle lamella in the earlywood. The resistance decreased with increasing relative humidity in all locations. The resistance decreased more rapidly with relative humidity in the S2 layer than in the middle lamella. These results give insight into how some moisture-dependent wood properties affecting ion movement may be partitioned across cell wall layers.

Keywords: wood-moisture relations, electrical properties of wood, timber physics, percolation theory, wood damage mechanisms

Introduction

Wood-moisture relations have long been studied using electrical measurements at the macroscopic level (Stamm 1929). Recently, Zelinka et al. (2008) proposed a new mechanism for electrical conduction in wood based upon percolation theory. The theory describes the rapid increase in conductivity of wood as a function of moisture content (MC) between roughly 15-30% moisture content in terms of a percolating network through which ion movement occurs. One key feature of the model is that there is a percolation threshold, the MC at which the percolating network first forms and below which ionic conduction cannot occur. Above the percolation threshold, the conductivity increases with a power-law behavior. Because the percolation threshold represents the lower bound for ionic conduction, it also represents the moisture content below which wood damage mechanisms that rely on ion transport cannot occur (Jakes et al. 2013). Jakes et al. (2013) developed a model for chemical movement in cell walls that is consistent with the percolation model for ionic conduction. In this model chemical movement occurs in regions of the cell where the hemicelluloses have softened through a moisture induced glass transition. Under dry conditions, the hemicelluloses in wood have a glass transition between 150 and 220°C, however, the glass transition temperature decreases with moisture content and eventually crosses room temperature when in equilibrium with a relative humidity (RH) of somewhere between 60% to 80% RH (Cousins 1976, 1978; Kelley et al. 1987; Olsson and Salmen 2004). Above the glass transition temperature, the hemicellulose backbones twist and bend facilitating movement of ions and other chemicals between energetically favorable sites. Just below the percolation threshold, some of the hemicelluloses have adsorbed enough moisture to soften at room temperature. As the relative humidity increases, the number and size of softened regions grows until there is a continuous pathway of softened regions through which chemicals and ions can have long range diffusion.

The percolation model developed by Zelinka et al. was based upon macroscale measurements of the electrical conductivity and implicitly treats the wood material as homogenous. The transport mechanism proposed by Jakes et al. depends upon a moisture induced glass transition occurring in the hemicelluloses. This theory suggests that there are likely differences in the threshold moisture content for moisture transport between different regions in the cell wall. For instance, the secondary cell wall contains cellulose microfibrils, amorphous cellulose, hemicelluloses, and lignin, where hemicelluloses are preferentially oriented along the microfibrils (Hafren et al. 2000;

Åkerholm and Salmén 2001; Stevanic and Salmén 2009). In contrast, in the middle lamella hemicelluloses exist in an irregular network of lignin (Hafren et al. 2000). Because of the differences in the arrangement and amount of hemicelluloses between these two cell wall regions, it is likely that these regions might exhibit differences in how the conductivity increases with moisture content. Since there are differences in the orientation and amount of the hemicelluloses between the secondary cell wall and middle lamella, it's possible that transport occurs differently between these two cell wall layers, and these differences may give further insight into moisture induced changes in wood.

Materials and Methods

Tests were conducted on microtome-cut transverse sections of Southern pine (*Pinus* sp.) wood. Although the exact species could not be determined, the tree was harvested from a plantation where over 90% of the trees were slash pine (*Pinus elliottii)*. Section thickness was examined as an experimental variable and was controlled with the microtome thickness settings: measurements were taken on 20, 40, and 60 µm sections. Sections were stored in ethanol to prevent microbial degradation. Immediately prior to testing, the sections were rinsed with water, placed in the sample holder, and conditioned at 50% RH and 22°C. Additionally, measurements were attempted on 500 µm sections cut by a fine saw; however, the surface roughness of these samples was too high to get reproducible results.

Making good electrical contact with the wood sample was challenging since the sections were prone to curling. To ensure good electrical contact, a sample holder was developed to press the section onto a conductive metal plate while still allowing the top to be accessed with the tungsten probe and exchange moisture with the environment. The sample holder consisted of an acrylic plate with a hole in the center (Figure 1). The section sat between the acrylic plate and an aluminum plate which was used as one of the electrodes. Bolts were used to tighten the acrylic plate to the aluminum plate and an extra bolt was attached to the aluminum so that a wire could be connected to it for the electrical measurements. The second electrode in the measurement was a tungsten probe with a 1 µm tip diameter (Electron Microscopy Sciences, Hartfield, PA).

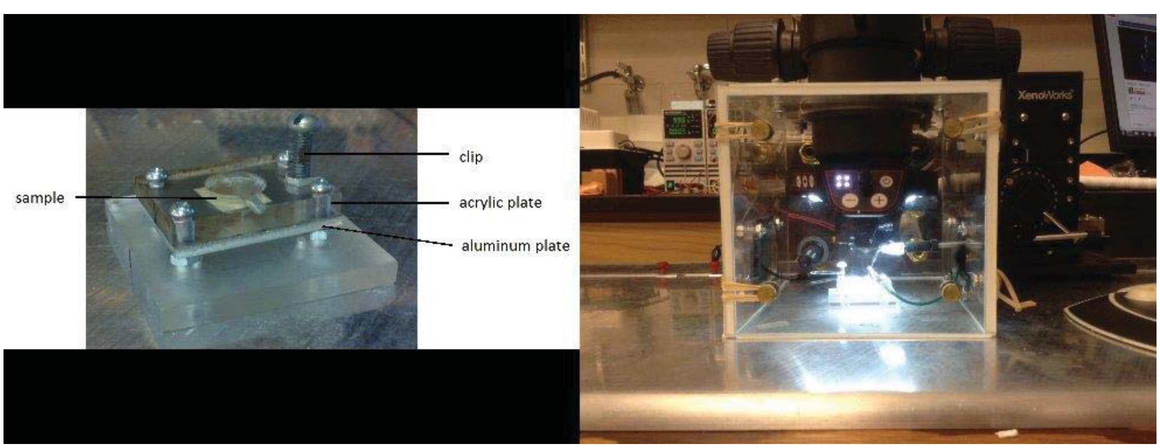

Figure 1: Left: Sample holder used to hold the sections against the aluminum electrode. Right: Chamber built around the stereomicroscope to control the relative humidity conditions.

Measurements were taken in a custom chamber built around a S8APO stereomicroscope (Leica, Wetzlar, Germany) (Figure 1). The chamber was built to house the tungsten probe and the objective of the stereomicroscope. The probe was positioned with a Xenoworks micromanipulator (Sutter, Novato, CA) with a minimum step size of 62.5 nm. Constant RH was maintained by a 2 L min^{-1} flow of conditioned air into the chamber from a HumiSys RH generator (InstruQuest, Coconut Creek, FL) that relied on an RH sensor placed inside the chamber.

For each relative humidity condition, the probe was placed in contact with a cell and the electrical resistance was measured. The RH was then increased, and the section was allowed to condition for 25 minutes at the new RH, this time allowed these thin specimens to get fairly close to equilibrium conditions. Then the measurements were repeated on the same ten cells that had been measured at the previous RH condition. Measurements were taken at seven different relative humidity conditions starting at 50% RH (50%, 57%, 64%, 71%, 78%, 85%, 95%).

Measurements in the earlywood could only be taken at the compound corner middle lamella at the intersection of four cells (Figure 2). Because the cell walls in the earlywood are so thin, the cell wall away from the middle lamella could not be individually measured with the probe we used. In the latewood, the cell wall thickness permitted measurements in both the S2 layer of the cell wall and in the compound corner middle lamella.

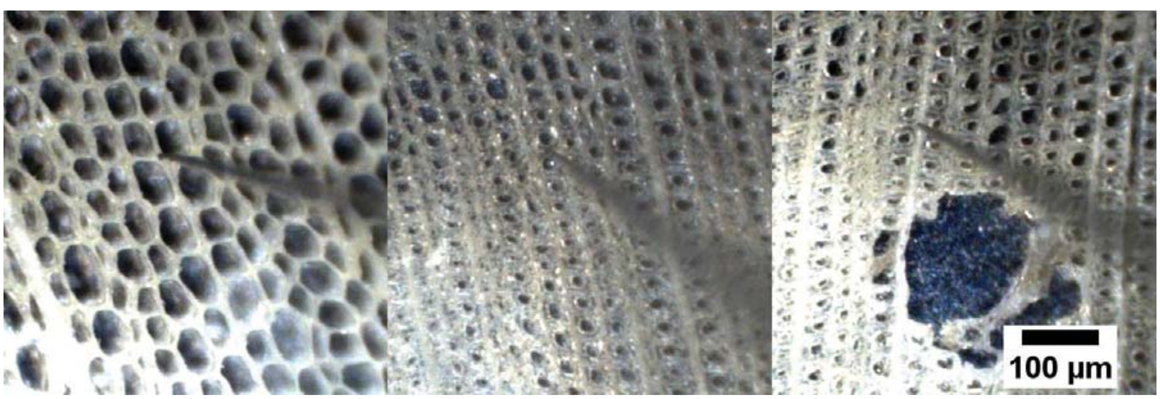

Figure 2: From left to right: example images showing probe placement in earlywood cells, in the S2 layer of latewood cells, and in the middle lamella in the latewood cells.

The resistance measurements were performed with an apparatus designed to minimize polarization effects and to allow for consistent and repeatable measurements (Boardman et al. (2012). The system applies 10 V across a 10 MΩ precision resistor in series with the specimen; polarization is prevented by switching the polarity of the bias voltage at a frequency of 1 Hz and averaging four measurements. The resistance of the wood is determined from measuring the voltage drop across the precision resistor, resulting in uncertainty of less than 6 % at 100 GΩ.

Results

The results of the measurements taken in the earlywood for the three different thicknesses are shown in Figure 3. The resistances range from nearly 50 GΩ at 50% RH to less than 5 GΩ at 95% RH. There is no apparent trend of resistance with section thickness. At the lowest RH conditions, the 60 µm thick sections have the highest resistance but between 70-90% RH, the 20 µm thick sections have the highest resistance. The data appear to have a nearly linear decrease in resistance as the relative humidity increases.

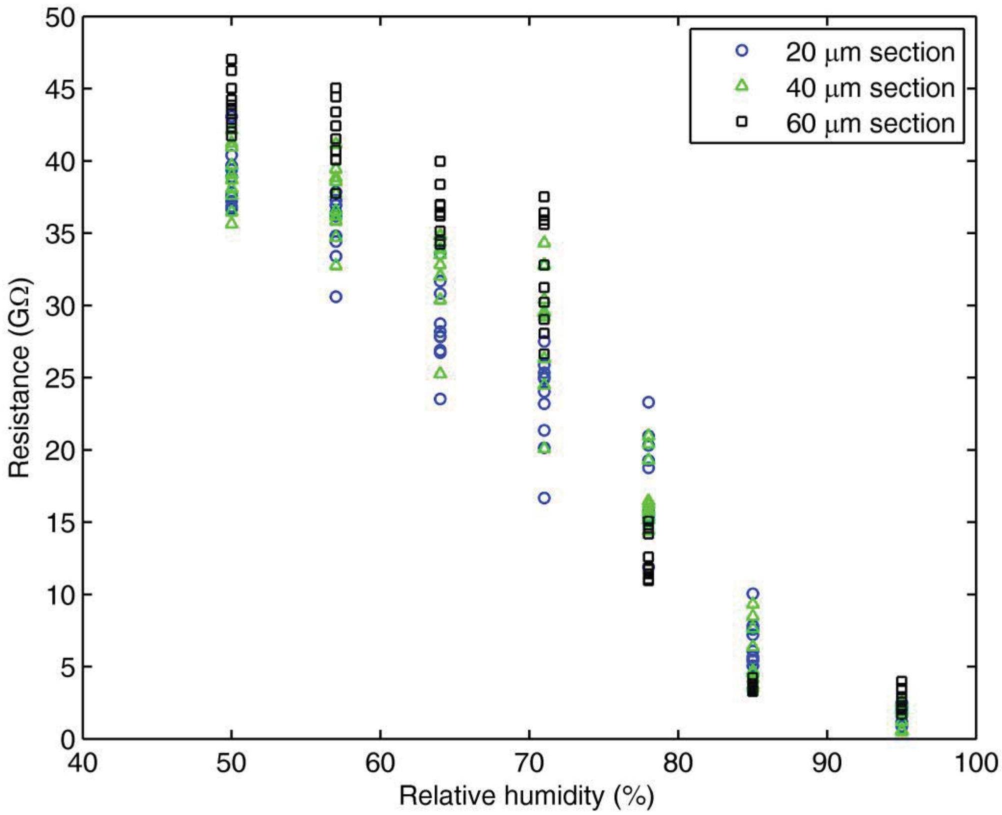

Figure 3: Resistance measurements taken in the compound corner middle lamella of the earlywood as a function of relative humidity.

The results of the latewood measurements taken from the 20 µm thick section are shown in Figure 4. Clear differences are visible in the behavior of the cell wall layers. At the 50% RH condition, the resistance of both layers is approximately equal. However, in the S2 layer, the resistance exhibits a steep drop between 50% and 70% RH. The measurements taken in the middle lamella appear similar to those taken in the earlywood, where the resistance decreased nearly linearly with increasing relative humidity.

Discussion

The measured resistances were independent of the section thickness. This is not surprising as the measurements were taken with a probe with a very sharp radius of curvature. Zelinka et al. (in press) used finite element models to show that for pin-type electrical measurements in wood, the resistance was independent of electrode spacing. Furthermore, when one of the electrodes is a point source, the resistance (R) depends upon only the resistivity of the material (ρ) and the radius of curvature (r)

$$\rho = 4\pi r R \quad \text{(Eq 1).}$$

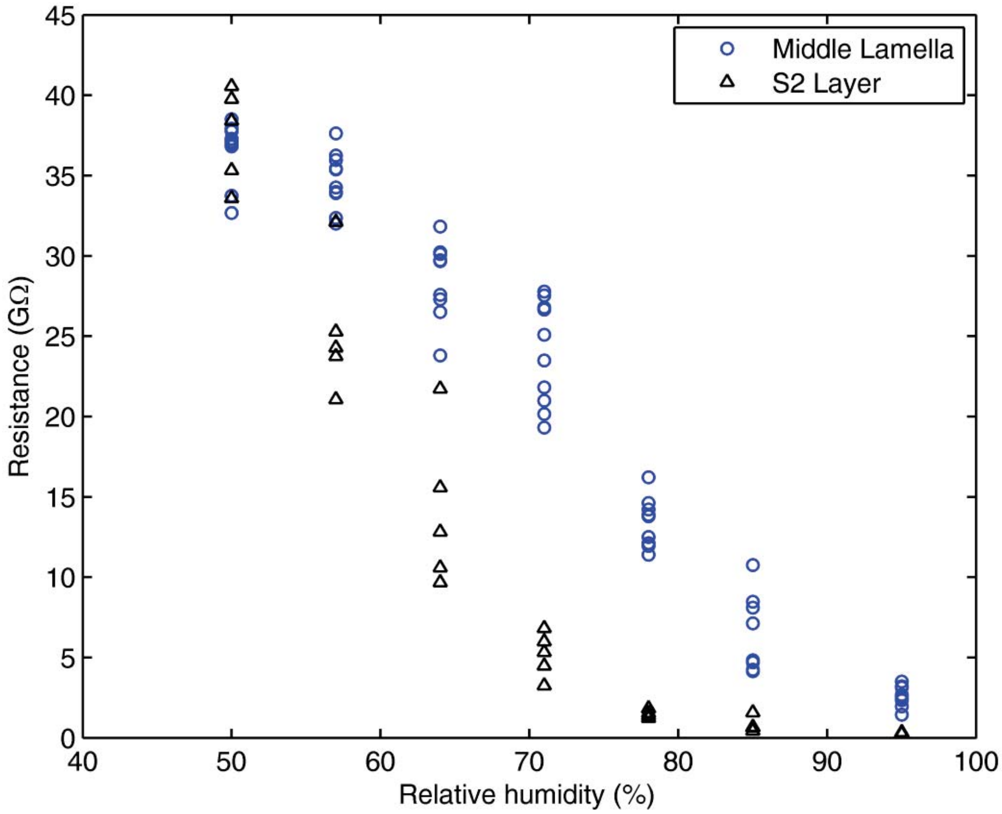

Figure 4: Resistance measurements taken in the compound corner middle lamella and S2 layers of the cell wall in the latewood as a function of relative humidity.

(Telford et al. 1990). Therefore, it is not surprising that there was no trend in the measurements with increasing thickness, and the measurements taken at different thicknesses help define the range of expected values for these measurements.
The resistance measurements taken in the compound corner middle lamella in the earlywood are almost identical to those taken in the same location in the latewood.

It is worthwhile to compare these data to those collected at the macroscale. Traditionally, electrical measurements in wood have plotted conductivity (σ, the reciprocal of the resistivity) as a function of the wood moisture content. Using Eq. 1, the conductivity ranges from $10^{-6}\ \Omega^{-1}m^{-1}$ at 50% RH for both the S2 and middle lamella to $10^{-4}\ \Omega^{-1}m^{-1}$ and $5\cdot10^{-5}\ \Omega^{-1}m^{-1}$ at 95% RH for the S2 layer and the middle lamella, respectively. From sorption measurements previously taken on material from the same parent board (Zelinka et al. 2014), these RH conditions correspond with wood moisture contents of 7.8% and 22.4% MC, respectively. The macroscopic measurements of Stamm (1929) used to develop the percolation model ranged from $10^{-7}\ \Omega^{-1}m^{-1}$ at 9% MC to $4\cdot10^{-5}\ \Omega^{-1}m^{-1}$ at 22% MC; and are within an order of magnitude of the range of values found at the subcellular level. Furthermore, the relative change in the resistivity of the macroscopic measurements is similar to the relative change in resistivity of the measurements taken in the S2 layer.

The increase in conductivity with moisture content is important as it is a way to measure the mobility of ions at different moisture contents. Jakes et al. (2013) hypothesized that several wood damage mechanisms require chemical diffusion within the cell wall and that a better understanding of the diffusion of ions and other chemicals through the cell wall may lead to new ways of protecting wood from moisture-induced damage. In these measurements, it appears that there are clear differences in conductivity between the S2 layer and the middle lamella, and that movement increases more rapidly in the S2 layer than in the middle lamella as wood moisture content increases.

These measurements may give insight into where a percolating network first occurs in wood and how it may be related to mechanical softening. Specifically, the conductivity increases most rapidly in the S2 layer where the hemicelluloses are more regularly oriented, whereas in the middle lamella, there does not appear to be a sharp increase in the conductivity with moisture content. If a rapid increase in conductivity is indeed controlled by the hemicelluloses passing through a moisture induced glass transition, then these measurements suggest that the moisture content at which the glass transition occurs is different in the S2 layer and middle lamella and that the S2 layer is the first to soften. These measurements suggest treatments that preferentially affect the S2 layer may be more beneficial in reducing chemical movement in wood at moisture contents below fiber saturation, thereby protecting wood from moisture-induced damage.

Conclusions

Electrical resistance was measured across microtomed wood sections as a function of relative humidity using a 1 µm diameter probe contacting the secondary cell wall and compound corner middle lamella of southern pine. Several conclusions can be drawn from these measurements:

- The measured resistances were independent of section thickness between 20-60 µm. A smooth, microtomed surface was necessary to make good electrical contact and obtain reproducible results.

- Measurements could only be taken in the compound corner middle lamella in the earlywood. Measurements taken in the earlywood in the middle lamella were almost identical to those taken in the latewood in the middle lamella.
- The resistance decreased as the relative humidity of the chamber increased. The resistance of the S2 layer decreased more rapidly than the middle lamella.

Acknowledgements

Funding for J.L.C.Q. was provided through the Summer Research Experience for Undergraduates (SURE) program as administered by the University of Wisconsin, Madison. The authors acknowledge experimental assistance of Keith Bourne and the contributions of David Eustice of the Forest Products Laboratory machine shop.

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