

Mechanism of Transport Through Wood Cell Wall Polymers

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Abstract- The movement of chemicals through wood is necessary for decay and fastener corrosion to occur in forest products. However, the mechanism responsible for the onset of fastener corrosion and decay in wood is not known. The onset occurs before the formation of free water in wood cavities and aqueous chemical transport would be possible. Here, we propose that the onset mechanism is the hemicelluloses going through a moisture-induced glass transition. As nm-scale regions of mechanically softened hemicelluloses in cell walls percolate, pathways for chemical transport are created. The ability of chemicals to move in cell walls enables fastener corrosion and decay to occur. This mechanism suggests that wood treatments preventing the glass transition of hemicelluloses will inhibit fastener corrosion and wood decay. The identification of this mechanism should accelerate the development of wood treatments to improve forest products durability.

Index Terms- Durability, Fastener Corrosion, Ionic Conduction, Micromechanical Response, Sorption Hysteresis, Water

I. INTRODUCTION

Wood's lack of durability severely limits its potential end uses, wastes resources, and impacts forest management.

It is estimated that 10% of the lumber cut each year is used to replace wood that has decayed or molded in service, [1] costing billions of U.S. dollars per year. [2,3]. A better understanding of the fundamental mechanisms that enable wood degradation will lead to improved treatments to inhibit degradation, increase the value of wood products, and improve utilization of the forest resource. Water is necessary for wood degradation; if wood is kept dry, it can last for centuries [4].

Wood is hygroscopic and its moisture content (MC) is defined as water mass divided by oven-dried wood mass [5]. Traditionally it is believed that at low MC water in wood is bound only to the cell wall polymers. Above a particular MC, called the fiber saturation point (FSP), [6] water begins to exist as "free" (unbound) water in wood cavities like cell lumina. The FSP occurs at roughly 30% MC for many wood species [7].

II. MECHANISM FOR CHEMICAL TRANSPORT IN WOOD CELL WALLS

Despite the dichotomy of bound and free water, the FSP is not the threshold MC for the onset of fastener corrosion and wood decay. Corrosion of embedded metals begins to occur at 15-18% MC, [8-10] and wood decay fungi also act below FSP (Table 1) [11-14]. Movement of chemicals is an important aspect of both fastener corrosion and wood decay. Fastener corrosion is an oxidation/reduction reaction that requires transport of ions to and from the fastener surface. [9, 15, 16] Fig. 1 shows a cellular-level schematic of a fastener embedded in wood. At MC's above the FSP aqueous ion transport to and from the fastener surface could occur through free water in the lumina. However, below the FSP there is no free water and the chemical transport to and from the fastener surface likely occurs at the fastener interface with secondary cell walls and middle lamellae.

Ions also play a critical role in wood decay. The primary decay agents are fungi, which grow by extending filaments, called hyphae, through wood lumina (Fig. 1). As enzymes are too large to enter cell walls, [17-18] fungal enzymes in hyphae produce small diffusible oxidants that depolymerize the cell walls, releasing carbohydrates which diffuse back to the fungal hyphae and are metabolized. The primary decay agents in brown rot decay are diffusible Fenton reagents, Fe²⁺ chelates and H₂O₂. [19,20] White rot decay are thought to also use various diffusible ions such as Mn³⁺ chelates, fatty acid peroxides, and uncharged species. [21,22] Because damage occurs microns below the cell wall surface, [17] chemical transport must occur through the cell wall.

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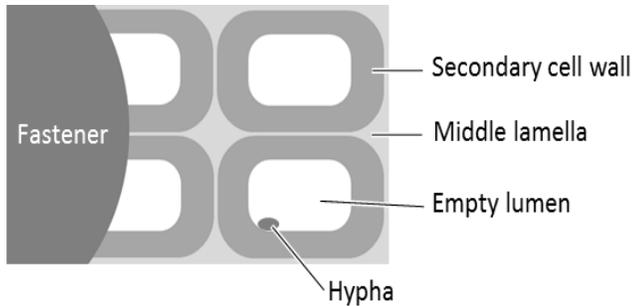


Fig. 1: Schematic of wood cell cross sections next to a fastener and a fungal hypha growing through an empty lumen.

**TABLE I
PROCESSES THAT REQUIRE THE CONDUCTION OF IONS AND OCCUR BELOW FIBER SATURATION**

Phenomena	Moisture content of 1 st appearance	Citations
Ionic Conduction	16%	23
Corrosion	15%-18%	8-10
Wood Decay	20%,23-25% ≥25%	11-14

Ion transport through wood cell walls has been observed below the FSP although the mechanism of transport is not understood. Using radioactive sodium and iodide ions in an electric field, Lin has shown that long range transport begins in wood cell walls at a MC as low as 16% [23]. Also, based on impedance measurements Zelinka et al. recently showed that ionic conduction in wood could be described by a percolation model, where the percolation threshold physically represents the MC at which there is a continuous pathway for ion conduction [24]. When the percolation threshold was set to 16%, based upon the measurement of Lin, the percolation model yielded a good fit to electrical conductivity measurements as a function of MC [25]. We had previously hypothesized that the percolation threshold of ions was related to the so-called “Type II” or “loosely-bound” water found in DSC and NMR measurements which was proposed to solvate ions and facilitate transport [24, 26, 27]. However, we have recently shown that the Type II water visible in DSC experiments is an artifact of sample preparation,[28] and therefore ion conduction is not occurring in “Type II” water.

Here, we hypothesize chemical transport in cell walls below the FSP occurs through interconnecting networks of moisture-softened hemicelluloses, analogous to the hydrophilic phase in ionomers [29]. The secondary cell walls are nano-fiber-reinforced composites of highly oriented, semicrystalline cellulose microfibrils embedded in a matrix of amorphous cellulose, hemicelluloses, and lignin. Within the secondary cell walls hemicelluloses are preferentially oriented with the cellulose microfibrils and form a continuous sheath around the cellulose microfibril [30-32]. Hemicelluloses oriented perpendicular to the cellulose microfibrils has also been proposed [33]. And in the middle lamella, hemicelluloses are

embedded as an irregular, interconnecting network in a matrix of lignin [32]. Under dry conditions, hemicelluloses have glass transition temperatures (T_g) estimated between 150 and 220°C [34-35]. However, moisture plasticization brings the T_g down to room temperature at an estimated 60% relative humidity (RH) for intact hemicelluloses in wood and 80% RH for extracted hemicelluloses [35-37]. In contrast, the glass transition temperature of lignin never drops below ambient temperature even at moisture contents above the FSP [38]. The 60-80% RH range in which the T_g of hemicelluloses drops below ambient conditions corresponds to the MC range leading up to the percolation threshold (11-15% MC) and at which MC moisture-induced structural damage mechanism begins (Table 1). Our recent work studying shape memory effects in wood slivers also supports the primary softening of hemicelluloses occurs in the 60-80% RH range [39].

We illustrate our proposed mechanism for chemical transport in Fig. 2 for both the secondary cell wall and the middle lamella of softwood, noting that the percolation threshold may be different in these two types of cell walls. Briefly, as the cell wall adsorbs moisture, local regions of the hemicelluloses undergo glass transition. As the MC rises, more softened regions exist, and their size increases. Finally, at the percolation threshold, the interconnecting network of softened hemicelluloses is continuous and facilitates chemical transport. Because lignin remains glassy throughout all moisture contents below FSP, it does not contribute to percolation. We also expect that the MC threshold for chemical transport will depend on the size and solubility parameters of the migrating chemical, with larger chemicals having a higher MC threshold than metal ions.

There are many practical and theoretical implications if indeed the softening of the hemicelluloses facilitates chemical transport, and in turn wood degradation, below FSP. Practically, this could lead to new methods of wood preservation in humid environments, with potentially a large economic impact; wood preservation is a 4 billion dollar (USD) industry in the US alone [40]. Instead of incorporating toxic biocides, it may be possible to protect wood by raising the T_g of the hemicelluloses. This would in turn raise the RH threshold for the onset of fastener corrosion and decay. Such a hypothetical preservative could only be suitable for outdoor environments where the MC of the wood would be above FSP if the treatment could completely prevent cell wall chemical transport.

III. CONCLUSIONS

Moisture-induced damage to wood structures, including fungal decay and fastener corrosion, require transport of chemicals. This chemical transport must occur through the cell walls. We propose that above approximately 15% MC, the hemicelluloses' T_g drops below room temperature and interconnecting networks of mechanically softened hemicelluloses percolate within cell walls to facilitate chemical transport. We also propose it is not coincidental that the onset

of ionic conduction occurs at the same MC as fastener corrosion and wood decay. We therefore conclude that treatments engineered to prevent hemicelluloses passing

through their glass transition, and thus preventing chemical transport through wood cell walls, have promise for inhibiting fastener corrosion and wood decay.

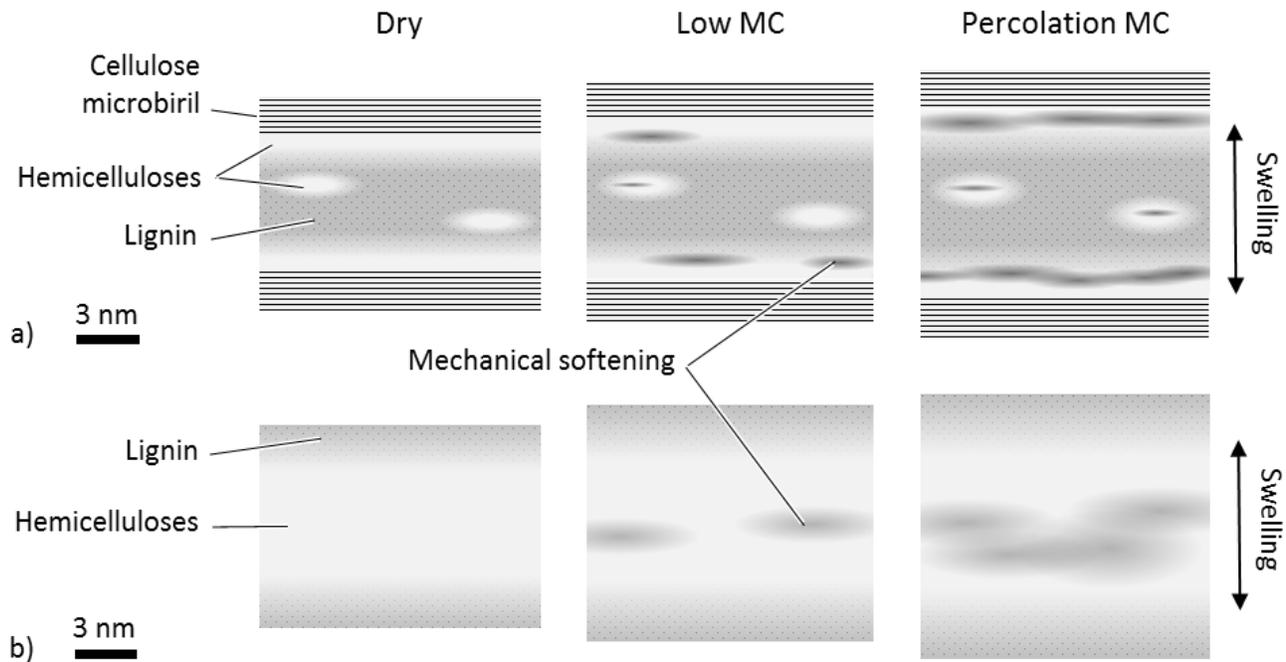


Fig. 2. Hypothesized effect of moisture uptake on ultrastructure of a) secondary cell wall and b) middle lamella

REFERENCES

- [1] J. J. Morrell, "Protection of wood-based materials," in *Handbook of Environmental Degradation of Materials*, M. Kutz, Ed., ed Norwich, NY: William Andrew Publishing, 2005, pp. 299-317.
- [2] D. Mudarri and W. J. Fisk, "Public health and economic impact of dampness and mold," *Indoor Air*, vol. 17, pp. 226-235, 2007.
- [3] V. Yang and C. Clausen, "Inhibitory effect of essential oils on decay fungi and mold growth on wood," presented at the Proceedings of the One Hundred Third Annual Meeting of the American Wood Protection Association, St. Louis, MO, 2007.
- [4] C. Clausen and S. V. Glass, *Build Green: Wood Can Last for Centuries*. Madison, WI: Forest Service, Forest Products Laboratory, General Technical Report, FPL-GTR-215, 2012.
- [5] S. V. Glass and S. L. Zelinka, "Moisture Relations and Physical Properties of Wood," in *Wood Handbook. Wood as an Engineering Material.*, R. J. Ross, Ed., ed: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 2010.
- [6] H. D. Tiemann, *Effect of moisture upon the strength and stiffness of wood. U.S. Department of Agriculture. Forest Service - Bulletin 70*. Washington, D.C.: Government Printing Office, 1906.
- [7] A. J. Stamm, "Review of nine methods for determining the fiber saturation points of wood and wood products," *Wood Science*, vol. 4, pp. 114-128, 1971.
- [8] N. R. Short and J. K. Dennis, "Corrosion resistance of zinc-alloy coated steel in construction industry environments," *Transactions of the Institute of Metal Finishing*, vol. 75, pp. 47-52, 1997.
- [9] A. J. Baker, "Corrosion of metals in preservative-treated wood," in *Wood Protection Techniques and the Use of Treated Wood in Construction*, M. Hamel, Ed., ed Madison, Wisconsin: Forest Products Society, 1988, pp. 99-101.
- [10] J. K. Dennis, *et al.*, "Corrosion behaviour of zinc and zinc alloy coated steel in preservative treated timber," *Transactions of the Institute of Metal Finishing*, vol. 75, pp. 96-101, 1995.
- [11] D. Griffin, "Water potential and wood-decay fungi," *Annual Review of Phytopathology*, vol. 15, pp. 319-329, 1977.
- [12] C. Carll and T. L. Highley, "Decay of wood and wood-based products above ground in buildings," *Journal of Testing and Evaluation*, vol. 27, pp. 150-158, 1999.
- [13] J. Wang and P. I. Morris, "A review on conditions for decay initiation and progression," presented at the International Research Group on Wood Protection, Biarritz France, 2010.
- [14] H. Viitanen and L. Paajanen, "The critical moisture and temperature conditions for the growth of some mould fungi and the brown rot fungus *Coniophora puteana* on wood.," in *International Research Group on Wood Protection*, Madrid, Spain, 1988, p. IRG/WP 1369.
- [15] S. L. Zelinka and D. S. Stone, "Corrosion of metals in wood: Comparing the results of a rapid test method with long-term exposure tests across six wood treatments," *Corrosion Science*, vol. 53, pp. 1708-1714, 2011.
- [16] A. J. Baker, "Corrosion of metal in wood products," in *Durability of Building Materials and Components. ASTM STP 691.*, ed West Conshohocken, PA: American Society for Testing and Materials, 1980, pp. 981-993.
- [17] R. A. Blanchette, *et al.*, "Cell wall alterations in loblolly pine wood decayed by the white-rot fungus, *Ceriporiopsis subvermispora*," *Journal of Biotechnology*, vol. 53, pp. 203-213, 1997.

- [18] D. S. Flourmoy, *et al.*, "Wood decay by brown-rot fungi: changes in pore structure and cell wall volume," *Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood*, vol. 45, pp. 383-388, 1991.
- [19] D. Wei, *et al.*, "Laccase and its role in production of extracellular reactive oxygen species during wood decay by the brown rot basidiomycete *Postia placenta*," *Applied and environmental microbiology*, vol. 76, pp. 2091-2097, 2010.
- [20] P. Baldrian and V. Valášková, "Degradation of cellulose by basidiomycetous fungi," *FEMS microbiology reviews*, vol. 32, pp. 501-521, 2008.
- [21] V. Arantes, *et al.*, "Lignocellulosic polysaccharides and lignin degradation by wood decay fungi: the relevance of nonenzymatic Fenton-based reactions," *Journal of industrial microbiology & biotechnology*, vol. 38, pp. 541-555, 2011.
- [22] K. E. Hammel and D. Cullen, "Role of fungal peroxidases in biological ligninolysis," *Current opinion in plant biology*, vol. 11, pp. 349-355, 2008.
- [23] R. T. Lin, "A study of electrical conduction in wood," State College of Forestry at Syracuse University, 1965.
- [24] S. Zelinka, *et al.*, "A Percolation Model for Electrical Conduction in Wood with Implications for Wood-Water Relations," *Wood and Fiber Science*, vol. 40, pp. 544-552, 2008.
- [25] A. J. Stamm, "The fiber-saturation point of wood as obtained from electrical conductivity measurements," *Industrial and Engineering Chemistry, Analytical Edition*, vol. 1, pp. 94-97, 1929.
- [26] K. Nakamura, *et al.*, "Studies on bound water of cellulose by differential scanning calorimetry," *Textile research journal*, vol. 51, pp. 607-613, 1981.
- [27] L. Thygesen and T. Elder, "Moisture in Untreated, Acetylated, and Furfurylated Norway Spruce Monitored During Drying Below Fiber Saturation Using Time Domain NMR," *Wood and Fiber Science*, vol. 41, pp. 194-200, 2009.
- [28] S. L. Zelinka, *et al.*, "Examination of water phase transitions in Loblolly pine and cell wall components by differential scanning calorimetry," *Thermochimica Acta*, vol. 533, pp. 39-45, 2012.
- [29] J. Li, *et al.*, "The role of water in transport of ionic liquids in polymeric artificial muscle actuators," *Soft Matter*, vol. 5, pp. 2596-2602, 2009.
- [30] M. Åkerholm and L. Salmén, "Interactions between wood polymers studied by dynamic FT-IR spectroscopy," *Polymer*, vol. 42, pp. 963-969, 2001.
- [31] J. S. Stevanic and L. Salmén, "Orientation of the wood polymers in the cell wall of spruce wood fibres," *Holzforschung*, vol. 63, pp. 497-503, 2009.
- [32] J. Hafren, *et al.*, "Ultrastructural changes in the compound middle lamella of *Pinus thunbergii* during lignification and lignin removal," *Holzforschung*, vol. 54, pp. 234-240, 2000.
- [33] N. Terashima, *et al.*, "Nanostructural assembly of cellulose, hemicellulose, and lignin in the middle layer of secondary wall of ginkgo tracheid," *Journal of Wood Science*, vol. 55, pp. 409-416, 2009.
- [34] E. Back and L. Salmen, "Glass transitions of wood components hold implications for molding and pulping processes," *TAPPI J*, vol. 65, pp. 107-110, 1982.
- [35] S. S. Kelley, *et al.*, "Relaxation behaviour of the amorphous components of wood," *Journal of Materials Science*, vol. 22, pp. 617-624, 1987.
- [36] W. Cousins, "Young's modulus of hemicellulose as related to moisture content," *Wood Science and Technology*, vol. 12, pp. 161-167, 1978.
- [37] A. M. Olsson and L. Salmen, "The softening behavior of hemicelluloses related to moisture," 2004.
- [38] W. Cousins, "Elastic modulus of lignin as related to moisture content," *Wood Science and Technology*, vol. 10, pp. 9-17, 1976.
- [39] N. Plaza, *et al.*, "Plant-based torsional actuator with memory," *Smart Materials and Structures*, vol. 22, p. 072001, 2013.
- [40] R. P. Vlosky, "Statistical overview of the U.S. wood preserving industry: 2007" Vancouver, WA: North American Wood Pole Council, 2009.