The Role of Chemical Transport in the Decay Resistance of Modified Wood

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Keywords: diffusion, percolation, glass transition temperature, brown rot decay, hemicelluloses

ABSTRACT

A 2014 review by Ringman *et al*. examined established theories addressing why modified wood has increased decay resistance and concluded that the most probable cause of inhibition and/or delay of the initiation of brown rot decay is lowering the equilibrium moisture content for given environmental conditions. A 2013 paper by Jakes *et al*. examined moisture induced wood damage mechanisms that do not appear in dry wood but have onsets at moisture contents below fibre saturation, including wood decay and fastener corrosion, and observed that these damage mechanisms require chemical transport through wood cell walls. They proposed the mechanism for chemical transport within the wood cell walls was controlled by a moisture induced glass transition in interconnected networks of hemicelluloses and amorphous cellulose. Here we show how these models jointly suggest a mechanism by which wood modifications can inhibit brown rot. Alternative mechanisms are also discussed. These models can be used to understand the performance of modified wood and in the development of new modification systems.

INTRODUCTION

As a building material, wood is unique in that it is a completely renewable resource that can sequester carbon during the life of the building (Falk 2009). Furthermore, wood has an excellent strength to weight ratio and is frequently cited as having a warm, pleasing, appearance (Rice *et al.* 2006). However, the interaction of wood with moisture can cause a host of undesirable consequences that, in-part, limit the usefulness of wood as a building material. When the moisture content within the wood is sufficiently high, it is susceptible to biotic attack and becomes corrosive towards embedded metal fasteners. Furthermore, repeated large changes in the hygroscopic range of wood moisture content cause dimensional instability, which can lead to the formation of splits and checks within the wood and failures at wood-adhesive bond lines. When non-durable wood and wood-based products are selected for an application where it will become repeatedly wet in-service, preservative (biocidal) treatments are frequently specified. These treatments protect the wood by excluding fungi or insects that attack the wood through

repellent, biostatic, or biocidal actions. However, almost all preservative treatments are regulated pesticides, and their use and availability is subject to their ability to maintain their regulation (Lebow 2004). Over the last 50+ years, wood modifications have been developed as a potential alternative to preservative treatments for use when wood will be exposed to damp conditions.

In contrast to preservative treated wood, where biocidal chemicals (mainly heavy metals) are injected into the wood, wood modification changes the wood structure through a chemical, thermal, or thermochemical process to make it less susceptible to degradation. Common wood modification methods include acetylation, furfurylation, cross-linking agents, such as dimethylol dihydroxyethyleneurea (DMDHEU), and several variations of thermal modifications. All of these modifications have been shown to improve the dimensionally stability and the decay resistance of wood. However, there are differences between the treatments in their ability to resist decay (Temiz *et al*. 2006, Rowell *et al.* 2009, Lande *et al.* 2004, Thybring 2013, Verma *et al.* 2009). Several possible mechanisms have been proposed for how wood modifications protect wood (Boonstra *et al*. 2007, Boonstra and Tjeerdsma 2006, Rowell *et al.* 2009, Rowell 2005, Hill *et al.* 2005, Papadopoulos and Hill 2002). Testing these mechanisms and identifying how wood modifications enhance durability are the keys to finding the preferred uses for modified wood as well as refining the modification techniques for optimum performance and cost.

Here we review recent advances in the understanding of brown rot decay in modified wood and a new model for chemical transport in wood. We then discuss potential mechanisms by which decay resistance occurs in modified wood in light of these recent advances. With each potential mechanism, we clearly highlight testable hypotheses so that future work can test these hypotheses. Finally, the paper highlights the most crucial open questions that can be used to determine the mechanisms resulting in the decay resistance of modified wood.

BROWN ROT DECAY RESISTANCE IN MODIFIED WOOD

Brown-rot decay is characterised by significant reductions in strength even at low mass loss. The brown rot degradation process is divided into two parts: i) chelator-mediated Fenton (CMF) degradation, in which hydroxyl radicals depolymerise polysaccharides in addition to modifying lignin, and ii) enzymatic degradation, in which cellulases and hemicellulases hydrolyse the polysaccharides (Goodell *et al.* 1997, Baldrian and Valášková 2008, Arantes *et al*. 2012). Ringman *et al*. (2014) recently conducted a review of theories of how modification imparts decay resistance to wood and presented four different potential mechanisms:

1. There may not be enough easily accessible nutrients, such as hemicelluloses, in the modified wood material to provide energy for initial degradation, since hemicelluloses are degraded or heavily modified in e.g. thermally modified and acetylated wood (Rowell *et al.* 2009, Boonstra *et al.* 2007). It has also been argued that e.g. arabinose is the trigger of wood degradation (Rowell *et al*. 2009). However, Ringman *et al*. pointed out that celluloses and hemicelluloses are degraded by the same mechanisms so if there are no hemicelluloses, the fungi would most probably degrade cellulose instead. Furthermore, this mechanism would not inhibit CMF degradation.
2. The fungal metabolism process may be disrupted by wood modification through modification of the wood polymers so they are unable to be broken down by fungal enzymes (Rowell, 2005). This mechanism also seems unlikely

to be solely responsible for the enhanced durability of modified wood since brown rot fungi are able to break down wood through CMF degradation.

3. Wood modification may close micropores in the wood cell wall preventing enzymes entering the cell wall. However, Hill *et al*. (2005) showed that for acetylated wood, the entire size range of micropores is accessible to CMF degradation agents in highly modified wood even though the total volume of micropores has decreased.
4. Diffusion of fungal CMF degradation agents may be inhibited since wood modification reduces the equilibrium moisture content by decreasing the free volume within the cell wall (Papadopoulos and Hill 2002, Boonstra and Tjeerdsma 2006). Taking the brown rot degradation process into account, Ringman *et al*. (2014) concludes that out of the four established theories, this is the most plausible one. However, mechanisms 2 and 3 may reduce the rate of the enzymatic breakdown.

We next focus on the relationship between wood moisture content and intra-cell-wall diffusion to show how wood modifications may inhibit diffusion at a given moisture content and how by reducing the moisture content generally, there is a reduction in diffusion.

CHEMICAL TRANSPORT IN WOOD CELL WALLS

A mechanism recently proposed to control the onset of decay in wood was the percolation of rubbery regions in hemicelluloses and amorphous cellulose networks that facilitate the necessary transport of CMF degradation chemicals through wood cell walls (Jakes *et al*. 2013). This onset mechanism was developed based on the observations in the literature that:

1. CMF degradation chemical transport must occur through wood cell walls because the onset 20-25% moisture content for wood decay is below fibre saturation (Griffin 1977, Carll and Highley 1999, Viitanen and Paajanen 1988), suggesting free water is not readily present in the wood structure to facilitate chemical transport
2. Hemicelluloses and amorphous cellulose are proposed to form interconnected networks in wood cell walls. In secondary wood cell walls, amorphous cellulose is found within cellulose microfibrils. Glucomannan is mechanically associated with cellulose microfibrils (Åkerholm and Salmén 2001) and may create a sheath around the microfibril (Terashima *et al.* 2009) or even be present within a microfibril (Salmén and Fahlen 2006). Additionally, xylan forms networks both parallel (Stevanic and Salmén 2009) and perpendicular (Terashima *et al*. 2009) to the cellulose microfibrils in secondary wood cell walls. Hemicelluloses are also embedded as an irregular, interconnected network in lignin to form the middle lamella (Hafren *et al*. 2000).
3. The moisture-induced glass transition of hemicelluloses occurs at lower moisture content than wood decay. The range assessed using mechanical spectroscopy is between 60-80% relative humidity (Kelley *et al.* 1987, Cousins 1978, Olsson and Salmén 2004) at room temperature, which corresponds approximately with 11-15% wood moisture content (MC).
4. Ionic conduction in polymers is much higher in the rubbery state above their glass transition than in the glassy state below their glass transition (Ferry 1980).
5. Ionic conduction in wood as a function of moisture content can be fit with a percolation threshold at 16% moisture content (Zelinka *et al.* 2008).

A schematic of the proposed formation of percolated regions of softened hemicelluloses in the secondary cell wall and middle lamella of two adjacent cell walls is shown in Figure 1. An experiment to test the proposed mechanism and effects of moisture on ionic diffusion in wood cell walls was recently developed using synchrotron-based X-ray fluorescence microscopy (Zelinka *et al.* 2015). In these experiments, a sharp concentration gradient of ions was implanted into thin sections of wood and the relative humidity controlled *in situ* during imaging to allow the observation of humidity thresholds for ion diffusion. It was observed that the threshold moisture content for observable diffusion depended on the ion (Cu, Zn, K, or Cl), cell wall layer (S2 or middle lamella), and orientation (longitudinal or. transverse). The threshold for diffusion was found to be as low as 60% RH for K and Cl ions and potentially be as high as 90% RH for Zn ions in the longitudinal direction. This range of humidity corresponds to the proposed 60-80% RH range for the hemicelluloses passing through their moisture-induced glass transition, supporting the theory that percolated networks of rubbery hemicelluloses and amorphous cellulose could be responsible for ion transport through wood cell walls. Additionally, for all experiments a low RH bound was observed over which no ion diffusion could be observed during the experiment (~10 minutes). The difference in onset RH for different ions might relate to size requirements to the diffusion pathways in the percolated network.

The moisture content threshold of the hemicelluloses glass transition observed using mechanical spectroscopy and ion movement in the XFM experiments may not be the same as the onset moisture content for wood decay. It could be that the CMF degradation chemicals require a different moisture threshold for transport through wood cell walls. Or the time scale of the XFM experiments may be different than the relevant time scales in chemical transport in wood decay. Nevertheless, if the relationship between the moisture threshold of ion diffusion in wood cell walls observed with XFM and onset moisture for wood decay can be further substantiated, the XFM experiments would be a valuable to tool to directly predict the efficacy of a wood treatment on decay resistance.

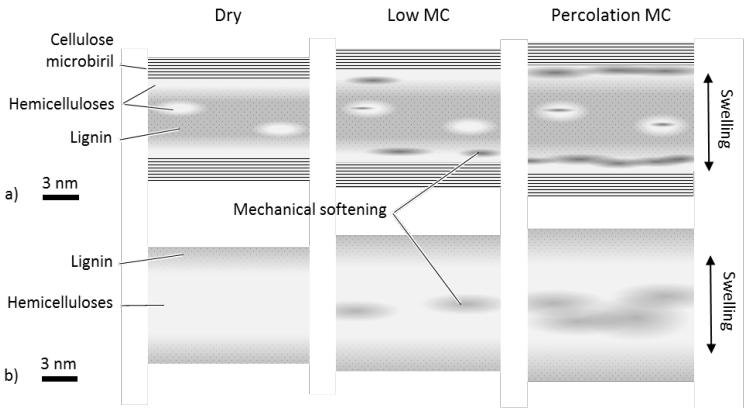

Figure 1: Mechanism of transport proposed by Jakes et al. where transport occurs in interconnected regions of softened hemicelluloses in the (a) S2 layer and (b) middle lamella

DISCUSSION- POTENTIAL MECHANISMS OF DECAY RESISTANCE IN MODIFIED WOOD BASED UPON TRANSPORT THEORIES

In this section we present potential mechanisms by which wood modifications may result in decay resistant wood based upon the recent advances in understanding of brown rot decay and chemical transport in wood presented earlier. Even with these

recent advances, there is not yet enough information to know the exact mechanism. Therefore, we present three potential mechanisms by which modified wood may inhibit brown rot decay. Along with each mechanism, we present testable hypotheses; experiments that can prove or disprove each of these mechanisms.

Transport of fungal CMF degradation agents is inhibited by preventing softening of the hemicelluloses

The percolation model of Zelinka *et al*. (2008) and extended transport model of Jakes *et al*. (2013) both suggest that a threshold moisture content exists below which diffusion of at least some chemical species does not occur. One possible mechanism for the decay resistance of modified wood is that diffusion of CMF degradation compounds are inhibited because the percolation threshold has not been reached. In this case, a percolating network would not be achieved because the hemicelluloses remain in their glass state.

Mechanism of decay resistance

This mechanism provides decay resistance by inhibiting the transport of CMF degradation compounds. Chemical modifications that increase the humidity required for hemicelluloses to pass through a glass transition should improve decay resistance. A modification that prevents a hemicellulose glass transition under water saturated conditions should be an effective wood protection treatment because the initial CMF degradation mechanisms are prevented.

Testable hypotheses of this mechanism

If decay resistance was imparted by inhibiting diffusion by stopping the moisture induced glass transition of the hemicelluoses, then there would be no observable diffusion at high moisture contents and the hemicelluloses would be stiffer than in untreated wood at high moisture contents. Previously, XFM was used to examine the diffusion thresholds for unmodified wood (Zelinka *et al.* 2015); this work could be extended to study whether the threshold moisture content changes in modified wood. Furthermore, *in-situ* measurements of the glass transition temperature of hemicelluloses in unmodified and modified wood across a range of moisture contents could determine if the glass transition moisture content tracked with the diffusion threshold.

Transport of fungal CMF degradation agents is inhibited by preventing percolation

Another possibility is that there is softening of the hemicelluloses, but a percolating network does not form in modified wood. The transport mechanism presented by Jakes *et al*. showed correlation between percolation and the softening of hemicelluloses but did not prove causation. Therefore, it is possible that chemical modifications do not affect the glass transition of hemicelluloses but do prevent percolation and diffusion. In this case, even though the hemicelluloses may have softened, the heavy presence of embedded entities from the modification (e.g. acetyl groups in acetylated wood) may prevent a continuous, percolating network through which diffusion can occur.

Mechanism of decay resistance

In this case, the mechanism of decay resistance is the same as in the previous section; the diffusion of fungal CMF degradation compounds is inhibited. However, in contrast to the previous mechanism, this lack of diffusion is not related to vitrified hemicelluloses, but instead comes from lack of percolation.

Testable hypotheses of this mechanism

Similar to the previous mechanism, testing this mechanism would require testing both whether or not diffusion can occur in modified wood as well as testing whether or not the in-situ glass transition temperature of the hemicelluloses has changed. In this case, diffusion would not be observed, but the hemicelluloses would be softened.

Transport of CMF degradation agents is not inhibited

In unmodified wood, the diffusion threshold (~16% MC) (Zelinka *et al.* 2008) is well below the threshold moisture content at which brown rot decay is first observed (>20% MC) (Carll and Highley 1999, Griffin 1977, Viitanen and Paajanen 1988). Clearly diffusion is a necessary but not sufficient condition for brown rot decay to occur. Furthermore, it is unclear what other changes are occurring to the wood between the percolation threshold and the decay threshold that makes decay possible.

Previous research on modified wood has found linkages between the moisture exclusion efficiency (MEE) and decay resistance across various wood modifications (Thybring 2013) with completely different chemistry and mode of action (bulking, grafting, cross-linking). MEE is a measure at how effectively wood modifications reduce the equilibrium moisture content below fibre saturation. The relationship between MEE and decay resistance for modifications which presumably has a diverse effect on the hemicellulose softening, suggests that decay resistance may be directly controlled by the amount of water inside cell walls, although the exact mechanism is yet unclear.

One possibility is that it is not the diffusion threshold that is important to the fungi, but rather, a minimum rate of diffusion that is needed to produce a favourable decay reaction. In this case, while there may be sufficient moisture to create a percolating system, the diffusion rate is not high enough to sustain the degradation process. In terms of modified wood, it could be that even at the highest possible moisture content within cell wall diffusion is simply too slow for decay to occur (note that this does not exclude the possibility that percolation occurs in modified wood).

Conversely, it is also possible that diffusion is freely able to occur and that the decay resistance of modified wood is caused by an as yet undetermined mechanism that may or may not be related to the wood moisture content. For example, the reactions leading up to the formation of hydroxyl radicals in the CMF degradation are pH sensitive and may therefore be inhibited by the altered pH in some modified wood materials.

Mechanism of decay resistance

In this case, it is unclear the exact mechanism of decay resistance. It could be that while there is diffusion, it is not fast enough to sustain decay, or it could be that the mechanism of decay resistance is not linked to transport.

Testable hypotheses of this mechanism

If diffusion experiments show transport in decay resistant modified wood, then clearly diffusion of fungal agents is not excluded and an alternative mechanism must be responsible for the decay resistance of modified wood.

CONCLUSIONS

In this paper, we discuss newly published findings on chemical transport in wood and brown rot decay in modified woods. These new findings jointly suggest that transport of low molecular weight compounds in wood cell walls play an important role in the decay process and theories of chemical transport suggest some potential mechanisms by

which transport might be inhibited. However, at this stage, there is not enough research to definitively identify the role of chemical transport in the decay resistance of modified wood. Based on the current understanding, we suggest that there are three possibilities: (1) That diffusion is inhibited by making the hemicelluloses glassy at high moisture contents (2) That diffusion is inhibited even though the hemicelluloses are softened because they do not form a percolated network, and (3) That decay resistance is not related to chemical transport. We presented several testable hypotheses to differentiate between these mechanisms with the hope that future research will be able to more clearly identify the mechanism of decay resistance in modified wood.

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Citation:

S. Zelinka, R. Ringman, A. Pilgård, E.E. Thybring, E. Jakes Joseph, K. Richter, The role of chemical transport in the decay resistance of modified wood, in: M. Hughes, L. Rautkari, T. Uimonen, H. Militz, B. Junge (Eds.) Proceedings of the eighth European conference on wood modification, Ålto University School of Chemical Technology, Helsinki, Finland, 2015, pp. 35-43.