 moisture in modified wood and its relevance for fungal decay

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Water plays an essential role in fungal decay of wood, and limiting the cell wall moisture content by chemical modification can effectively improve the durability of the material. Investigating the wood-water relations of modified material under climatic conditions relevant for fungal decay are, however, experimentally challenging. Most studies in literature therefore focus on moisture sorption under conditions outside those of importance for fungal decay. This review discusses the validity of such data for characterising the wood-water relations at very humid climatic conditions, relevant for fungal decay. Moreover, the review attempts to cover the basics of fungal decay, the important role of water, and how controlling water content by modification can improve durability.

Keywords: Modification, Wood, Moisture, Experimental Techniques

Introduction

Some of the most widespread, economically important, and devastating wood-decaying organisms are basidiomycetes fungi (Viitanen & Ritschkoff 1991, Duncan & Lombard 1965, Alfredsen et al. 2005, Schmidt 2007). A lot of research is therefore dedicated to understand their degradation mechanisms and the basic conditions necessary for decay (Alfredsen et al. 2013, Thybring 2013, 2017, Ringman et al. 2014a, 2014b, 2017, Zelinka et al. 2016b, Kirker et al. 2017, Ommondroyd et al. 2017), in order to prevent fungal attack of wood. Protection of wood structures has traditionally been accomplished by using toxic preservatives, i.e., fungicides, but environmental concerns and restrictions of their use have increased the focus on non-toxic alternatives such as chemical modification (Hill 2006). A large number of physico-chemical modification processes exist aimed at improving various aspects of the performance of wood materials. In this review, the focus is on modifications targeting an improved durability, and how their performance is linked to wood-water relations of the modified material. Recent years have seen several new findings regarding the protection mechanism, and this review attempts to cover both the basics of fungal decay, the important role of water, and how controlling water content by modification can improve durability.

Fungal decay mechanisms and the importance of water

Fungi employ enzymes for the conversion of cell wall polymers into smaller fragments which can be consumed. However, as cell wall pores, even in the water-saturated state, are too small for enzymes to enter (Srebotnik et al. 1988, Daniel et al. 1989, 1990, 2004), fungi break up cell walls by oxidative action (Cragg et al. 2015). While fungi classified as white-rot fungi rely on enzymes for this task (Vaalje-Kolstad et al. 2010, Horii et al. 2013, Riley et al. 2014), another class of fungi termed brown-rot fungi have evolved a non-enzymatic strategy based on Fenton chemistry to disrupt cell walls in the initial stage of attack (Goodell et al. 1997, Xu & Goodell 2001, Halliwell 2003, Arantes & Milagres 2007, Hastrup et al. 2013, Schilling et al. 2013, Ringman et al. 2014a, Zhang et al. 2016). It is speculated that through transportation of chelated iron ions into wood cell walls and reaction of these with hydrogen peroxide, brown-rot fungi create highly reactive free radicals which disrupt chemical bonds of the cell wall constituents. This mechanism can work at a distance of several microns from the fungi to create pathways within cell walls, through which the lignocellulosic enzymes can penetrate (Grethlein et al. 1984, Grethlein 1985, Wong et al. 1988, Arantes & Milagres 2007, Arantes et al. 2011, Ringman et al. 2014a, Hosseinporuia & Mai 2016). That such a combination of non-enzymatic and enzymatic degradation machinery is effective is apparent from the high relative occurrence (73-85 %) of brown-rot in decaying wooden structures compared with white-rot decay (Duncan & Lombard 1965, Viitanen & Ritschkoff 1991, Alfredsen et al. 2005, Schmidt 2007).

A prerequisite for fungal decay is sufficient ambient temperature and moisture conditions of the wood. Being a hygroscopic material, wood can absorb/desorb and exchange water molecules with the surrounding air. Water in wood, often termed moisture, can be found both within cell walls as bound water and outside cell walls in the void wood structure (pits, lumens, vessels, etc.) as capillary water or vapour (Engelund et al. 2013). The moisture distribution between cell walls and voids depends on the climatic conditions. Thus, for relative humidity (RH) levels up to about 97-98 %, the moisture content in equilibrium with the ambient RH is dominated by bound water (Engelund et al. 2010). However, as the RH approaches saturation (100% RH) the contribution from capillary water held in the void structure becomes significant and eventually dominates the moisture content at very high (>99 %) RH (Stone & Scallan 1967, Griffin 1977, Fortin 1979, Cloutier & Fortin 1991, Almeida & Hernandez 2006, Almeida & Hernandez 2007, Fredriksson et al. 2013, Fredriksson & Johansson 2016). In line with common practice within building materials research, the RH-range from 6% to 97-98 %...
is in this review referred to as “hygroscopic” and the range above as “over-hygroscopic” (see Fig. 1).

It is often assumed that liquid water, e.g., capillary water in the wood void structure, should be available for fungal decay to be possible (Kirk & Cowling 1984, Schmidt 2007). While it is evident that fungal decay is only relevant at high RH (Fig. 1) and that in general wood moisture contents of 40–70 % are most favourable for decay (Vitainen & Ritschkoff 1991), the essential presence of capillary water is questionable. For instance, the lowest RH capable of supporting brown-rot decay is around 92–97 % RH (Griffin 1977, Clarke et al. 1980, Vitainen 1997, Schmidt 2007), the exact threshold depending on temperature and fungal species (Vitainen 1997). Wood in equilibrium with this level of RH only contains minuscule amounts of capillary water that is found in pores smaller than 70 nm. For Norway spruce, this amount of water outside cell walls is of the order of 10 µg water per gram wood (Engelund et al. 2010). The question of whether capillary water is essential for fungal decay is, however, obscured by experimental limitations. It is difficult to maintain a stable climate above 97 % RH (Griffin 1977), and studies of moisture in wood in the over-hygroscopic regime therefore requires special techniques, e.g., pressure plate. For this reason, studies on the effect of initial wood moisture conditions on fungal decay often employ wood specimens exposed to liquid water and perhaps partially dried to specific wood moisture contents (Peterson & Cowling 1973). This inevitably causes moisture gradients in the specimens, but further complications arise with controlling the moisture conditions during decay tests (Ammer 1964). During such tests both the hygroscopicity of the material changes (Buro 1954, Ammer 1963, Schulze-Dewitz et al. 1969, Winandy & Morrell 1993, Anagnost & Smith 1997), and the amount of water increases due to fungal respiration (Mez 1908, Hoffmann 1910, Lehmann & Scheible 1923, Weigl & Ziegler 1960, Thybring 2017). These issues of lack of climate control and changes in the substrate during the tests seriously complicate the interpretation of the limiting moisture conditions for decay.

**Improving durability by chemical modification**

Since sufficient moisture conditions are central to fungal decay, it has long been recognised that durability can be obtained by keeping wood dry (Levi 1973, Kirk & Cowling 1984, Clausen & Glass 2012). However, for some applications keeping wood dry is impossible, e.g., under direct exposure to rain or in very humid environments. In these cases, alternative strategies are needed to avoid fungal decay. While traditional wood protection depends on toxic preservatives, chemical modification improves the durability the modified material by non-toxic means. The exact mechanisms behind the increased resistance to fungal decay observed for several kinds of chemical modification are not fully clear, but it is undoubtedly linked with reductions in the moisture content of cell walls (Thybring 2013). Thus, even at high moisture contents where fungal decay of untreated wood is possible, modified wood can be decay resistant (Cardias 1992, Forster 1998, Farahani 2003, Williams & Hale 2003, Hill et al. 2006, Thybring 2017). This illustrates that the total amount of water available to fungi is not a predictor of the potential for wood decay as sufficient cell wall moisture content needs to be present as already speculated a century ago (Zeller 1926).

As described previously, investigating the wood-water relations in the over-hygroscopic regime, relevant for fungal decay, is challenging. Therefore, the vast majority of studies of wood-water relations for modified wood focus on the over-hygroscopic range, while the over-hygroscopic range is only covered in two studies on modified wood (Thygesen et al. 2010, Zauer et al. 2016) and few more for unmodified wood (Stone & Scallan 1967, Griffin 1977, Fortin 1979, Cloutier & Fortin 1991, Almeida & Hernandez 2006, Almeida & Hernandez 2007, Fredriksson et al. 2013, Fredriksson & Jønsson 2016, Zelinka et al. 2016a). This raises the important question of whether observations about wood-water relations in the hygroscopic range are valid for the over-hygroscopic range as well. For instance, Thybring (2013) found a common moisture threshold for decay in several different types of modified wood, where a reduction of about 40 % in moisture content at similar hygroscopic RH conditions (in the range 30-90 %) was found to correlate with resistance to fungal decay across widely different modifications. One exception is thermally modified wood which is not fully decay resistant (Kamdem et al. 2002, Welzbacher & Rapp 2007, Kymäläinen et al. 2015), despite a 40 % reduction in moisture content under hygroscopic conditions. This illustrates the need for determining wood-water relations at moisture conditions relevant for fungal decay (Fig. 1).

**Potential mechanisms for improved durability of modified wood towards brown-rot decay**

It is apparent that the durability of wood can be improved by reducing the cell wall moisture content through modification, but the actual mechanism of protection has not yet been resolved. In a recent review, Zelinka et al. (2016b) discuss the potential mechanisms behind decay resistance from modification based on the observation by Zelinka et al. (2015) that ions within cell walls have a threshold moisture content below which they cannot diffuse. Ion transport in wood has been linked with the formation of a continuous network of cell wall water (a percolation threshold – Zelinka et al. 2008, Zelinka & Glass 2010, Jakes et al. 2015), and limiting the cell wall moisture might prevent the formation of such a network, hereby disrupting the physical pathways for transport of solutes. As the initial stage of brown-rot attack involves the transport of ions into cell walls
(Kirker et al. 2017), it seems reasonable that the formation of a continuous water-swollen porosity of sufficient pore size is a prerequisite for this transport. Hosseinpourpia & Mai (2016a, 2016b, 2016c) have conducted a series of experiments where modified wood veneers are exposed sequentially to solutions of iron ions and hydroxide peroxide, mimicking the oxidative Fenton chemistry of brown-rot fungi. Their results show that for acetylated and pheno-formaldehyde modified wood, hydroxide peroxide is not consumed in a solution with iron ions and modified wood after 48 hours of exposure given that the modification intensity (WPG) is high enough (Hosseinpourpia & Mai 2016a, 2016b). Moreover, controls of modified wood of adequately high WPG exposed only to the iron ion solution did not take up iron during the 48 hour experiment. The threshold WPG in both cases was consistent with the 17-20 % WPG reported for acetylated exposed in laboratory and field tests (Peterson & Thomas 1978, Kumar & Agarwal 1983, Tahakashi et al. 1989, Beckers et al. 1994, Breid et al. 2000, Papadopoulos & Hill 2002, Mohrhy 2003, Hill et al. 2006, Papadopoulos 2006, Breid & Westin 2007, Hill et al. 2009). For thermally modified wood, the uptake of iron ions and consumption of hydroxide peroxide was markedly reduced during the 48 hour exposure time for wood of high modification intensity (Hosseinpourpia & Mai 2016c), but no threshold was found. This indicates that solute transport is slowed but not hindered in thermally modified wood, since fungal agents presumably can be transported in the micro-porosity created as cell wall material is lost during modification (Kymäläinen et al. 2014, Kymäläinen et al. 2015). If the pore size is sufficiently large, enzymes may even be transported into the cell walls. This is seen for pretreated wood material where the water-swollen volume in cell walls accessible to 5.1 nm probe molecules correlates linearly with hydrolysis yield (Grethlein et al. 1984, Grethlein 1985, Wong et al. 1988). Perhaps the durability of thermally modified wood could be optimised further if the created micro-porosity could be tuned. This would require detailed investigations of the cell wall micro-porosity in thermally modified wood, and how processing conditions potentially affect it.

**Conclusion**

Water plays an essential role in fungal decay of wood, and limiting the cell wall moisture content by chemical modification can effectively improve the durability of the material. Investigations of the wood-water relations under climatic conditions relevant for fungal decay are, however, difficult, and thus many studies focus on the relative humidity (RH) range below 95 %. While the cell wall moisture content in the over-hygroscopic range (> 98 % RH) is underesti- mated by extrapolation of data obtained below 95 % RH, the relative reductions in cell wall moisture content appear similar for acetylated wood. This might not be the case for other types of modification.

Reductions in cell wall moisture content are thought to prevent fungal decay by hindering transport of fungal agents into the cell walls, presumably from a disruption of the continuous water network within cell walls otherwise found in untreated wood at high moisture contents.

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**References**


