DOI 10.1515/hf-2013-0057 — Holzforschung 2014; 68(2): 239–246

Review

Rebecka Ringman*, Annica Pilgård, Christian Brischke and Klaus Richter

Mode of action of brown rot decay resistance in modified wood: a review

Abstract: Chemically or physically modified wood materials have enhanced resistance to wood decay fungi. In contrast to treatments with traditional wood preservatives, where the resistance is caused mainly by the toxicity of the chemicals added, little is known about the mode of action of nontoxic wood modification methods. This study reviews established theories related to resistance in acetylated, furfurylated, dimethylol dihydroxyethyleneurea-treated, and thermally modified wood. The main conclusion is that only one theory provides a consistent explanation for the initial inhibition of brown rot degradation in modified wood, that is, moisture exclusion via the reduction of cell wall voids. Other proposed mechanisms, such as enzyme nonrecognition, micropore blocking, and reducing the number of free hydroxyl groups, may reduce the degradation rate when cell wall water uptake is no longer impeded.

Keywords: acetylated wood, basidiomycetes fungi, DMDHEU-treated wood, furfurylated wood, mode of action, thermally modified wood

***Corresponding author: Rebecka Ringman,** SP Technical Research Institute of Sweden, Wood Technology, Box 857, SE-501 15 Borås, Sweden, e-mail: rebecka.ringman@sp.se
Annica Pilgård: SP Technical Research Institute of Sweden, Borås, Sweden; and Technische Universität München, München, Germany
Christian Brischke: Leibniz University Hannover, Hannover, Germany
Klaus Richter: Technische Universität München, München, Germany

Introduction

At present, the use of traditional toxic wood preservatives is being questioned and their application is restricted (Hingston et al. 2001; Ibach 2005; Townsend et al. 2005). As alternatives to these preservatives, wood can be modified by nontoxic chemicals and/or by physical treatments (Hill 2006). The optimization of processes and product properties could be further improved by a better understanding of the underlying mechanisms of inhibition or delay of biological degradation after nontoxic modifications. Decay resistance has been reviewed independently for acetylated wood (Papadopoulos 2010) and thermally modified wood (Esteves and Pereira 2009) as well as in a combined review (Rowell et al. 2009). Previous research concerning the degradation of cellulose by brown rot fungi was summarized by Baldrian and Valaskova (2008). Aro et al. (2005) reviewed the transcriptional regulation of enzymes involved in the breakdown of cell wall biopolymers by filamentous fungi. The biochemical mechanisms that underlie nonenzymatic degradation of wood were recently summarized in a comprehensive review (Arantes et al. 2012). However, general comparative reviews are not available in terms of the modes of action of different wood modification methods. In particular, only a few studies are dealing with the biochemical mechanisms of decay resistance in modified woods.

Thus, the present review attempts a comparative evaluation of established theories related to the mode of action of brown rot fungi resistance in modified woods with biochemical mechanisms in focus. The following modifications are considered: acetylated wood (Militz 1991; Larsson Brelid et al. 2000), furfurylated wood (Schneider 1995; Westin 1996; Lande et al. 2008; Bryne and Wålinder 2010; Thygesen et al. 2010), dimethylol dihydroxyethyleneurea (DMDHEU)-treated wood (Militz 1993; Dieste et al. 2009b), and thermally modified wood (Tjeerdsma et al. 1998; Welzbacher 2007; Windeisen et al. 2009; Pfriem et al. 2010).

Degradation of wood by brown rot

Brown rot wood degradation has been studied mainly based on *Gloeophyllum trabeum*, although some mechanisms have also been confirmed in *Postia placenta*, *Serpula lacrymans*, and others (Goodell et al. 1997; Shimokawa et al. 2004; Martinez et al. 2009). Differences between species have also been reported, which support the theory of the repeated evolution of brown rot fungi from white rot fungi (Green and Highley 1996; Hibbett and Donoghue 2001; Niemenmaa et al. 2008; Kang et al. 2009).

Degradation of polysaccharides

Details of polysaccharide degradation by brown rot are summarized in Figure 1, which is based mainly on studies by Goodell et al. (1997), Baldrian and Valaskova (2008), and Arantes et al. (2012). Brown rot fungi degrade polysaccharides via oxidative and enzymatic activities (Eriksson et al. 1990; Eaton and Hale 1993; Goodell 2003; Aro et al. 2005; Fackler et al. 2010). The fungus induces the production of hydroxyl radicals within the polymer matrix by the secretion of reductants and hydrogen peroxide (Goodell et al. 1997). The reductants reduce ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}), which reacts with hydrogen peroxide to produce hydroxyl radicals via the Fenton reaction (Fenton 1894). The hydroxyl radicals then depolymerize hemicelluloses and cellulose and modify lignin (Halliwell 1965; Cohen et al. 2002; Kaneko et al. 2005). During these reactions, microcapillary pathways are generated so that hydrolyzing enzymes, which are too large to penetrate the intact wood cell wall, can diffuse into the previously damaged matrix. In this way, the degradation of polysaccharides is initiated, in the course of which oligomers, dimers, and monomers via enzymatic hydrolysis arise. Enzymatic degradation, which becomes noticeable by compositional changes, can be detected only in the advanced state of the decay process (Fackler et al. 2010).

The first signs of brown rot decay are visible in the outer regions of the cell wall, that is, in the middle lamella, S1, and the outer parts of S2 (Irbe et al. 2006; Fackler et al. 2010). The S3 layer remains intact throughout the early stages of decay, which contributes to the limited permeability of enzymes into the S2 layer (Highley et al. 1985; Eriksson et al. 1990; Kleman-Leyer et al. 1992). The formation of hydroxyl radicals only inside the wood cell wall and the delayed degradation of the S3 layer may protect the hyphae from oxidative injuries.

Hemicelluloses surround the cellulose fibrils (Zabel and Morell 1992) and they are amorphous compared with to the mainly crystalline cellulose. Their higher accessibility is the reason why hemicelluloses are degraded before cellulose (Curling et al. 2002; Irbe et al. 2006; Fackler et al. 2010).

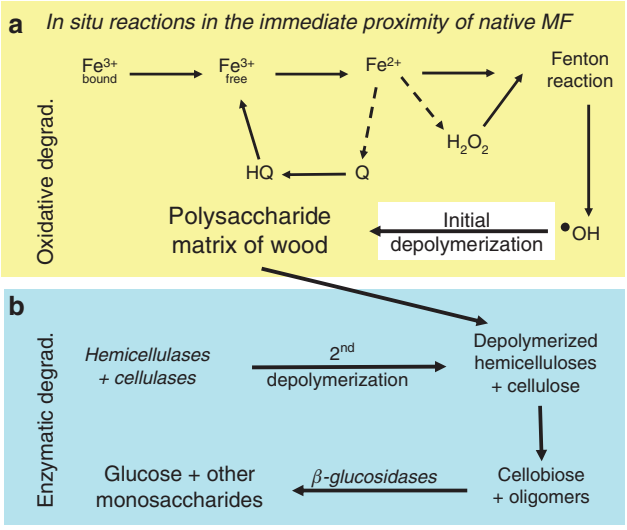

Figure 1 Polysaccharide degradation in untreated wood. Based on Goodell et al. (1997), Arantes et al. (2012), and Baldrian and Valaskova (2008). HQ, hydroquinone; MF, microfibrils; Q, quinone.

Oxidation of lignin

Brown rot fungi circumvent lignin mineralization and degrade the polysaccharides in a straightforward manner (Koenig et al. 2010; Martinez et al. 2011). Lignins maintain their macromolecular nature throughout brown rot decay (Kirk 1975; Niemenmaa et al. 2008; Yelle et al. 2008), but their structure is modified substantially by hydroxyl radicals (Yelle et al. 2008, 2011; Arantes et al. 2009, 2011; Martinez et al. 2011). This can be detected in the outer parts of the cell wall based on increases in the carbonyl group content and demethylation (Eriksson et al. 1990; Filley et al. 2002; Fackler et al. 2010). Lignin modification contributes to the formation of microcapillary pathways that allow enzymes to penetrate the wood cell wall (Arantes et al. 2012). It has been suggested that fragments of oxidatively remodeled lignin in brown-rotted wood may contribute to the formation of hydroxyl radicals (Xu and Goodell 2001; Filley et al. 2002; Goodell et al. 2006) as an integral part of the redox processes. The strong relationship between lignin demethylation and polysaccharide degradation suggests that these processes are mechanistically interlinked (Filley et al. 2002). However, no water-soluble lignin products with Fe^{3+}-reducing activities have been detected in brown rotted wood (Aguiar et al. 2013).

Mode of action theories from a biochemical perspective

Table 1 provides an overview of established theories related to the protective effects of wood modification. Despite the higher decay resistance of modified wood, these modifications do not inhibit the expression of the fungal genes required for degradation. Alfredsen and Fossdal (2010) showed that genes encoding enzymes involved in oxidative degradation are expressed at higher

Table 1 Theoretical modes of action of brown rot decay resistance in modified wood.

Mode of action	Principle of action	Proposed mechanism	References
Biochemical	Unavailability of easily accessible nutrients	Lack of easily accessible nutrients, such as hemicelluloses, and this prevents cellulose from fungal decay.	Boonstra et al. 2007; Rowell et al. 2009
	Enzyme nonrecognition	Wood polymers are modified in such a way that fungal enzymes no longer recognize them; therefore, enzymatic hydrolysis is not possible.	Rowell 2005
Physical	Micropore blocking	Micropores in the cell wall are blocked, so that fungal reductants and enzymes penetrate the cell wall at a slower rate.	Hill et al. 2005
	Moisture exclusion		
	OH-group blocking/ reduction	OH-groups in the cell wall are blocked or hindered, so that less water binding sites are available, which leads to a less efficient hydrolysis of polysaccharides.	Rowell et al. 2009
	Reduction in void volume	The amount of free water in the cell wall is diminished through bulking of voids by chemicals or by reduction of void sizes, so that diffusion of fungal reductants and enzymes is impeded.	Papadopoulos and Hill 2002; Boonstra and Tjeerdsma 2006

levels in furfurylated wood than in untreated one. Pilgård et al. (2012) reported similar findings for acetylated wood. However, it is not known whether these genes are translated into proteins that can induce the formation of hydroxyl radicals in the wood cell wall.

Role of accessible nutrients

As pointed out above, brown rot fungi degrade hemicelluloses before cellulose (Militz 2002; Weiland and Guyonnet 2003; Rowell et al. 2009) and this order of degradation is considered by many investigators to be a key step (Boonstra et al. 2007; Rowell et al. 2009). Rowell et al. (2009) proposed that arabinose, which is the only L-pentose sugar found in wood, is a key compound that triggers the chain reactions of degradation and that its absence would prevent the initiation of degradation. Indeed, most hemicelluloses are degraded in thermally modified wood (Boonstra et al. 2007) and hemicelluloses are considerably modified by acetyl groups in acetylated wood (Rowell et al. 2009).

However, the biochemical mechanism of brown rot does not support this theory. Hemicelluloses are degraded in the same manner as cellulose; oxidative degradation occurs, which is mediated by hydroxyl radicals followed by enzymatic hydrolysis (Arantes and Milagres 2006; Fackler et al. 2010; Arantes et al. 2011). Cellulases are constitutively expressed at a low level and are up-regulated when the fungus starts to metabolize any type of sugar (Aro et al. 2005), which shows that the degradation of hemicelluloses is not necessary for the expression of cellulases. It seems unlikely that a microorganism would not degrade one particular nutrient in the absence of another one. Most microorganisms, including fungi, can degrade many different types of nutrient sources (Wainwright 1988).

Nonrecognition of substrates by enzymes

Rowell (2005) proposed that fungal enzymes are unable to recognize their substrates in modified wood (Figure 2A). This theory may be supported by the fact that hemicellulases and cellulases are less efficient in thermally modified, DMDHEU-treated, and furfurylated wood (Lekounougou et al. 2008; Venås 2008; Verma and Mai 2010). Their action is, however, not inhibited. Furthermore, the nonspecific oxidative degradation that precedes enzymatic degradation is highly effective even without enzymatic hydrolysis (Verma and Mai 2010). Thus, this theory does not provide an explanation for the initial inhibition of oxidative degradation.

Blocking of micropores

Hill et al. (2004) suggested that a decrease in the micropore size might reduce the rate of diffusion into the wood cell wall by fungal reductants. The bulking effect caused by acetylation and DMDHEU treatment has been shown to reduce the size of micropores (Hill et al. 2004; Dieste et al. 2009b).

However, this theory does not explain the initial inhibition of decay, because micropore blocking can only reduce rate of diffusion of fungal reductants rather than inhibit their diffusion (Hill et al. 2005). Thus, micropore

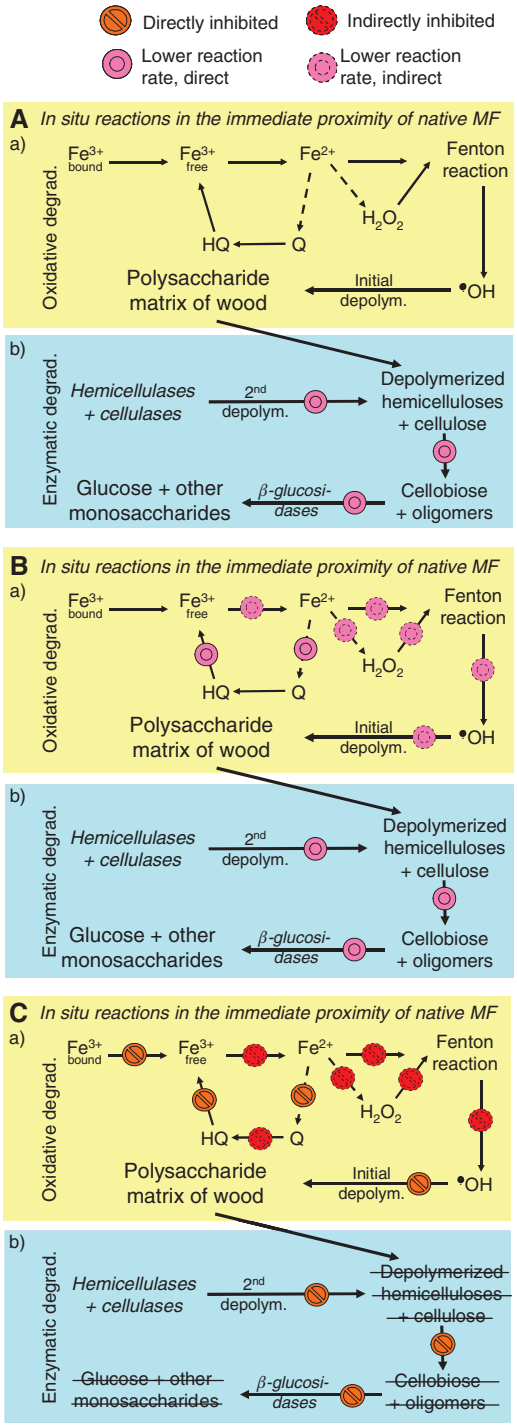

Figure 2 Illustration of the effects of different mechanisms of brown rot decay resistance wood polysaccharide degradation as described in Table 1.
(A) Enzyme nonrecognition and moisture exclusion due to the reduced availability of free OH-groups. (B) Micropore blocking. (C) Moisture exclusion by reducing of the cell wall void volume.

blocking will only slow down oxidative degradation and the formation of the microcapillary pathways required for enzyme diffusion and subsequent hydrolysis (Figure 2B).

Exclusion of moisture via the reduction of accessible OH-groups

It has been suggested that the reduced availability of water binding sites may lead to a lower equilibrium moisture content (EMC) observed in modified wood (Rowell et al. 2009). The same authors have also proposed that a lack of water bound to OH-groups may impede the hydrolysis of glycosidic bonds and the subsequent formation of cellobiose and monomeric sugars.

OH-groups are blocked by acetylation and reduced in number by thermal modification because of the loss of hemicelluloses (Phuong et al. 2007; Rowell et al. 2009). However, Hill et al. (2005, 2009) and Papadopoulos and Hill (2002) showed that the number of OH-groups blocked in acetylated wood do not correlate with decay resistance. Accordingly, the loss of hemicelluloses from thermally modified wood does not correlate with decay resistance (Hakkou et al. 2006; Welzbacher 2007). The number of available (free) OH-groups is increased in DMDHEU-treated wood, which supports the subordinate role of free OH-groups in decay resistance (Dieste et al. 2009a). The loss of water from glycosidic bonds may reduce the efficiency of fungal hydrolases but not completely inhibit it (Lekounougou et al. 2008; Venås 2008; Verma and Mai 2010). Furthermore, oxidative degradation would not be affected.

Exclusion of moisture through decrease in cell wall void volume

Reduction in the wood cell wall void volume may mean that there is insufficient water inside the wood cell wall to allow diffusion (Papadopoulos and Hill 2002; Rapp et al. 2008). If fungal reductants, hydrogen peroxide, and oxalic acid cannot diffuse into the wood cell wall, hydroxyl radicals will not be formed and oxidative degradation will not occur.

The bulking effect of acetylation leads to a reduced EMC (Ibach and Rowell 2000; Papadopoulos and Hill 2003). The correlation between weight percent gain and decay resistance was unambiguous in Corsican pine (*Pinus nigra*), whereas the results were less clear or even contradictory in a number of other wood species (Hill et al. 2004, 2009; Hill 2009). The more even distribution of acetyl groups in Corsican pine may explain the effectiveness of decay prevention (Habu et al. 2006) compared with Scots pine investigated by Hill et al. (2004, 2009). Crosslinking in thermally treated wood reduces the swelling capacity and lowers EMC, which correlates

well with decay resistance (Hakkou et al. 2006; Rapp et al. 2008). After the heat-induced cross-linking was disrupted by treatment with KOH, EMC and decay resistance declined to the levels found in untreated wood (Rapp et al. 2008). The bulking effect and the subsequent exclusion of moisture from the smaller voids are most important for the decay resistance caused by DMDHEU modification (Dieste et al. 2009a,b). Reducing of the void volume via bulking is a possible explanation for the increased decay resistance in furfurylated wood (Venås 2008).

The theory of moisture exclusion by reducing the void volume may explain the inhibition of oxidative and enzymatic degradation (Figure 2C). Furthermore, it explains the delayed but eventual onset of degradation, because the EMC will increase with time due to moisture uptake from the surrounding air via mall cracks and voids in the wood cell wall (Welzbacher and Rapp 2004; Thygesen et al. 2010).

Proposed mechanism

No degradation occurs during the first contact between brown rot fungi and modified wood. Brown rot fungi colonize modified wood only when sufficient water has accumulated in the lumen. The fungi secrete reductants, hydrogen peroxide, and oxalic acid, but they are unable to diffuse into the cell wall matrix due to lack of water for diffusion. Thus, hydroxyl radicals cannot be formed and oxidative degradation does not occur (Figure 2Ca). The reductants can diffuse only if the cell walls lose their ability to resist water uptake. This process may be slowed down because of micropore blocking (Figure 2Ba). Hydroxyl radicals are formed that react with hemicelluloses and lignin. After the hemicelluloses have been degraded sufficiently to expose the cellulose, the hydroxyl radicals start to depolymerize the cellulose, beginning with its paracrystalline moieties. Lignin modification by hydroxyl radicals facilitates the penetration of hydrolyzing enzymes.

The rate of the enzymatic hydrolysis of hemicelluloses and cellulose may be lower than that in untreated wood because of three reasons: (1) micropore blocking leads to a slower rate of enzyme diffusion into the wood cell wall (Figure 2Bb); (2) the lack of water bound to OH-groups decreases the enzyme efficiency (Figure 2Ab); and (3) the recognition of modified polysaccharides by enzymes is hindered (Figure 2Ab). In summary, moisture exclusion delays the onset of degradation, and micropore blocking, insufficient amounts of water bound to OH-groups, and enzyme nonrecognition slow down degradation after its initiation.

Discussion and conclusions

This review considers only brown rot fungi and four types of modification. Different mechanisms may apply to white rot fungi. The mechanisms of fungal degradation are known to be species specific (Green and Highley 1996; Niemenmaa et al. 2008; Kang et al. 2009) as well as dependent on the growth medium and wood species attacked (Tomberg and Olsson 2002; Vanden Wymelenberg et al. 2011). The multitude of wood modification methods and the different methods for evaluating fungal decay also aggravates a comparative evaluation and general conclusions. However, focusing on EMC and mass loss (ML) during decay may facilitate comparisons of different mechanisms. Standardized decay tests, which are designed to assess the durability of wood products, may also pose problems. First, they give an illusion of a threshold level that will prevent decay, but the "threshold" will change if the decay test is run for a longer time (Hill et al. 2009). Second, decay test standards (the European standards EN 113 (1996) and EN 252 (1989) and the American standard ASTM E10) accept a level of treatment that results in a ML of 3%, but this can be misleading. A ML of 3% might be a critical limit for determining the durability of a certain type of wood material, but it is not helpful for evaluating the protective mechanism (Brischke et al. 2008). Third, standardized decay tests for assessing the durability of modified wood were originally designed for testing preservative treated wood. Environmental conditions, such as wetness, are less important for the durability of preservative treated woods than in case of modified woods (Junga and Militz 2005; Meyer et al. 2012).

The present evaluation of theories related to the mode of action of brown rot decay resistance with four types of wood modification suggests that moisture exclusion caused by reductions in the wood cell wall void volume is the most essential parameter that delays the onset of wood decay. Other mechanisms, such as enzyme nonrecognition, micropore blocking, and reduced number of free OH-groups, probably affect the degradation speed after water uptake is initiated.

Acknowledgments: The authors gratefully acknowledge financial support from The Swedish Research Council Formas 213-2011-1481 and Gry Alfredsen for useful discussions.

Received April 2, 2013; accepted July 23, 2013; previously published online August 15, 2013

References

Alfredsen, G., Fossdal, C.G. (2010) *Postia placenta* gene expression during growth in furfurylated wood. IRG/WP 10-10734. In: Proceedings, International Research Group on Wood Protection, 9–13 May, Biarritz, France.

Aguiar, A., Gavioli, D., Ferraz, A. (2013) Extracellular activities and wood component losses during *Pinus tadea* biodegradation by the brown-rot fungus *Gloeophyllum trabeum*. Int. Biodeter. Biodegr. 82:187–197.

Arantes, V., Milagres, A.M. (2006) Degradation of cellulosic and hemicellulosic substrates using a chelator-mediated Fenton reaction. J. Chem. Tech. Biotechnol. 81:413–419.

Arantes, V., Qian, Y., Kelley, S.S., Milagres, A.M.F., Filley, T.R., Jellison, J., Goodell, B. (2009) Biomimetic oxidative treatment of spruce wood studied by pyrolysis-molecular beam mass spectrometry coupled with multivariate analysis and ^{13}C-labeled tetramethylammonium hydroxide thermochemolysis: implications for fungal degradation of wood. J. Biol. Inorg. Chem. 14:1253–1263.

Arantes, V., Milagres, A.M., Filley, T.R., Goodell, B. (2011) Lignocellulosic polysaccharides and lignin degradation by wood decay fungi: the relevance of nonenzymatic Fenton-based reactions. J. Ind. Microbiol. Biotechnol. 38:541–555.

Arantes, V., Jellison, J., Goodell, B. (2012) Peculiarities of brown-rot fungi and biochemical Fenton reaction with regard to their potential as a model for bioprocessing biomass. Appl. Microbiol. Biotechnol. 94:323–338.

Aro, N., Pakula, T., Penttila, M. (2005) Transcriptional regulation of plant cell wall degradation by filamentous fungi. FEMS Microbiol. Rev. 29:719–739.

Baldrian, P., Valaskova, V. (2008) Degradation of cellulose by basidiomycetous fungi. FEMS Microbiol. Rev. 32:501–521.

Boonstra, M.J., Tjeerdsma, B. (2006) Chemical analysis of heat treated softwoods. Holz Roh- Werkst. 64:204–211.

Boonstra, M.J., Van Acker, J., Kegel, E., Stevens, M. (2007) Optimisation of a two-stage heat treatment process: durability aspects. Wood Sci. Technol. 41:31–57.

Brischke, C., Welzbacher, C.R., Huckfeldt, T. (2008) Influence of fungal decay by different basidiomycetes on the structural integrity of Norway spruce wood. Holz Roh- Werkst. 66:433–438.

Bryne, L.E., Wålinder, M.E.P. (2010) Ageing of modified wood. Part 1: wetting properties of acetylated, furfurylated, and thermally modified wood. Holzforschung 64:295–304.

Cohen, R., Jensen, K.A., Houtman, C.J., Hammel, K.E. (2002) Significant levels of extracellular reactive oxygen species produced by brown rot basidiomycetes on cellulose. FEBS Lett. 531:483–488.

Curling, S.F., Clausen, C.A., Winandy, J.E. (2002) Relationships between mechanical properties, weight loss and chemical composition of wood during incipient brown-rot decay. For. Prod. J. 52:34–39.

Dieste, A., Krause, A., Mai, C., Militz, H. (2009a) The calculation of EMC for the analysis of wood/water relations in *Fagus sylvatica* L. modified with 1,3-dimethylol-4,5-dihydroxyethyleneurea. Wood Sci. Technol. 44:597–606.

Dieste, A., Krause, A., Mai, C., Sèbe, G., Grelier, S., Militz, H. (2009b) Modification of *Fagus sylvatica* L. with 1,3-dimethylol-4,5-dihydroxy ethylene urea (DMDHEU). Part 2: pore size distribution determined by differential scanning calorimetry. Holzforschung 63:89–93.

Eaton, R.A., Hale, M.D.C. Decay, Pests and Protection. Chapman & Hall, Cambridge, 1993.

Eriksson, K.E.L., Blanchette, R.A., Ander, P. Microbial and Enzymatic Degradation of Wood and Wood Components. Springer, Berlin, 1990.

Esteves, B., Pereira, H.M. (2009) Wood modification by heat treatment: a review. BioResources 4:370–404.

EN 252 (1989) Field test method for determining the relative protective effectiveness of a wood preservative in ground contact. European Committee for Standardization (CEN), Brussels, pp. 12.

EN 113 (1996) Wood preservatives – test method for determining the protective effectiveness against wood destroying basidiomycetes: determination of toxic values. European Committee for Standardization (CEN), Brussels, Belgium, pp. 31.

Fackler, K., Stevanic, J.S., Ters, T., Hinterstoisser, B., Schwanninger, M., Salmen, L. (2010) Localisation and characterisation of incipient brown-rot decay within spruce wood cell walls using FT-IR imaging microscopy. Enzyme Microbial. Technol. 47:257–267.

Fenton, H.J.H. (1894) Oxidation of tartaric acid in the presence of iron. J Chem. Soc. 65:899–911.

Filley, T.R., Cody, G.D., Goodell, B., Jellison, J., Noser, C., Ostrofsky, A. (2002) Lignin demethylation and polysaccharide decomposition in spruce sapwood degraded by brown rot fungi. Org. Geochem. 33:111–124.

Goodell, B. (2003) Brown-rot fungal degradation of wood: our evolving view. In: Wood deterioration and preservation. Eds. Goodell, B., Nicholas, D.D., Schultz, T.P., vol. 845. ACS Symposium Series, Washington, DC. pp. 97–118.

Goodell, B., Jellison, J., Liu, G., Daniel, A., Paszcynski, F., Fekete, S., Krishnamurthy, L., Jun, L., Xu, G. (1997) Low molecular weight chelators and phenolic compounds isolated from wood decay fungi and their role in the fungal biodegradation of wood. J. Biotechnol. 53:133–162.

Goodell, B., Daniel, G., Jellison, J., Qian, Y. (2006) Iron-reducing capacity of low-molecular-weight compounds produced in wood by fungi. Holzforschung 60:630–636.

Green, F., Highley, T.L. (1996) Mechanism of brown-rot decay: paradigm or paradox. Int. Biodeter. Biodegr. 39:113–124.

Habu, N., Nagasawa, Y., Samejima, M., Nakanishi, T.M. (2006) The effect of substituent distribution on the decay resistance of chemically modified wood. Int. Biodeter. Biodegr. 57:57–62.

Hakkou, M., Pétrissans, M., Gérardin, P., Zoulalian, A. (2006) Investigations of the reasons for fungal durability of heat-treated beech wood. Polym. Degrad. Stabil. 91: 393–397.

Halliwell, G. (1965) Catalytic decomposition of cellulose under biological conditions. Biochem. J. 95:35–40.

Hibbett, D.S., Donoghue, M.J. (2001) Analysis of character correlations among wood decay mechanisms, mating systems, and substrate ranges in homobasidiomycetes. Syst. Biol. 50:215.

Highley, T., Murmanis, L., Palmer, T. (1985) Micromorphology of degradation in western and sweetgum by the brown-rot fungus *Postia placenta*. Holzforschung 39:73–78.

Hill, C. Wood Modification: Chemical, Thermal and Other Processes. John Wiley and Sons, Chichester, 2006.

Hill, C.A.S. (2009) Why does acetylation protect wood from microbiological attack? Wood Mater. Sci. Eng. 4:37–45.

Hill, C.A.S., Papadopoulos, A.N., Payne, D. (2004) Chemical modification employed as a means of probing the cell-wall micropore of pine sapwood. Wood Sci. Technol. 37:475–488.

Hill, C.A.S., Forster, S.C., Farahani, M.R.M., Hale, M.D.C., Ormondroyd, G.A., Williams, G.R. (2005) An investigation of cell wall micropore blocking as a possible mechanism for the decay resistance of anhydride modified wood. Int. Biodeter. Biodegr. 55:69–76.

Hill, C.A.S., Curling, S.F., Kwon, J.H., Marty, V. (2009) Decay resistance of acetylated and hexanoylated hardwood and softwood species exposed to *Coniophora puteana*. Holzforschung 63:619–625.

Hingston, J.A., Collins, C.D., Murphy, R.J., Lester, J.N. (2001) Leaching of chromated copper arsenate wood preservatives: a review. Environ. Pollut. 111:53–66.

Ibach, R. (2005) Biological properties. In: Handbook of Wood Chemistry and Wood Composites. Ed. Rowell, R.M., Taylor & Francis, Boca Raton.

Ibach, R., Rowell, R.M. (2000) Improvements in decay resistance based on moisture exclusion. Mol. Cryst. Liq. Cryst. 353:22–33.

Irbe, I., Andersons, B., Chirkova, J., Kallavus, U., Andersone, I., Faix, O. (2006) On the changes of pinewood (*Pinus sylvestris* L.) Chemical composition and ultrastructure during the attack by brown-rot fungi *Postia placenta* and *Coniophora puteana*. Int. Biodeter. Biodegr. 57:99–106.

Junga, U., Militz, H. (2005) Particularities in agar block tests of some modified woods caused by different protection and decay principles. In: Proceedings of the 2nd European Conference on Wood Modification. Eds. Militz, H., Hill, C. University of Göttingen, Göttingen, Germany. pp. 354–362.

Kaneko, S., Yoshitake, K., Itakura, S., Tanaka, H., Enoki, A. (2005) Relationship between production of hydroxyl radicals and degradation of wood, crystalline cellulose, and a lignin-related compound or accumulation of oxalic acid in cultures of brown-rot fungi. J. Wood Sci. 51:262–269.

Kang, Y.-M., Prewitt, M.L., Diehl, S.V. (2009) Proteomics for biodeterioration of wood (*Pinus taeda* L.): challenging analysis by 2-D PAGE and MALDI-TOF/TOF/MS. Int. Biodeter. Biodegr. 63:1036–1044.

Kirk, T. (1975) Effects of the brown-rot fungus *Lentzites trabea*, on lignin in spruce wood. Holzforschung 29:99–107.

Kleman-Leyer, K., Agosin, E., Conner, A., Kirk, K. (1992) Changes in molecular size distribution of cellulose during attack by white rot and brown rot fungi. Appl. Environ. Microbiol. 58: 1266–1270.

Koenig, A.B., Sleighter, R.L., Salmon, E., Hatcher, P.G. (2010) NMR structural characterization of *Quercus alba* (white oak) degraded by the brown rot fungus *Laetiporus sulpureus*. J. Wood. Chem. Technol. 30:61–85.

Lande, S., Eikenes, M., Westin, M., Schneider, M. (2008) Furfurylation of wood: chemistry; properties and commercialization. Development of commercial wood preservatives. ACS Symp. Ser. 982:337–355.

Larsson Brelid, P., Simonson, R., Bergman, Ö., Nilsson, T. (2000) Resistance of acetylated wood to biological degradation. Holz Roh- Werkst. 58:331–337.

Lekounougou, S., Pétrissans, M., Jacquot, J.P., Gelhaye, E., Gérardin, P. (2008) Effect of heat treatment on extracellular enzymatic activities involved in beech wood degradation by *Trametes versicolor*. Wood Sci. Technol. 43:331–341.

Martinez, D., Challacombe, J., Morgenstern, I., Hibbett, D., Schmoll, M., Kubicek, C.P., Ferreira, P., Ruiz-Duenas. F.J., Martinez, A.T., Kersten, P., Hammel, K.E., Vanden Wymelenberg, A., Gaskell, J., Lindquist, E., Sabat, G., Splinter BonDurant, S., Larrondo, L.F., Canessa, P., Vicuna, R., Yadav, J., Doddapaneni, H., Subramanian, V., Pisabarro, A.G., Lavín, J.L., Oguiza, J.A., Master, E., Henrissat, B., Coutinho, P.M., Harris, P., Magnuson, J.K., Baker, S.E., Bruno, K., Kenealy, W., Hoegger, P.J., Kües, U., Ramaiya, P., Lucas, S., Salamov, A., Shapiro, H., Tu, H., Chee, C.L., Misra, M., Xie, G., Teter, S., Yaver, D., James, T., Mokrejs, M., Pospisek, M., Grigoriev, I.V., Brettin, T., Rokhsar, D., Berka, R., Cullen, D. (2009) Genome, transcriptome, and secretome analysis of wood decay fungus *Postia placenta* supports unique mechanisms of lignocellulose conversion. Proc. Natl. Acad. Sci. USA 106:1954–1959.

Martinez, A.T., Rencoret, J., Nieto, L., Jiménez-Barbero, J., Gutiérrez, A., Del Río, J.C. (2011) Selective lignin and polysaccharide removal in natural fungal decay of wood as evidenced by in situ structural analyses. Environ. Microbiol. 13:96–107.

Meyer, L., Brischke, C., Pilgård, A. (2012) Modified timber in various above ground exposures – durability and moisture performance. In: Proceedings of the 6th European Conference on Wood Modification. Eds. Hill, C.A.S., Militz, H., Pohleven, F. Ljubljana, Slovenia.

Militz, H. (1991) Die Verbesserung das Schwind- und Quellverhaltens und der Daurhaftigkeit von Holz mittels Behnadlung mit unkatalysiertem Essigsäureanhydrid. Holz Roh- Werkst. 49:147–152.

Militz, H. (1993) Treatment of timber with water-soluble dimethylol resin to improve their dimensional stability and durability. Wood Sci. Technol. 27:347–357.

Militz, H. (2002) Thermal treatment of wood: European processes and their background. IRG/WP 02-40241. In: Proceedings, International Research Group on Wood Protection, 12–17 May, Cardiff.

Niemenmaa, O., Uusi-Rauva, A., Hatakka, A. (2008) Demethoxylation of [$O_{14}CH_3$]-labelled lignin model compounds by the brown-rot fungi *Gloeophyllum trabeum* and *Poria* (*Postia*) *placenta*. Biodegradation 19:555–565.

Papadopoulos, A.N. (2010) Chemical modification of solid wood and wood raw material for composites production with linear chain carboxylic acid anhydrides: a brief review. BioResources 5:499–506.

Papadopoulos, A.N., Hill, C.A.S. (2002) The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against *Coniophora puteana*. Holz Roh- Werkst. 60:329–332.

Papadopoulos, A.N., Hill, C.A.S. (2003) The sorption of water vapour by anhydride modified softwood. Wood Sci. Technol. 37:221–231.

Pfriem, A., Zauer, M., Wagenführ, A. (2010) Alteration of the unsteady sorption behaviour of maple (*Acer pseudoplatanus* L.) and spruce (*Picea abies* (L.) Karst.) due to thermal modification. Holzforschung 64:235–241.

Phuong, L.X., Takayama, M., Shida, S., Matsumoto, Y., Aoyagi, T. (2007) Determination of the accessible hydroxyl groups in heat-treated *Styrax tonkinensis* (Pierre) Craib ex Hartwich wood

by hydrogen-deuterium exchange and ^{2}H NMR spectroscopy. Holzforschung 61:488–491.

Pilgård, A., Alfredsen, G., Fossdal, C.G., Long, I.C.J. (2012) The effects of acetylation on the growth of *Postia placenta* over 36 weeks. IRG/WP 12-40589. In: Proceedings, International Research Group on Wood Protection, 6–10 May, Kuala Lumpur.

Rapp, A.O., Brischke, C., Welzbacher, C.R. (2008) Increased resistance of thermally modified Norway spruce timber (TMT) against brown rot decay by *Oligoporus placenta* – a study on the mode of protective action. Wood Res. 53:13–26.

Rowell, R.M. (Ed.) (2005) Handbook of Wood Chemistry and Wood Composites. Taylor & Francis, Boca Raton.

Rowell, R.M., Ibach, R.E., McSweeny, J., Nilsson, T. (2009) Understanding decay resistance, dimensional stability and strength changes in heat-treated and acetylated wood. Wood Mater. Sci. Eng. 4:14–22.

Shimokawa, T., Nakamura, M., Hayahashi, N., Ishihara, M. (2004) Production of 2,5-dimethoxyhydroquinone by the brown-rot fungus *Serpula lacrymans* to drive extracellular Fenton reaction. Holzforschung 58:305–310.

Schneider, M.H. (1995) New cell wall and cell lumen wood polymer composites. J. Wood Sci. Technol. 29:121–127.

Thygesen, L.G., Tang Engelund, E., Hoffmeyer, P. (2010) Water sorption in wood and modified wood at high values of relative humidity. Part I: results for untreated, acetylated, and furfurylated Norway spruce. Holzforschung 64:315–323.

Tjeerdsma, B.F., Boonstra, M., Pizzi, A., Militz, H. (1998) Characterisation of thermally modified wood: molecular reasons for wood performance improvement. Holz Roh- Werkst. 56:149–153.

Tomberg, K., Olsson, S. (2002) Detection of hydroxyl radicals produced by wood-decomposing fungi. FEMS Microbiol. Ecol. 40:13–20.

Townsend, T., Dubey, B., Tolaymat, T., Solo-Gabriele, H. (2005) Preservative leaching from weathered CCA-treated wood. J. Environ. Manage. 75:105–113.

Wainwright, M. (1988) Metabolic diversity of fungi in relation to growth and mineral cycling in soil – a review. Trans. Br. Mycol. Soc. 90:159–170.

Vanden Wymelenberg, A., Gaskell, J., Mozuch, M., BonDurant, S.S., Sabat, G., Ralph, J., Skyba, O., Mansfield, S.D., Blanchette, R.A., Grigoriev, I.V., Kersten, P.J., Cullen, D. (2011) Significant alteration of gene expression in wood decay fungi *Postia placenta* and *Phanerochaete chrysosporium* by plant species. Appl. Environ. Microbiol. 77:4499–4507.

Weiland, J.J., Guyonnet, R. (2003) Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. Holz Roh- Werkst. 61:216–220.

Welzbacher, C.R. (2007) Performance of spruce and pine timber, treated by novel thermal modification processes, in consideration of the durability against wood-destroying microorganisms (in German). University of Hamburg, Hamburg.

Welzbacher, C.R., Rapp, A.O. (2004) Determination of the water sorption properties and preliminary results from field tests above ground of thermally modified material from industrial scale process. IRG/WP 04- 40279, The International Research Group on Wood Protection, 6–10 June, Ljubljana.

Venås, T.M. (2008) A study of mechanisms related to the fungal decay protection rendered by wood furfurylation. University of Copenhagen, Copenhagen.

Verma, P., Mai, C. (2010) Hydrolysis of cellulose and wood powder treated with DMDHEU by a hydrolase enzyme complex, Fenton's reagent, and in a liquid culture of *Trametes versicolor*. Holzforschung 64:69–75.

Westin, M. (1996) Development and evaluation of new alternative wood preservation treatments. Final report to the Swedish Council for the Forestry and Agricultural Research (SJFR). p. 25.

Windeisen, E., Bächle, H., Zimmer, B., Wegener, G. (2009) Relations between chemical changes and mechanical properties of thermally treated wood. 10th EWLP, Stockholm, Sweden, August 25–28, 2008. Holzforschung 63:773–778.

Xu, G., Goodell, B. (2001) Mechanisms of wood degradation by brown rot fungi: Chelator mediated cellulose degradation and binding of iron by cellulose. J. Bacteriol. 87:43–57.

Yelle, D.J., Ralph, J., Lu, F., Hammel, K.E. (2008) Evidence for cleavage of lignin by a brown rot basidiomycete. Environ. Microbiol. 10:1844–1849.

Yelle, D.J., Wei, D., Ralph, J., Hammel, K.E. (2011) Multidimensional NMR analysis reveals truncated lignin structures in wood decayed by the brown rot basidiomycete *Postia placenta*. Environ. Microbiol. 13:1091–1100.

Zabel, R.A., Morell, J.J. Wood microbiology: Decay and Its Prevention. Academic Press, San Diego, 1992.