Decay resistance of ash, beech and maple wood modified with N-methylol melamine and a metal complex dye

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A R T I C L E   I N F O
Article info
Article history:
Received 17 September 2013
Received in revised form 10 January 2014
Accepted 11 January 2014
Available online xxx

Keywords:
Melamine modification
Metal-complex dye
Wood decay
Brown rot
White rot
Soft rot

A B S T R A C T
This study evaluated the decay resistance of ash (Praxinus excelsior L.), beech (Fagus sylvatica L.), and maple (Acer platanoides L.) wood impregnated by a full cell process with N-methylol melamine (NMM) and combined NMM-metal complex dye (NMM-BS) in aqueous solutions. Basidiomycete decay testing involved incubation with Coniophora puteana (brown rot) and Trametes versicolor (white rot) according to a modified EN 113 (1996) standard, while for the soft rot fungal resistance was evaluated following the standard ENv 807 (2001). NMM and NMM-BS modifications at a WPG range of 7–11% provided decay protection against brown rot resulting in a mass loss less than the required limit (3%). The NMM and NMM-BS modified wood showed increased resistance to white rot decay; however, a higher WPG is needed to prohibit attack from this hardwood specific fungus. The metal-complex dye alone revealed biocidal effects against basidiomycetes. An increased WPG in NMM or NMM-BS had a positive impact against soft rot decay and the lowest mass losses after 32 weeks of exposure were obtained with NMM modification at about 18–21% WPG. NMM modification at this WPG range, however, was not sufficient to protect the wood from soft rot decay. The wood of beech and maple showed slightly higher resistance to all decay types than ash, probably due to the poorer degree of modification of the latter.

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1. Introduction

It is well recognized that wood modification is able to provide protection against decay fungal attack (Stamm and Baechler, 1960; Rowell, 2005). It is an alternative approach to traditional preservation treatments of wood with biocides and refers to thermal, chemical and impregnation modification. Chemical modification involves a reaction between the hydroxyl groups of cell wall polymers and the reagent molecules leading to covalent bonding. Various mechanisms have been proposed for the protection imparted by chemical wood modification systems. Especially for brown and soft rot decay, it was concluded that the main protection mechanism is based on cell wall bulking rather than a chemical one caused by blockage of the OH-groups as suggested for anhydride-modified wood (Hill, 2006). The incorporated adduct occupies spaces within the cell wall and thus, the penetration of decay agents released by fungi might be prevented due to a blocking of the cell wall micro-pores and a reduction in the cell wall moisture content (Peterson and Thomas, 1978; Suttie et al., 1999; Larsson Brelid et al., 2000; Lade et al., 2004; Rowell, 2006; Verma et al., 2009). Cross-linking of cell wall polymers reduces swelling of wood in water which results in more pronounced reduction of cell wall moisture than with of cell wall bulking; therefore, cross-linking was assumed to be more efficient in preventing wood degradation by basidiomycetes than cell wall bulking (Stamm and Baechler, 1960; Xiao et al., 2012). In the case of passive impregnation modification, the mechanism of decay protection is attributed to cell wall bulking. Although in this case no reaction occurs between the impregnation reagent and the cell wall polymers, the reagent molecules are deposited within the cell wall and polymerise therein (Norimoto and Gril, 1993). Pore size in the cell wall matrix is reduced and less space can be occupied by the water molecules, resulting in reduced cell wall moisture content and limited access to the cell wall interior by the degradation agents (Stamm, 1964; Lukowsky, 1999). Improved decay resistance of thermally modified wood is based on changes in the chemical structure of the cell walls and auto-cross-linking of cell wall polymers making it more difficult for fungi to attack the wood material (Hakkou et al., 2006; Lekounougou et al., 2009). Loss of hemicelluloses lowers the hydrophilicity of the material, and the process may generate new extractives, which may...
have fungicidal or fungistatic effects (Kamdem et al., 2000; Weiland and Guynnoet, 2003).

NMM resins are able to penetrate into the cell wall and different morphological regions of wood tissues by diffusion (Rapp et al., 1999; Gindl et al., 2002, 2003; Mahnert et al., 2013; Sint et al., 2013), while after curing fixation is provided by the formation of a three-dimensional network with corresponding increase in molar mass within the cell wall rather than covalent bonding to the wood matrix (Lukowsky, 1999). Various resin formulations have been used showing the ability of NMM-treatment to enhance physico-mechanical properties and hydrophobicity of wood (Inoue et al., 1993; Pittman et al., 1994; Miroy et al., 1995; Rapp and Peek, 1999; Gsöls et al., 2003; Gindl et al., 2004; Krause et al., 2004; Hansmann et al., 2006). Fungal tests have also shown high decay resistance, mainly depending on the amount of resin used (Lukowsky, 1999; Gsöls et al., 2003; Krause et al., 2004).

Recent studies reported on the modification of three hardwood species (ash, beech, maple), which are extensively used in wooden structures, with an aqueous NMM solution containing a metal-complex dye (Kielmann et al., 2012, 2013a,b). The aim was not only to improve the performance of wood exposed outdoors but also to enhance its aesthetic quality by a permanent staining of the whole wood substrate. By means of UV micro-spectrophotometry and x-ray micro-analysis it was shown that the combined resin modification and staining of the three wood species is possible and that NMM causes fixation of the water-soluble dye (Kielmann et al., 2013a). Previous results (Kielmann et al., 2012) indicated the potential of the combined modification to improve the performance of wood under conditions with high humidity and high biological activity. Performance of the modified wood in soil contact (use class 4; EN 335-2, 2006), however, was not reported. With respect to strength changes, the modified wood appeared suitable for most structural uses, but the known problems associated with the reduction of impact bending strength should be considered (Kielmann et al., 2013b). The present study further reports on the properties of the combined NMM-dye treated wood of ash, beech, and maple by evaluating the durability improvement towards brown, white and soft rot fungi.

2. Materials and methods

2.1. Wood and chemicals

The wood material used in this study was ash (Fraxinus excelsior L.), beech (Fagus sylvatica L.), and maple (Acer platanoides L.)

![Fig. 1. Mass loss of unmodified and NMM or NMM-BS modified ash, beech and maple wood after 16 weeks' incubation with T. versicolor (A) and C. puteana (B) according to EN 113 (1996). n = 10; mean values ± SD.](image)

![Fig. 2. Mass loss of untreated and BS-treated (metal-complex dye) beech wood after 16 weeks of incubation with T. versicolor and C. puteana according to EN 113 (1996), n = 10; mean values ± SD.](image)

Table 1
<table>
<thead>
<tr>
<th>Species/Treatment</th>
<th>WPG (%)</th>
<th>EN 113</th>
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<tbody>
<tr>
<td></td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
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<tr>
<td>Ash</td>
<td></td>
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<tr>
<td>10.0% NMM</td>
<td>7.1 ± 0.8</td>
<td>8.3 ± 0.8</td>
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<tr>
<td>10.0% NMM-BS</td>
<td>10.4 ± 0.7</td>
<td>9.4 ± 0.6</td>
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<tr>
<td>20.0% NMM</td>
<td>17.7 ± 0.8</td>
<td>17.5 ± 0.8</td>
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<tr>
<td>20.0% NMM-BS</td>
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<tr>
<td>Beech</td>
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<tr>
<td>2.5% BS</td>
<td>1.0 ± 0.2</td>
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<tr>
<td>7.5% BS</td>
<td>2.9 ± 0.3</td>
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<tr>
<td>15.0% BS</td>
<td>6.5 ± 0.5</td>
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<tr>
<td>10.0% NMM</td>
<td>10.5 ± 1.0</td>
<td>11.1 ± 0.9</td>
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<tr>
<td>10.0% NMM-BS</td>
<td>11.2 ± 0.8</td>
<td>13.3 ± 0.9</td>
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<tr>
<td>20.0% NMM</td>
<td>20.3 ± 1.2</td>
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<tr>
<td>20.0% NMM-BS</td>
<td>22.9 ± 1.4</td>
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<tr>
<td>Maple</td>
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<tr>
<td>10.0% NMM</td>
<td>11.6 ± 1.0</td>
<td>11.3 ± 1.2</td>
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<tr>
<td>10.0% NMM-BS</td>
<td>17.2 ± 1.5</td>
<td>16.4 ± 1.0</td>
<td></td>
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</tr>
<tr>
<td>20.0% NMM</td>
<td>21.0 ± 1.6</td>
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</tr>
<tr>
<td>20.0% NMM-BS</td>
<td>27.2 ± 1.5</td>
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</table>

* 10 replicates per treatment.
* 40 replicates per treatment.
originating from air-dried boards. Wood specimens with a size of 50 × 25 × 15 mm³ (L × R × T) were prepared for white and brown rot testing, and mini-stakes measuring 100 × 10 × 5 mm³ (L × R × T) for soft rot testing. The specimens were oven-dried at 103 ± 2 °C for 48 h and weighed. Prior to treatment, the dried wood specimens were conditioned at 20 °C and 65% RH to a constant weight.

The N-methylol melamine resin Madurit MW840/75WA (NMM) was supplied as an aqueous stock solution with a solid content of approximately 75% and a specific gravity of 1.245–1.260 g ml⁻¹ at 23 °C (Ineos Melamines GmbH, Frankfurt, Germany). The aqueous metal-complex dye Basantol™ Brown 269 liquid (BS) was supplied with 30% solid content, density of 1.14 g cm⁻³, pH 6.5 and fastness 6–7 (BASF SE, Ludwigshafen, Germany).

### 2.2. Micro-organisms

The brown rot fungus Coniophora puteana (Schum.: Fr.) Karst. strain BAM Ebw. 15 (DSM No. 3085) and the white rot fungus Trametes versicolor (Linneus) L. Quélet strain CTB 863 A (DSM No. 3086) were obtained from the German Collection of Microorganisms and Cell Cultures (DSMZ). The cultures of C. puteana and T. versicolor were maintained on 4% malt extract agar medium at 30°C and sub-culturing was done in intervals of 4 weeks. The cultures were supplied as an aqueous stock solution with a solid content of 30% and a specific gravity of 1.285 g ml⁻¹ at 23 °C. Basantol™ Brown 269 liquid (BS) was supplied with 30% solid content, density of 1.14 g cm⁻³, pH 6.5 and fastness 6–7 (BASF SE, Ludwigshafen, Germany).

### 2.3. NMM-dye treatment

For brown and white rot testing, solutions with 10% NMM solid content (wt/vol) as well as NMM-dye solutions consisting of 10% NMM solid content (wt/vol) and 5% BS (vol/vol) of stock solution were prepared by diluting with tap water. For soft rot testing, additional solutions of 20% NMM and 20% NMM-5% BS were also prepared. The solutions were sterilized in an autoclave with water vapour at 121 °C for 20 min and incubated at 22 °C ± 1 °C and 70% RH with C. puteana and T. versicolor in Kölle flasks for 16 weeks. Each flask contained an untreated specimen and a modified one (10% NMM, 10% NMM-BS, and 2.5, 7.5, 15.0% BS treated beech specimen). Ten replicates (flasks) were tested per treatment. After incubation, the specimens were oven-dried to determine the mass loss.

### 2.4. White and brown rot testing

Basidiomycetes decay testing was done according to a modified EN 113 (1996) standard. The specimens were sterilized in an autoclave with water vapour at 121 °C for 20 min and incubated at 22 °C ± 1 °C and 70% RH with C. puteana and T. versicolor in Kölle flasks for 16 weeks. Each flask contained an untreated specimen and a modified one (10% NMM, 10% NMM-BS, and 2.5, 7.5, 15.0% BS treated beech specimen). Ten replicates (flasks) were tested per treatment. After incubation, the specimens were oven-dried to determine the mass loss.

### 2.5. Soft rot testing

The resistance of mini-stakes against soft rot fungi was evaluated in unsterile soil following the standard ENv 807 (2001) by using 40 replicates per treatment (10% and 20% NMM, 10% and 20% NMM-BS). Untreated stakes served as controls. After 8, 16, 24, and 32 weeks of exposure, 10 specimens per treatment were withdrawn and the dry weight was measured to determine the mass loss.

### 3. Results and discussion

#### 3.1. White and brown rot decay

A mass loss of approximately 30% was observed for the unmodified control specimens of the three species after 16 weeks incubation with T. versicolor (white rot). Both NMM and NMM-BS modifications significantly increased the resistance of wood to white rot decay (Fig. 1A). This was especially true for NMM-modified beech and followed by maple where the mass loss diminished to 8.0% and 12.4%, respectively. The combined NMM-BS modification further increased the resistance, as the mass loss caused by T. versicolor diminished to almost half in comparison to the above mentioned values (4.0% and 5.3%); this effect was not observed for ash. Ash samples modified with NMM and NMM-BS exhibited a higher mass loss (14.0–17.6%) than modified beech and maple specimens; this is attributable to the lower WPG of ash (Table 1) which was also reported previously (Kielmann et al., 2013a). Decay protection against C. puteana (brown rot) resulting in a mass loss below the 3%-limit (EN 113, 1996) was achieved with all species by both NMM and NMM-BS treatments with mass losses ranging from 0.5 to 3.0% (Fig. 1B). While the modified wood
was protected from C. puteana at a WPG threshold of 7–11% (Table 1), the WPG values established were not high enough to obtain a mass loss caused by T. versicolor, a white rot fungus generally associated with hardwoods, below the 3%-limit of EN 113 (1996). The effect of the modification on fungal resistance appears to depend on the wood species, as for example, a WPG of 13% was sufficient to protect the NMM-BS treated wood of beech inducing a minor loss of almost 4% but a much higher WPG (17%) in maple did not have a similar effect.

Due to its metal content such as chromium (Kielmann et al., 2013a), BS dye indicated to have a biocide effect with stronger effects on C. puteana than on T. versicolor (Fig. 2). BS treatment alone protected beech wood from decay by C. puteana at a WPG threshold of about 3%, while at least the double amount was required to provide protection against T. versicolor (see Table 1 and Fig. 2). The mechanism for the improved resistance of NMM-BS treated wood to basidiomycete decay might be a combined effect of blocking micro-pores in the cell wall and lowering cell wall moisture content which hinder the penetration of enzymes and low molecular weight decay agents (Sutte et al., 1999; Sailer and van Etten, 2004; Rowell, 2006; Hill et al., 2006) as well as a biocidal effect of the BS dye.

3.2. Soft rot decay

Untreated ash wood showed a slightly higher resistance to soft rot fungi and soil inhabiting micro-organisms (mass loss 33%) than untreated beech and maple, which had a similar mass loss of about 40% after 32 weeks of incubation (Fig. 3). With all species, mass loss of untreated control specimens continuously increased with the exposure time in the soil. The modifications resulted in lower mass losses during the incubation period with beech and maple showing slightly higher resistance than ash. For both NMM and NMM-BS modifications, higher WPG of the specimens enhanced the resistance to soft rot decay. The lowest mass losses in the species after 32 weeks of exposure were obtained with NMM modification at about 18–21% WPG (see Table 1 and Fig. 3). Even these mass losses (approx. 8–13%) were significantly higher than the 3%-threshold of ENv 807 (2001) indicating the inefficiency of the modification to protect the wood against soft rot decay at this WPG range. For two Bombax species modified with NMM, a WPG of 24–37% was needed to ensure resistance to soft rot decay (Sint, 2010). The addition of BS dye in the NMM solutions caused no further decay reduction (Figs. 3 and 4). The protection mechanism against soft rot fungi is assumed to be similar to that discussed above for basidiomycete decay. NMM is able to penetrate different morphological regions of the wood cells while during curing the monomers condense and form a 3D network within the cell wall (Mahnert et al., 2013; Sint et al., 2013; Kielmann et al., 2013a). This mechanical incorporation of NMM in the cell wall results in a reduction of cell wall moisture content and acts as a physical barrier to destroying decay agents (Rapp et al., 1999; Rowell, 2006).

4. Conclusions

NMM and NMM-BS modifications were able to increase the resistance of ash, beech and maple wood to basidiomycete decay. A WPG threshold of 7–11% could prevent brown rot decay, while these WPG values were not high enough to fully protect wood from white rot. WPG correlated positively with the resistance to soft rot decay, but higher WPGs are needed than the obtained 18–21% WPG to avoid soft rot decay in the species. The metal-complex dye, which contains chromium, provided additional resistance toward basidiomycetes, especially to brown rot, but had no effect against soft rot.

Acknowledgements

The authors would like to thank the companies BASF SE and Ineos Melamines GmbH for their cooperation. The support from AIF through the ZIM cooperation program (KF 2454601GZ9) is also acknowledged.

References


Fig. 4. Photos of unmodified and NMM or NMM-BS modified ash (A), beech (B), and maple (C) wood stakes after 32 weeks of exposure in soil according to ENv 807. In every photo, the stakes from left to right are: unmodified control, 10% NMM, 20% NMM, 10% NMM + BS, 20% NMM + BS.