ORIGINALS ORIGINALARBEITEN

Weathering characteristics of wood treated with water glass, siloxane or DMDHEU

Antje Pfeffer · Carsten Mai · Holger Militz

Received: 5 November 2009 / Published online: 28 January 2011 © The Author(s) 2011. This article is published with open access at Springerlink.com

Abstract Specimens of Scots pine sapwood (Pinus sylvestris) and beech wood (Fagus sylvatica) were treated with a sodium water glass solution, an amino-alkyl-functional oligomeric siloxane and 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU). The specimens were exposed outside without ground contact for 24 months. Colour measurements during outside exposure showed a discoloration of all wood specimen surfaces. FTIR spectroscopy displayed lignin degradation of all specimens during the initial exposure time. Chemical treatments decelerated fungal infestation of wood, while their effect on lignin degradation was not discernible. SEM studies revealed that fungal infestation was affected by the different treatments. The untreated specimens showed radial penetration of fungal hyphae through the pits. Only superficial infestation and no radial penetration were visible at water glass and siloxane treated specimens. A significantly reduced radial penetration of fungal hyphae was exhibited at DMDHEU treated specimens. Fungal infestation through the pits was not visible.

Bewitterungseigenschaften von Wasserglas, Siloxan, DMDHEU behandeltem Holz

Zusammenfassung Prüfkörper aus Kiefer (*Pinus sylvest-ris*) und Buche (*Fagus sylvatica*) wurden mit einem Natri-umwasserglas, einem Amino-Alkyl-funktionellem oligomeren Silansystem, und 1,3-dimethylol-4,5-dihydroxyethylene-urea (DMDHEU) behandelt. Unbehandelte und behandelte Prüfkörper wurden für die Dauer von 24 Monaten einer Freilandbewitterung ohne Bodenkontakt ausgesetzt. Ei-

A. Pfeffer (☑) · C. Mai · H. Militz Wood Biology and Wood Products, Georg-August-Universität Göttingen, Göttingen, Germany e-mail: apfeffe@gwdg.de ne Farbveränderung der Holzoberfläche während der Bewitterung war bei allen untersuchten Prüfkörpern sichtbar. FTIR-Spektroskopie zeigte einen Ligninabbau bei allen untersuchten Prüfkörpern schon nach kurzer Bewitterungszeit. Der Befall durch holzverfärbende Pilze war bei den behandelten Prüfkörpern verzögert, der Ligninabbau dagegen nicht. In SEM-Studien wurde der Einfluss der Behandlung auf den Pilzbefall untersucht. Die unbehandelten Prüfkörper zeigten eine radiale Eindringung der Pilzhyphen in das Holz durch die Tüpfel. Bei den Siloxan und Wasserglas behandelten Prüfkörpern war ein Befall der Prüfkörperoberfläche sichtbar, aber keine radiale Eindringung der Pilzhyphen. Bei den DMDHEU behandelten Prüfkörpern war die radiale Eindringung stark vermindert und kein Durchwachsen der Tüpfel sichtbar.

1 Introduction

The surface of wood rapidly deteriorates during unprotected outside exposure. Major aspects of the weathering of wood are aesthetic effects such as changes in colour, roughness, surface checking, dirt uptake and growth of sapstaining fungi. These initial surface changes can be quite rapid followed by longstanding periods without any signs of decay (Feist 1982). Influencing factors for surface degradation are sunlight (UV- and visible light) and water in the form of rain and humidity (Hon 2001). The energy of UV-light is sufficient to cleave bonds of wood cell wall components.

Lignin is most susceptible to UV-light degradation, but also holocellulose showed some severe breakdown (Feist 1990; Hon 1981; Plackett et al. 1996). Lignin in cell corners and in the compound middle lamellae is degraded during the early stages of irradiation (Miniutti 1964; Hon and Feist 1986). Leaching of photo-degraded wood fragments (mainly from lignin) by rain results in increased surface roughness.



After leaching of UV degradation products, subjacent cell layers are exposed to erosion (Feist 1982).

The degradation products of weathering are also nutrients for surface micro-organisms such as blue stain fungi and moulds (Schoeman and Dickinson 1997). Naturally weathered wood surfaces adopt a grey colour due to colonisation by staining fungi. These fungi are able to metabolize breakdown products of lignin and holocellulose (Eaton and Hale 1993; Schmidt 2006).

One aspect to reduce the infestation of staining fungi on wood surfaces is a reduction of the lignin breakdown products as potential nutrient source. The variety of methods protecting the wood substrate against UV-degradation and fungal infestation includes coatings as well as pre-treatments for enhanced weathering stability of wood in exterior application. Chemical modification can enhance the weathering performance (Evans et al. 2000). Furthermore wood modification can influence the amount and accessibility of soluble nutrients (Verma et al. 2008) thus an effect on spore germination and growth of sapstain fungi is to be considered.

Treatments of wood with water glass solutions were shown to increase the resistance against brown rot fungi in laboratory tests and to decrease fungal colonisation (Furuno et al. 1991, 1992; Furuno and Imamura 1998; Dellith 2006). Further studies on water glass treatments did not reveal any infestation of blue stain fungi after three years above ground weathering (Dellith 2006).

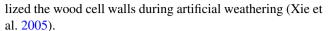
A treatment with siloxanes increased the water repellency of wood (Donath et al. 2006, 2007), but did not considerably influence the sorption behaviour of wood. Siloxanes containing amino-functional groups showed protective effectiveness against wood destroying basidiomycetes particularly the brown rot fungi Coniophora puteana and Gloeophyllum trabeum in laboratory durability tests according to EN 113 (Donath 2004).

Wood modified with 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) was previously reported to be resistant against decay fungi (Militz 1993; Yusuf 1996; Van der Zee et al. 1998; Krause et al. 2003; Verma et al. 2005, 2008). DMDHEU treatment of thin veneer strips partially reduced the degradation of lignin and cellulose and stabi-

chemicals Tab. 1 Charakterisierung der Chemikalien

Table 1 Characterisation of

Trade name Chemical characterisation Concentration BETOL 39 T3 (Woellner, Sodium water glass with additives 15% wt/wt Ludwigshafen, Germany) DYNASYLAN® HS 2909 Amino-alkyl-functional oligomeric 20% wt/wt siloxane (Evonik, Rheinfelden, Germany) N-methylol compound, DMDHEU (BASF, Ludwigshafen, 1.3 M 1,3-dimethylol-4,5 dihydroxyethylen Germany) urea (catalyst MgCl2, 5% concentration related to the DMDHEU concentration)



This study investigates the outdoor weathering performance of water glass, siloxane and DMDHEU treated Scots pine sapwood and beech wood. Colour changes, fungal infestation as well as fungal penetration into the wood tissue and changes in the chemical structure of the wood surface were evaluated during and after outside weathering.

2 Material and methods

2.1 Treatment of the wood specimens

Specimens of Scots pine sapwood (Pinus sylvestris L.) and beech wood (Fagus sylvatica L.) free of knots and cracks were prepared with a size of $150 \times 74 \times 18 \text{ mm}^3$ (longitudi $nal \times tangential \times radial$). The modification chemicals that were used in this study are described in Table 1.

Impregnation of wood specimens was carried out by applying a vacuum of 60 mbar (30 min) and a subsequent pressure of 12 bar (2 h). All treatments were carried out in a laboratory scale process. After impregnation, siloxane impregnated specimens were pre-dried at 40°C (4 d). Curing of the siloxane was subsequently performed at 103°C (24 h). The water glass treated specimens were stored for three weeks in a desiccator under carbon dioxide atmosphere, which was established by floating the desiccator in regular steps with CO₂ from a gas bomb. DMDHEU impregnated specimens were cured in a hot steam dryer. The weight percent gain (WPG) of the specimens was determined from the dry masses before and after treatment.

2.2 Outside exposure and analyses of specimen surface

The specimens of Scots pine sapwood and beech wood were placed and fixed on weathering racks with a 45° slope direction towards south west. The weathering racks were located at the field of the University of Göttingen. Eight samples per treatment were used. Weathering was performed from August 2006 to August 2008.



2.2.1 Colour measurements

Colour change of specimen surfaces was evaluated every three months. Therefore the panels were removed from the weathering racks and their surface was scanned with an EP-SON Expression 10000XL at 300 dpi resolution. The colour changes were determined with Adobe Photoshop 7.0 software by using the integrated CIE-lab colour space of the software. These CIE-lab data have been corrected to make them comparable with data measured by a photospectrome-

The measured area of the specimens was defined by x and y coordinates to guarantee the same measuring area for every evaluation period. The surface colour was determined according to the Commission International de l'Eclairage (CIE) on the basis of the Lab colour space. The lightness (L)and absolute colour difference (ΔE) between two colours given in terms of L^*a^*b were determined during exposure time. Lightness is represented by the L axis running from black to white. The ΔE was calculated using the following equation:

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2},$$

L = Lightness (white-black axis), a = chromaticity coordinate (red-green axis), b = chromaticity coordinate (yellowblue axis), L_1 , a_1 , b_1 data before weathering, L_2 , a_2 , b_2 data after weathering period.

2.2.2 FTIR spectroscopy

Chemical changes of the specimen surfaces during the first year of outside exposure were evaluated by FTIR spectroscopy every three months. Therefore a FTIR spectrometer (Vector 22, Bruker, Bremen, Germany) with an ATRunit (DuraSamplIRII, SensIR Technologies, Danbury, USA) operating at 32 scans and at 4 cm⁻¹ resolution was used. Measurements at five randomly chosen spots on the earlywood parts of the specimen surface were taken. The spectra were baseline corrected and normalized to the highest peak.

Fig. 1 Change in lightness of Scots pine sapwood specimens exposed outside (error bars show standard deviation) Abb. 1 Änderung der Helligkeit von Kiefernsplintholz nach Freilandbewitterung (Fehlerindikatoren zeigen die Standardabweichung)

--■- Siloxane - ▲- Water glass 90 80 70 60 50 40 30 20 10 0 12 18 21 Exposure time [months]

untreated

2.2.3 Scanning-Electron-Microscopy (SEM)

The penetration of fungal hyphae into the wood tissue was studied by Scanning Electron Microscopy (SEM). SEM studies were carried out using a Leo Supra 45 (Leo Elektronenmikroskopie GmbH, Oberkochen, Germany). The instrument operated at an acceleration voltage of 5.01 kV and a working distance between 11 mm and 13 mm. The exposed surface layers of the panels were separated and transformed into smaller samples by splitting in radial direction. Thus exposed radial sections presented the object of observation of the depth and paths of penetration of fungi. The radial surface was coated with graphite by a low vacuum sputter coating to prevent accumulation of static electricity charge during electron irradiation.

3 Results and discussion

3.1 Colour changes

Within the initial 3 months of outside exposure, the lightness of all specimens decreased clearly, except for water glass treated specimens particularly in the case of Scots pine sapwood specimens (Figs. 1 and 2). Since the initial lightness was slightly decreased for all treated specimens, decline of lightness within the initial 3 months was lower compared to untreated specimens. During the subsequent exposure time the lightness of treated and untreated Scots pine sapwood specimens remained almost constant for up to 15 months. The lightness of untreated and siloxane treated specimens was lower than that of DMDHEU and water glass treated specimens. After 24 months outside exposure, all specimens reached approximately the same level of lightness except for the water glass treated specimens. The values of beech wood varied over the whole evaluation period. During 9 months of outside exposure all treated specimens displayed the lowest values of lightness. Subsequently the lightness increased

—×- DMDHEU



DMDHEU

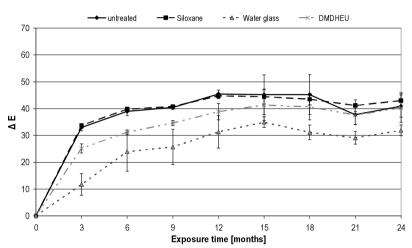
Fig. 2 Change in lightness of beech specimens exposed outside (error bars show standard deviation) Abb. 2 Änderung der Helligkeit von Buche nach Freilandbewitterung (Fehlerindikatoren zeigen die Standardabweichung)

90 80 70 60 50 40 30 20 3 12 15 18 21 24 n Exposure time [months]

- △- Water dass

◆ untreated

Fig. 3 Change in colour of Scots pine sapwood specimens exposed outside (error bars show standard deviation) Abb. 3 Farbänderung von Kiefernsplintholz nach Freilandbewitterung (Fehlerindikatoren zeigen die Standardabweichung)



and the untreated specimens showed the lowest values. After 15 months of outside exposure the lightness increased again particularly in the case of beech wood and water glass treated Scots pine. The variation of lightness is influenced by various factors such as wood moisture content and reflectance of light on the wood surface.

The dependence on different wood moisture contents is due to the effect of free water in the cells on the wood colour especially the L-values (Hon and Minemura 2001). The influence of wood moisture content could be reduced because the wood specimens were stored in a climatised room (20°C/65%RH) for three days to reach a climatised wood surface without any cluster of moisture. Furthermore the specimens were not evaluated after a rainfall period to prevent an evaluation of wet specimen surfaces.

Furthermore the surface layer of the specimens which is rich in cellulose fibres after lignin degradation reflects light non-uniformly which may result in a variability of lightness. An increase in lightness during weathering was also observed in previous investigations by Hon and Chang (1984), who reported regained brightness of some wood species

such as Redwood, Southern yellow pine and Douglas fir during outside weathering.

Scots pine sapwood exhibited a rapid change in colour during 6 months of outside exposure (Fig. 3). Siloxane treated and untreated specimens displayed the same level of colour change during the whole evaluation period. The DMDHEU and water glass treated specimens showed reduced change of colour.

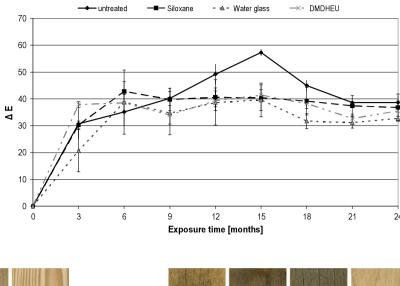
The untreated specimens of beech wood displayed an extensively changed colour within 3 months as well as between 9 and 18 months of outside exposure (Fig. 4). An increase of the overall colour change ΔE was observed in previous investigations during the initial stage of natural and accelerated weathering conditions (Feist and Hon 1984; Hon and Feist 1986). The extensive change of untreated beech wood after 9 months of exposure time can be explained by an increased growth of blue stain on the wood surface (pictures not shown). Between 15 and 18 months the surface of the specimens became greyer and the colour changed at decreased rate again.

The treated specimens showed fewer discolouration during 9 and 24 months of outside exposure.



beech specimens exposed outside (error bars show standard deviation) Abb. 4 Farbänderung von Buche nach Freilandbewitterung (Fehlerindikatoren zeigen die Standardabweichung)

Fig. 4 Change in colour of



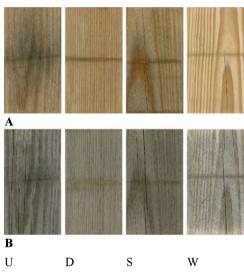


Fig. 5 Weathered specimens of untreated (U), DMDHEU (D), siloxane (S) and water glass treated (W) Scots pine sapwood after 3 months (A) and 12 months (B) of outside exposure

Abb. 5 Unbehandelte (U), DMDHEU (D), Siloxan (S) und Wasserglas (W) behandelte Prüfkörper, Kiefernsplintholz, nach 3-monatiger (A) und 12-monatiger (B) Freilandbewitterung

After three months of outside exposure the untreated specimens displayed an infestation of staining fungi (Figs. 5 and 6) visible as dark coloured spots on the weathered surface. The water glass treated specimens showed no signs of surface discoloration. The DMDHEU and siloxane treated specimens displayed the typical colour from light to dark grey usually found on exposed wood surfaces, but compared to untreated specimens, no dark coloured spots or streaks were visible. After 12 months of outside exposure all specimens showed visible surface discolouration which is attributable to a combination of fungal growth and photo degradation (Figs. 5 and 6). Various studies conclude that this grey surface discolouration of wood is a combined effect of photo degradation and the growth of fungi on the surface of the wood (Feist 1982; Sell 1975).

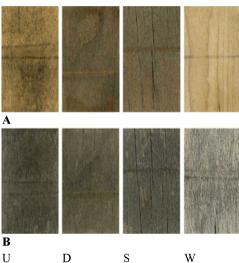


Fig. 6 Weathered specimens of untreated (U), DMDHEU (D), siloxane (S) and water glass treated (W) beech wood after 3 months (A) and 12 months (B) of outside exposure

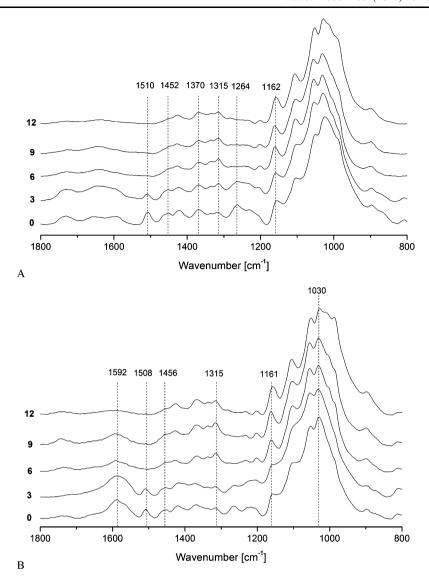
Abb. 6 Unbehandelte (U), DMDHEU (D), Siloxan (S) und Wasserglas (W) behandelte Prüfkörper, Buche, nach 3-monatiger (A) und 12-monatiger (B) Freilandbewitterung

3.2 Chemical changes

The chemical changes particularly lignin degradation was investigated by FTIR-spectroscopy. The lignin absorption of untreated Scots pine decreased with increasing exposure time, visible at the lignin absorption at 1510 cm⁻¹ (stretch vibration in aromatic ring), 1452 cm⁻¹ (CH₂-deformation) and 1264 cm⁻¹ (guaiacyl nuclei) (Schultz and Glasser 1986; Pandey and Theagarajan 1997). These absorptions were absent after 6 months of outside exposure. Absorptions at 1370 cm⁻¹, 1315 cm⁻¹ and 1162 cm⁻¹ which are assigned to cellulosic constituents (Pandey and Theagarajan 1997; Chang and Chang 2001) did not change significantly (Fig. 7). The lignin absorption of untreated beech wood was visible at 1507 cm⁻¹ (stretch vibration in aromatic ring),



Fig. 7 FTIR-spectra of untreated (A), water glass (B), siloxane (C) and DMDHEU (D) treated Scots pine sapwood before and after 3, 6, 9 and 12 months of outside exposure Abb. 7 FTIR-Spektren von unbehandeltem (A), Wasserglas (B), Siloxan (C) und DMDHEU (D) behandeltem Kiefernsplintholz nach 3-, 6-, 9-und 12-monatiger Freilandbewitterung



1459 cm⁻¹ (CH₂-deformation) and 1235 cm⁻¹ (syringyl nuclei). The lignin absorption decreased with increasing exposure time (Fig. 8).

Infrared spectra of water glass treated wood showed absorption at 1030 cm⁻¹ for the Si–O stretching of polysilicate and silica gel. But this absorption is partly overlaid by the C–O absorption bands in cellulose and hemicelluloses of wood. The spectra of water glass treated wood also revealed a reduced intensity of the lignin bands which is related to the lignin bands of untreated wood during 12 months of outside exposure.

The characteristic peaks of siloxane treated wood at 1229 cm⁻¹ (Scots pine) and 1231 cm⁻¹ (beech) assigned to the C–N vibration and at 1657 cm⁻¹ (Scots pine) and 1658 cm⁻¹ (beech) caused by NH₂-bending vibration (Gottwald and Wachter 1997; Bruker 2002) were not clearly visible. These bands were overlaid by absorption bands in untreated wood.

Infrared spectra of DMDHEU treated Scots pine and beech showed an increase in the carbonyl content (1709 and 1726 cm⁻¹) caused by carbonyl groups in DMDHEU (Petersen 1967; Schultz and Glasser 1986; Xie et al. 2005). This strong carbonyl band overlaid native carbonyl group absorptions in untreated wood. Additionally treated specimens displayed an absorbance maxima at 1237 cm⁻¹ (Scots pine) and 1232 cm⁻¹ (beech) for the C–O stretch vibration in the *N*-methylol group of DMDHEU.

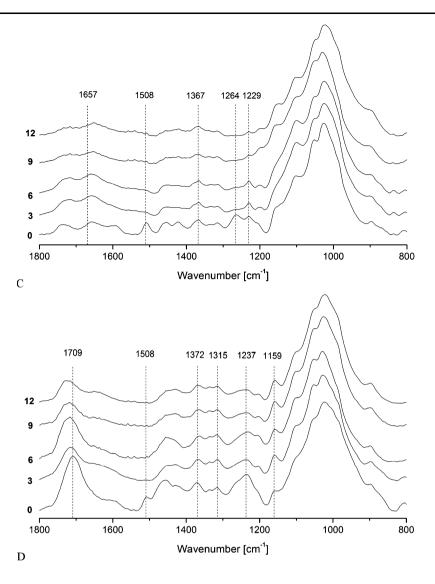
3.3 Weathering characteristics

Generally, the treatments did not prevent lignin from degradation during long-term outside weathering.

Irrespective of the treatments, absorptions of cellulosic constituents did not change significantly as a result of weathering.



Fig. 7 (Continued)



Colour measurements and FTIR spectroscopy showed distinct surface discolouration and lignin degradation during the initial exposure time (3–6 months). The degradation processes of lignin are accompanied by various changes in colour, depending on wood species, time of exposure and band width of the irradiation source (Hon and Minemura 2001). The grey surface colour is a result of the leaching of decay products of lignin (Feist 1983; Sell and Leukens 1971). The surface discolouration was a combination of fungal growth and photo degradation of lignin. The fungal infestation of all treated samples was retarded while the lignin degradation was not. Therefore the lignin degradation did not influence the initial fungal infestation on the treated wood surfaces.

Fungal infestation mostly resulted from wetting the wood surface with liquid water. Free water in the lumens of wood cells over longer periods is essential for fungal growth (Grosser 1985; Eaton and Hale 1993).

In the case of water glass treated specimens the inhibition of fungal growth is not influenced by reduced wood moisture content because the treatment resulted in a high hygroscopicity of silicate and sodium salts in the cell lumens (Furuno et al. 1991, 1992; Furuno and Imamura 1998). Rather the water glass treated specimens showed a highly alkaline pH-value before and after storage under carbon dioxide atmosphere. Highly alkaline pH values can influence spore germination, mycelia growth and fruit body formation (Schmidt 2006; Reiß 1997). Previous investigations also reported high resistance of water glass treated specimens against wood destroying basidiomycetes, because of the high pH-values and the insoluble silicates in the cell lumens (Furuno et al. 1992; Dellith 2006).

Treatments with siloxanes diminish the uptake of liquid water. The reduction in water uptake is caused by blocking the main penetration paths such as pits, ray cells and ray tracheids (Donath et al. 2006). However, the moisture content of the surface layer might still be high enough to allow



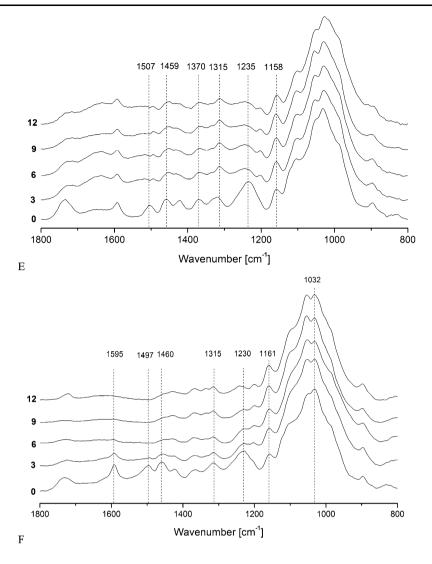
Fig. 8 FTIR-spectra of untreated (E), water glass (F), siloxane (G) and DMDHEU (H) treated beech wood before and after 3, 6, 9 and 12 months of outside exposure

Abb. 8 FTIR-Spektren von unbehandelter (E),

Wasserglas (F), Siloxan (G) und DMDHEU (H) behandelter

Buche nach 3-, 6-, 9und 12-monatiger

Freilandbewitterung



fungal infestation, particularly after rain periods with liquid water on the sample surface.

DMDHEU treatment reduces the speed of liquid water uptake caused by the inclusion of the chemical in the ray cells, the major penetration pathways for water in untreated wood (Xie et al. 2005, 2008). Therefore, fungal infestation particularly during initial stages of outside weathering can be reduced. The decelerated initial infestation is not attributable to a biocidal effect of DMDHEU, because most of the DMDHEU in wood is fixed through covalent bonding to the cell wall or self condensation (Verma et al. 2005). Rather the changed chemical structure of wood modified with DMDHEU particularly lignin and its breakdown products might have an impact to fungal growth on weathered wood surfaces.

Furthermore, a shift of the peak maximum of the carbonyl band of DMDHEU treated Scots pine sapwood from 1707 cm⁻¹ to 1718 cm⁻¹ occurred during weathering. An explanation for this might be the removal of DMDHEU which was linked to lignin molecules and a resultant over-

lapping of carbonyl bands in DMDHEU and those present in wood. These results correspond with those of previous studies (Xie et al. 2005).

3.4 Fungal penetration

In addition to the investigations on fungal growth on the specimen surface the radial penetration of fungal hyphae was studied by SEM.

All specimens were infested by staining fungi after 24 months of outside exposure. Furthermore, all specimens displayed cracks during and after outside exposure. The different treatments could not inhibit the formation of cracks. Sapstaining fungi colonise wood tissues by spreading from cell to cell primarily through pits (Liese and Schmid 1961, 1964; Eaton and Hale 1993). The cross-sectional view of staining fungi penetration (Figs. 9, 10, 11) revealed a radial penetration of fungal hyphae in untreated wood specimens. The untreated specimens exhibited a radial penetration of fungal



Fig. 8 (Continued)

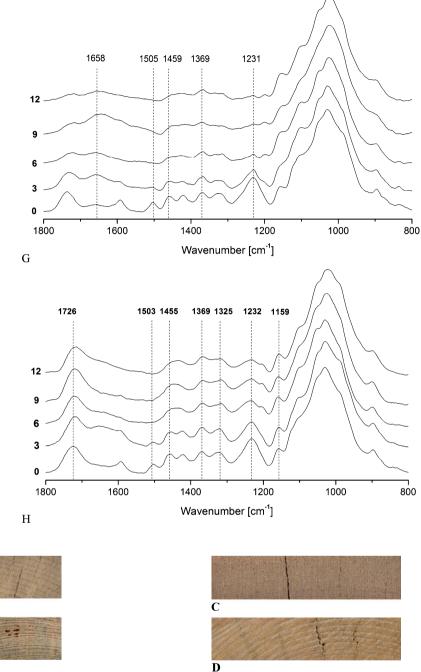


Fig. 9 Cross sectional view of staining fungi penetration in untreated beech wood (A) and Scots pine sapwood (B) after 24 months of outside exposure

В

Abb. 9 Querschnittsansicht der Eindringung von Bläuehyphen in unbehandelter Buche (A) und Kiefernsplintholz (B) nach 24-monatiger Freilandbewitterung

hyphae into the wood tissue (Fig. 12). The growth of fungal hyphae through the pits was clearly visible.

In the cross sectional view no differences of fungal penetration between the wood species were visible. Rather the fungal penetration was influenced by the different chemi-



Fig. 10 Cross sectional view of staining fungi penetration in DMD-HEU treated beech wood (C) and Scots pine sapwood (D) after 24 months of outside exposure

Abb. 10 Querschnittsansicht der Eindringung von Bläuehyphen in DMDHEU behandelter Buche (C) und Kiefernsplintholz (D) nach 24-monatiger Freilandbewitterung

cal treatments. SEM micrographs of wood were evaluated from specimens taken from the labelled area (see arrow in Fig. 9A). The SEM micrographs showed similar results. There were also no differences of fungal penetration depending on the wood species; rather the various treatments



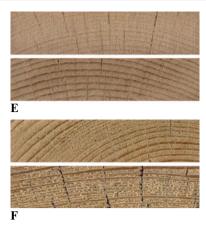


Fig. 11 Cross sectional view of staining fungi penetration in siloxane and water glass treated beech wood (E) and Scots pine sapwood (F) after 24 months of outside exposure

Abb. 11 Querschnittsansicht der Eindringung von Bläuehyphen in Siloxan und Wasserglas behandelter Buche (**E**) und Kiefernsplintholz (**F**) nach 24-monatiger Freilandbewitterung

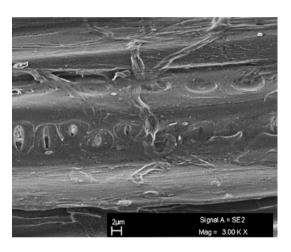


Fig. 12 Radial section of untreated beech wood after 24 months of outside exposure, $3000 \times$

 $\bf Abb.~12~$ Radialschnitt, unbehandelte Buche nach 24-monatiger Freilandbewitterung, $3000\times$

have an influence on fungal penetration into the wood tissue.

In water glass and siloxane treated specimens no radial penetration was visible. The cracks formed during outside weathering did not influence the penetration of fungal hyphae in the wood tissue. No penetration of hyphae was found in the crack areas (Fig. 11). The fungal penetration for untreated wood (Fig. 12), DMDHEU treated wood (Fig. 13), and siloxane and water glass treated wood (Figs. 14 and 15) are shown in the following SEM-micrographs. Only superficial infestation and no radial penetration of fungal hyphae were visible at SEM-micrographs for water glass and siloxane treated specimens, representatively shown in Fig. 14 for siloxane treated wood and Fig. 15 for water glass treated wood. Investigations on siloxane treated Scots pine sapwood

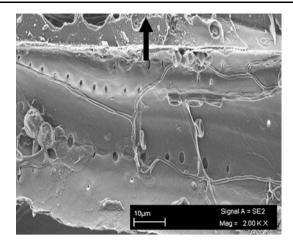


Fig. 13 Radial section of DMDHEU treated beech wood after 24 months of outside exposure, 2000×

Abb. 13 Radialschnitt, DMDHEU behandelte Buche nach 24-monatiger Freilandbewitterung, 2000×

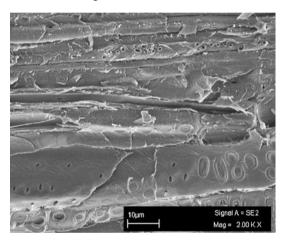


Fig. 14 Radial section of siloxane treated beech wood after 24 months of outside exposure, $2000 \times$

Abb. 14 Radialschnitt, Siloxan behandelte Buche nach 24-monatiger Freilandbewitterung, $2000 \times$

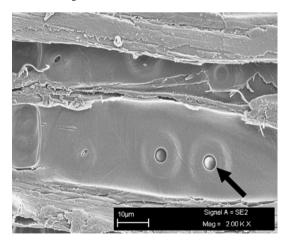


Fig. 15 Radial section of water glass treated Scots pine sapwood after 24 months of outside exposure, $2000 \times$

 ${\bf Abb.~15} \quad {\rm Radialschnitt,\,Wasserglas\,\,behandelte\,\,Kiefernsplintholz\,\,nach} \\ 24-monatiger\, Freilandbewitterung,\,2000 \times$



and beech wood have shown that deposits of siloxane occur in the cell lumens of ray cells and pits (Donath et al. 2006). This might be inhibiting the radial penetration through these pathways. Investigations by Dellith (2006) showed penetration of water glass into cell wall areas and cell lumens of ray cells and deposits onto the pits. The penetration of water glass within the pits is visible in Fig. 15 (see arrow). Hence these penetration paths for fungal hyphae are partly blocked.

In DMDHEU treated specimens radial penetration was reduced. Infestation was visible along the area of radial cracks. The radial penetration depth of fungi starting from the exposed specimens' surface was reduced in DMDHEU treated specimens. But hyphae growth was clearly visible near the weathered surface (Fig. 13, weathered surface in arrow direction). Any fungal infestation through the pits was not visible. The reduction of radial penetration on DMD-HEU treated wood might be caused by blocking of the penetration pathways because of the inclusion of the chemical in the ray cells (Xie et al. 2008).

Based on these results, it was assumed that there is an infestation of fungi with different physiology in treated and untreated specimens. In the case of treated specimens fungi might mainly utilise sugars in the superficial wood tissue and lignin breakdown products on the wood surface as nutritional source. In the case of untreated specimens the fungi are able to grow through the wood tissue along the rays consuming available sugars in these cells and in the superficial wood tissue.

4 Conclusion

Treatments with a sodium water glass solution, an oligomeric siloxane and DMDHEU did not prevent discolouration of the specimens during outside weathering. The chemical treatment did inhibit the infestation by sapstaining fungi on the specimen surface during the initial stage of outside weathering but did not prevent lignin degradation by UV-light. Hence, inhibition of fungal growth during the first months of outside exposure by hindering of lignin breakdown is to be excluded.

The main difference between treated and untreated specimens was the radial penetration of fungal hyphae. It was restricted during 24 months of outside exposure in treated wood specimens. The changes in the wooden structure and the blocking of the fungal penetration pathways caused by the different mode of action of the applied chemicals might be the main influencing factor for restricting fungal growth, particularly the radial penetration by fungal hyphae.

Acknowledgements We thank the "Deutsche Bundesstiftung Umwelt" (DBU) for granting Antje Pfeffer a doctoral scholarship.

Open Access This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

References

- Bruker (2002) Grundlagen der FTIR-Spektroskopie. Bruker Optics, Bremen
- Chang ST, Chang HT (2001) Comparisons of the photostability of esterified wood. Polym Degrad Stab 71:261–266
- Dellith W (2006) Beitrag zum alternativen Holzschutz durch modifizierte Alkalisilikatlösungen als Schutzmittel gegenüber holzzerstörenden Pilzen und Insekten. Dissertation, Bauhaus-Universität Weimar, Fakultät für Bauingenieurwesen
- Donath S (2004) Treatment of wood with silanes. PhD-thesis, University of Göttingen, Institute of Wood Biology and Wood Technology
- Donath S, Militz H, Mai C (2006) Creating water-repellent effects on wood by treatment with silanes. Holzforschung 60:40–46
- Donath S, Militz H, Mai C (2007) Weathering of silane treated wood. Holz Roh- Werkst 65:35–42
- Eaton RA, Hale MDC (1993) Wood—decay, pests and protection. Chapman & Hall, London
- Evans PD, AFA Wallis, Owen NL (2000) Weathering of chemically modified wood surfaces. Natural weathering of Scots pine acetylated to different weight gains. Wood Sci Technol 34:151–165
- Feist WC (1982) Weathering of wood in structural uses. In: Meyers R, Kellogg R (eds) Structural uses of wood in advers environments. Van Nostrand Reinhold, New York, pp 156–178
- Feist WC (1983) Weathering and protection of wood. In: Proceedings of the 79th annual meeting of the American Wood-Preservers Association, Kansas City, pp 195–205
- Feist WC (1990) Outdoor wood weathering and protection. In: Barbour RM, Rowell JR (eds) Archaeological wood: properties, chemistry and preservation. Am Chem Soc, Washington, pp 263–298
- Feist WC, Hon DNS (1984) Chemistry of weathering and protection. In: Rowell RM (ed) The chemistry of solid wood. Am Chem Soc, Washington, pp 401–451
- Furuno T, Imamura Y (1998) Combinations of wood and silicate. Part 6: biological resistances of wood-mineral composites using water glass-boron compound system. Wood Sci Technol 32:161–170
- Furuno T, Uehara T, Jodai S (1991) Combinations of wood and silicate. Part 1: impregnation by water glass and applications of aluminium sulfate and calcium chloride as reactants. Mokuzai Gakkaishi 37:462–472
- Furuno T, Shimada K, Uehara T, Jodai S (1992) Combinations of wood and silicate. Part 2: woodmineral composites using water glass and reactance of barium chloride, boric acid and borax and their properties. Mokuzai Gakkaishi 38:448–457
- Gottwald W, Wachter G (1997) IR-Spektroskopie für Anwender. Wiley VCH, Weinheim
- Grosser D (1985) Pflanzliche und tierische Bau- und Werkholzschädlinge. DRW-Verlag, Leinfelden-Echterdingen
- Hon DNS (1981) Photochemical degradation of lignocellulosic materials. In: Grassi N (ed) Developments in polymer degradation. Applied Science Publishers, London, pp 229–281
- Hon DNS (2001) Weathering and photochemistry of wood. In: Hon DNS, Shiraishi N (eds) Wood and cellulose chemistry. Dekker, New York, pp 513–546
- Hon DNS, Chang S-T (1984) Surface degradation of wood by ultraviolet light. J Polym Sci, Polym Chem Ed 22:2227–2241
- Hon DNS, Feist WC (1986) Weathering characteristics of hardwood surfaces. Wood Sci Technol 20:169–183



- Hon DNS, Minemura N (2001) Color and discoloration. In: Hon DNS, Shiraishi N (eds) Wood and cellulose chemistry. Dekker, New York, pp 385–442
- Krause A, Jones D, Van der Zee ME, Militz H (2003) Interlace treatment—wood modification with N-methylol compounds. In: Van Acker J, Hill CAS (eds) Proceedings of the first European conference on wood modification. Ghent. Belgium, pp 317–327
- Liese W, Schmid R (1961) Licht-und elektronenmikroskopische Untersuchungen über das Wachstum von Bläuepilzen in Kiefern- und Fichtenholz. Holz Roh- Werkst 19:329–337
- Liese W, Schmid R (1964) Über das Wachstum von Bläuepilzen durch verholzte Zellwände. Phytopathol Z 51:385–393
- Militz H (1993) Treatment of timber with water soluble dimethylol resins to improve their dimensional stability and durability. Wood Sci Technol 27:347–355
- Miniutti VP (1964) Microscale changes in cell structure at softwoods surfaces during weathering. For Prod J 14:571
- Pandey KK, Theagarajan KS (1997) Analysis of wood surfaces and ground wood by diffuse reflectance (DRIFT) and photoacoustic (PAS) Fourier transform infrared spectroscopic techniques. Holz Roh- Werkst 55:383–390
- Petersen H (1967) Beziehungen zwischen chemischer Konstitution und Methylolierbarkeit NH-gruppenhaltiger Verbindungen, 1 Mittelung. Textilveredelung 2:744–757
- Plackett DV, Dunningham EA, Singh AP (1996) Chemical modification of lignocellulosic materials. In: Hon DNS (ed) Chemical modification of lignocellulosic materials. Dekker, New York, pp 277–294
- Reiß J (1997) Schimmelpilze. Lebensweise, Nutzen, Schaden, Bekämpfung. Springer, Berlin
- Schmidt O (2006) Wood and tree fungi. Springer, Berlin
- Schoeman MW, Dickinson DJ (1997) Growth of *Aureobasidium pullulans* on lignin breakdown products at weathered wood surfaces. Mycologist 11:168–172

- Schultz TP, Glasser WG (1986) Quantitative structural analysis of lignin by diffuse reflectance Fourier transform infrared spectrometry. Holzforschung 40:37–44
- Sell J (1975) Basic requirements for the surface treatment of exterior wood: a review of partinent literature. Holz Roh- Werkst 33:336– 340
- Sell J, Leukens U (1971) Investigations of weathered wood surfaces— Part II: Weathering phenomena of unprotected wood species. Holz Roh- Werkst 29:23–31
- Van der Zee ME, Beckers EPJ, Militz H (1998) Influence of concentration, catalyst and temperature on dimensional stability of DMD-HEU modified Scots pine. Document No IRG/WP/98-40119. The International Research Group on Wood Preservation, Stockholm
- Verma P, Mai C, Krause A, Militz H (2005) Studies on the resistance of DMDHEU treated wood against white-rot and brown-rot fungi. Document No IRG/WP/05-10566. The International Research Group on Wood Protection, Stockholm
- Verma P, Dyckmans J, Militz H, Mai C (2008) Determination of fungal activity in modified wood by means of micro-calorimetry and determination of total esterase activity. Appl Microbiol Biotechnol 80:125–133
- Xie Y, Krause A, Mai C, Militz H, Richter K, Urban K, Evans PD (2005) Weathering of wood modified with the *N*-methylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea. Polym Degrad Stab 89:189–199
- Xie Y, Krause A, Militz H, Mai C (2008) Weathering of uncoated and coated wood treated with methylated 1,3-dimethylol-4,5-dihydroxyethyleneurea (mDMDHEU). Holz Roh-Werkst 66:455–464
- Yusuf S (1996) Properties enhancement of wood by cross-linking formation and its application to the reconstituted wood products. Wood Res 83:140–210

