Weathering Resistance of Modified Wood – A Review

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Abstract: Wood in exterior structures undergoes certain chemical and physical changes which cause slow degradation of its surface commonly known as weathering. Major aspects of the weathering of wood are aesthetic effects such as discolouration, loss of lightness, surface roughening, cracking, checking, dirt uptake, wood cell erosion and growth of mould and staining fungi. Wood modification becomes an ever-popular method of enhancing wood properties, primarily dimensional stability and biological resistance. The wood modification processes that have been successfully commercialized in Europe in the past two decades are presented briefly. To what extent modification of wood affects the resistance of wood to weathering is also an important aspect for exterior wood applications, especially where appearance is important. The aim of this paper is to review the literature on weathering resistance of wood modified by today's commercial modification techniques including thermal modification in various shield media, acetylation, furfurylation and modification with N-metylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU). The effect of modification on the weathering performance of wood during natural or artificial exposure was analysed with respect to optical appearance, surface erosion, crack formation, mould growth and performance of system coating - wood.

Keywords: weathering, thermally treated wood, acetylated wood, furfurylated wood**,** DMDHEU-modified wood

Introduction

Wood modification is an increasingly popular approach to improving wood properties such as dimensional stability, water resistance and durability (Hill, 2006). Due to environmental issues related to the use of toxic preservatives and tropical hardwood the research on wood modification has intensified in the last two decades although the first research on wood modification dates back to the first half of the 20th century (Stamm, Hansen, 1935, Stamm, 1946, Tarkow, 1946).

Among numerous methods of wood modification described in the literature, only a few of them have found successful industrial application. Among them are thermal treatment, acetylation, furfurylation and modification with N-methylol resin.

Modified wood is used for both interior and exterior applications, especially for decks and patios, outdoor claddings, facades, garden furniture, noise barriers, fences, ship decks etc. For these applications weathering resistance which affects aesthetic service life is very important to users. Weathering is the general term used to define the slow degradation of materials exposed to the weather (Williams, 2005). Sunlight (especially UV and visible light) and water play a major role in weathering of wood, although the synergistic contribution from the other factors (temperature, oxygen, pollutants) plays a significant role (Raczkowski, 1980, Derbyshire et al., 1997, Tolvaj et al., 2015, Varga et al., 2017). Photochemical degradation is manifested by an initial colour change, followed by loosening of wood fibers and gradual erosion of the wood surface (Williams et al., 1995). In addition to the slow erosion process (5-6 mm/century), other processes like checks developing, raising grain and mildew colonizing the surface also occur. The boards may warp and cup, particularly in decking applications (Williams et al., 1995). Chemical deterioration involves a complex sequence of free-radical reactions (Feist, 1988). Lignin has been found to be a major reactant in photochemical degradation where free radicals are involved (Hon, Feist, 1986, Hon, Ifju 1978, Hon et al., 1980). The photo degradation mechanism of lignin is complex with different pathways giving various types of phenoxy radicals leading to chain cleavage and coloured quinonoid molecules (Georg et al., 2005). It has been established that free radicals and singlet oxygen play important roles in discoloration and deterioration reactions of wood surfaces (Feist, Hon, 1984). At a microscopic level, the chemical nature of the weathered wood surface is changed, and the ultra structure of wood cell walls is damaged (Chang et al., 1982). Lignin is a much better absorber of light than cellulose and is therefore degraded faster than cellulose. Leaching of photo-degraded wood fragments (mainly from lignin) by rain results in increased surface roughness (washboard effect) and thereafter underlying cell layers are exposed to further erosion (Feist, 1988). Under artificial weathering conditions this process causes bleaching of wood due to the predominance of surface cellulose (Xie et al., 2008). However, another mechanism of surface greying of naturally weathered wood surfaces usually predominates, particularly in the presence of moisture, which is due to the colonisation so staining fungi. The most frequently observed species is *Aureobasidium pullulans*, which under favourable conditions grows not only on wood surfaces but also on the surface of coatings (Feist, 1988). This silver-gray adversely affects the appearance of wood even though does not degrade it. Although this weathering process develops primarily on the surface of wood, the susceptibility to photochemical degradation significantly reduces wood´s aesthetic values and performance (Jirous-Rajkovic et al., 2004).

Wood modification is carried out in order to improve biological resistance and dimensional stability of wood and to a secure high-performing, sustainable wood material. To what extent modification of wood affects the resistance to weathering is also an important aspect of wood application in outdoor conditions, especially as facade materials. This paper reviews the literature with regard to the weathering resistance of thermally modified wood, acetylated wood, furfurylated wood and DMDHEU modified wood.

Thermal modification

In recent years, wood products that do not contain toxic preservatives and which have increased performance and sustainability are increasingly demanded by customers, thus contributing to the popularity of thermally modified wood. Thermal modification or heat treatment is controlled pyrolysis of wood being treated at high temperatures between 180 °C and 240 °C under the oxygen free atmosphere to avoid burning, involving either steam, nitrogen or oil (Homan, Jorrisen, 2004). The treatment temperature and atmosphere are critical variables and the thermally induced chemical changes in the wood differ between various processes (Tjeerdsma et al., 2002). Higher temperature is known to lead to more severe degradation of the material. The process is selected to optimise the level of the thermally induced changes in the wood keeping the strength reduction and increase in brittleness under control (Homan, Jorrisen, 2004, Ormondroyd et al., 2015). Thermal modification changes the chemical composition of wood to some degree, resulting in mass loss of thermally treated wood, improvement in dimensional stability, reduction in the equilibrium moisture content, improvement in dimensional stability, improvement in decay resistance, reduced abrasion resistance, cracking tendency, reduction in impact toughness and modulus of rupture (MOR) for more intense treatments (Tjeerdsma et al., 1998, Kamdem et al., 2002, Mayes and Oksanen, 2002, Yildiz et al., 2005a, Yildiz et al., 2005b, Srinivas, Pandey, 2012, Xie et al., 2013, Ormondroyd et al., 2015). The process induces a darker coloration of wood depending to the type, duration and temperature of the process. The longer the treatment and the higher the temperature, the more intensive is colour change. Ddarkening during thermal modification is often attributed to the formation of coloured degradation products from hemicelluloses (Sehlstedt–Persson, 2003, Sundqvist, 2004) and to extractives that seem to participate in the colour formation of heat treated wood (Estevez et al., 2008, Sundqvist, Morén, 2002). This dark colour change is often seen positively, especially in hardwoods resembling tropical wood species (Chen et al., 2012, Bekhta, Niemz, 2003, Mitsui et al., 2003). It was shown that exposure of wood to high temperature changes both its chemical properties and its appearance (Nuopponen et al., 2004). Heat treatment is known to promote a range of chemical

changes of different wood constituents (Tjeerdsma et al., 1998). Thermal stability of the polymeric wood constituents of wood differs according to their chemical structure: hemicelluloses present a lower degree of polymerization and higher reactivity due to their amorphous structures, which are degraded first, followed by lignin and cellulose (Hakkou et al., 2005, Hakkou, 2006). The environmental impact of the heat treatment process is low, heat is introduced into the treatment system and smokes emitted from wood thermal degradation can be retrieved, condensed and purified (Petrissans, 2007 as cited in Candelier, 2016). It was reported that thermal modification generally reduced most of the strength properties of wood. Mechanical properties (bending strength, MOR, and bending stiffness, MOE) of heat-treated wood decreased regardless of process parameters. A decrease in hydroxyl groups reduced the hygroscopic nature, resulting in increased dimensional stability of thermally modified wood (Srinivas, Pandey, 2012). Reduction in the modulus of elasticity (MOE) is generally less than the modulus of rupture (MOR). Both the MOR of bending and impact strength decrease by up to 50 % (Xie et al., 2013). The mode of failure of thermally modified wood in mechanical tests is in most cases brittle and thermally modified wood and should therefore not be used in load-bearing structures (Hill, 2006). The degree of strength losses depends on temperature, treating period and shield gas used in the process (Xie et al., 2013).

Thermal modification processes are the most common and established wood modification methods, now commercialised in several European countries. Over the last decade, thermal modification has been developed in five main product markets in Europe; hardwood flooring, siding/cladding, decking, saunas/wall paneling, and specialties. Wood treated at a high temperature has always strong smell just after the treatment which decreased in intensity after a few days, but could remain for several months. It is believed to be related to the release of furfural (Militz, 2002). Miklečić et al. (2016) studied the influence of thermal modification of beech wood (*Fagus sylvatica* L.) on surface properties and reported that acidity and water contact angle on beech wood was higher and polar component of surface free energy was lower after the thermal modification, which might have an impact on wetting and adhesion of waterborne coatings.

The main commercial thermal modification processes are covered by patents, and products are treated under names such as *ThermoWood, Platowood*, *Retiwood* , *Le Bois Perdure* and, *Oil-Heat-Treated Wood* - OHT (Ormondroyd et al., 2015).

The *ThermoWood* process is the most common commercial thermal modification process. It is licensed to the members of the Finnish Thermowood Association and is divided into three phases: Phase 1. The kiln temperature is raised at a rapid speed using heat and steam to a level of around 100 ºC. Phase 2. Once the high temperature kiln drying has taken place the temperature inside the kiln is increased to a

level between 185 ºC and 230 ºC, and maintained at the target temperature for 2-3 hours. Phase 3. The final stage is to lower the temperature down using water spray systems and then once the temperature has reached 80-90 ºC remoisturising and conditioning takes place to bring the wood moisture content to a useable level over 4 % (Hill, 2006). ThermoWood is recommended for use in hazard classes 1 to 3 in accordance with EN-335-1 without the need for any further chemical protection.

The *Plato* process is a two –stage hygroterhmal process in relatively mild conditions. This process leaves high cellulose content in wood which is crucial to ensure final mechanical properties. The process was developed and is used by the Plato Company in the Netherlands for the production of flooring, cladding, decking and rough sawn timber (Ormondroyd et al., 2015, Sandberg et al., 2017).

The retification process is mild pyrolysis of wood in nitrogen atmosphere, industrialised in France and sold under name *Retiwood*. The name of process comes from the French word rétification, which is the abbreviation of réticulation (creation of chemical bonds between polymeric chains) and torréfaction (roasting).The second French process is named Le Bois Perdure (the Perdure process). This process is relative close to the retification process and the properties of modified wood processed with both methods are similar. The wood is heated up to 230 °C in a steam atmosphere, the steam being generated from the water from the green wood (Sandberg et al., 2017). The paint adhesion on this wood is drastically reduced (Homan, Orison, 2004).

The oil heat treatment process involves heating of wood in vegetable oil (sunflower, rape seed oil or linseed oil). Wood is immersed into hot oil and heated to temperatures between 180 and 220 °C to ensure optimal durability without strength reduction. The process was developed in Germany and is sold under name *Menz Holz –OHT.*

Weathering of thermally treated wood

It has been established that the brownish colour of thermally modified wood is not stable against light exposure (Jämsä, Viitaniemi, 2001, Temiz et al., 2006, Nuopponen et al., 2004, Hill, 2009). Wood treated at high temperature turns grey in colour after the exposition to sun and UV, for a few weeks and it is generally assumed that such grey colour is more homogenous than for untreated wood.

It was reported that short-term colour stability of retified ash, beech, poplar and pine wood exposed to artificial weathering was better than that of unmodified wood

(Ayadi et al., 2003).However, the original dark brown colour of the uncoated thermally treated spruce (*Picea abies*) and pine wood (*Pinus sylvestris*) panels were not stable when exposed outdoors and turning grey (Jämsä et al., 2000). The performance of the coated thermally modified and unmodified spruce wood and pine wood was monitored during five years of exposure. Although the moisture content of thermally modified wood was found to be at a lower level compared to unmodified wood, no decrease in surface growth of coated wood was detected. The thermally treatment used did not have an influence on mould and blue stain growth on coated wood in service (Aloha et al., 2002).

Thermally modified beech (*Fagus sylvatica*) in a nitrogen atmosphere was more resistant to natural and artificial weathering than unmodified control and showed a reduction of photochemical degradation and an improvement of the resistance against discolouring mold fungi during natural weathering. European spruce (*Picea abies*), conversely, exhibited minor part of these improvements (Feist, Sell, 1987). However, thermal modification of either species had small, but measurable effects on the performance and durability of semitransparent and film forming stains applied to the samples. Feist and Sell (1987) assume that reduced photochemical degradation after thermal modification might be due to low equilibrium moisture content of thermally modified wood because the wood moisture content strongly influences photochemical degradation (Hon, 1981). Nuopponen et al. (2004) studied chemical changes of thermally modified and unmodified Scots pine samples after 7 years of natural weathering in Finland and reported that the lignin content of thermally modified samples remained higher than of unmodified samples and degradation products did not leach out as easily as in the case of the unmodified samples. It might be due to the increased condensation of lignin induced by thermal treatment.

Miklečić et al. (2011) measured discoloration of uncoated and clear coated thermally modified three wood species: beech (*Fagus silvatica* L.), ash (*Fraxinus excelsior* L.) and hornbeam (*Carpinus betulus* L.) and established that modified wood samples discoloured slowly compared to unmodified samples. Accordingly, FTIR spectra of thermally modified ash, beech and hornbeam wood samples exposed to UV light showed similar chemical changes as unmodified wood samples exposed to UV light, but less pronounced.

Thermally treated Oriental beech (*Fagus orientalis* L.) wood also showed better colour stability compared to non treated samples after three months of natural weathering during winter. Natural weathering affected thermally modified beech wood samples less than unmodified samples in terms of gloss loss and surface roughness. Also, higher temperature and duration of thermal modification yielded better surface properties after natural weathering (Turkoglu et al., 2015).

Photo degradation of both thermally modified and unmodified Larix spp. wood was evaluated in terms of colour, microstructure, and chemical changes during accelerated weathering tests. Ultraviolet radiation caused immediate colour change and SEM observation showed deformations and cracks in both modified and unmodified samples. It was found that thermal modification was effective in improving colour stability only in the first stage of exposure to artificial weathering, but was ineffective in improving UV resistance of wood over long-term photo degradation conditions (Xing et al., 2015).

Thermally modified Scots pine (*Pinus sylvestris*) showed better surface characteristics than unmodified Scots pine after artificial weathering. Artificial weathering caused an increase in surface roughness and a decrease in glossiness of Scots pine wood. In general, higher temperature and duration of thermal modification resulted in lower surface roughness and higher gloss of Scots pine wood after artificial weathering (Baysal et al., 2013).

Deka et al. (2008) found that colour changes of thermally modified spruce wood (*Picea abies* L.) were lower than unmodified spruce wood after long term artificial UV-light exposure. It might be due to an increase in lignin stability by condensation at the time of the thermal modification process at 210 C. Similarly, oil-heat-treated pine wood (Pinus sylvestris) exhibited lower colour differences after one year of outdoor exposure in comparison to colour changes of weathered untreated wood (Petrič et al., 2007).

Yildiz et al. (2011) studied colour stability and chemical changes of thermally treated alder wood (*Alnus glutinosa* L.) after natural weathering. They reported that thermal modification delayed/decreased the rate of colour change caused by weathering factors but did not prevent it. FTIR-ATR spectroscopy showed significant deformation and degradation in wood components, especially in the hemicelluloses of thermally modified samples. Increasing the heat temperature and exposure time affects degradation of hemicelluloses.

There is inconsistency in the literature about whether thermally modified wood is susceptible to cracking when it is exposed outdoors.

Vernois (2001) reported that cracking due to dimensional changes was reduced by heat treated wood in comparison to natural wood.

Conversely, cracking of the thermally modified spruce and pine wood exposed outdoors without coating was at the same level as that of the unmodified wood and application of unpigmented or low build stains and oils did not prevent cracking of the thermally modified wood (Jämsä et al., 2000).

Miklečić et al. (2010) reported that uncoated unmodified samples of all three wood species (oak, ash and beech) had less surface cracks than thermally modified uncoated samples during accelerated weathering. Oil treatment reduced the cracking of thermally modified samples. Since the oil finish is also susceptible to photochemical degradation, the regular maintenance according to the manufacturer´s instructions is essential for a pleasant appearance of oiled surface during outdoor use.

Feist and Sell (1987) found more cracking and grain-raising on thermally modified spruce wood in nitrogen atmosphere than on unmodified wood, and surfaces were noticeably rougher after 14 months of outdoor exposure. On the contrary, thermally modified beech wood samples were smoother than unmodified ones with little noticeable differences in cracking. Both semitransparent penetrating and film-forming stains performed worse on thermally modified spruce samples than on the unmodified samples. The semitransparent stains performed somewhat better on thermally modified beech wood than on unmodified samples, while the film-forming stain performed poorly on both thermally modified and unmodified samples (Feist, Sell, 1987.). Vernois (2001) reported that surface tension of wood is drastically affected after heat treatment and that painting and finishing usually used for untreated wood cannot be used. Regardless of that, Jämsä et al. (2000) reported that thermally modified wood is comparable to untreated wood as a substrate for coatings and no alterations in coating recommendations are needed when considering coating of thermally modified wood.

Normal painting processes present no problems, but when electrostatic painting is used, heat-treated wood requires extra moisturising (Jämsä, Viitaniemi, 2001). Deka and Petrič (2008) studied the effect of two water-borne acrylic coating on photo degradation of thermally modified wood and unmodified wood and established that whole substrate-coating system showed better photo stability when thermally modified wood was used as substrate.

Pavlič (2009) studied the compatibility of nine different coatings with thermally modified Scotch pine wood (*Pinus sylvestris* L.). Coatings applied on thermally modified wood exhibited better performance than coatings on unmodified wood. This could be explained by the changed characteristics of thermally modified wood such as lower equilibrium moisture content, lower water permeability, increased dimensional stability, better UV stability and resistance to blue stain fungi in comparison to unmodified wood.

Better penetration of the coating into modified wood and better wetting of thermally modified wood with coatings were also shown. After one year of exterior weathering the solvent borne coatings exhibited better performance than waterborne coatings (Pavlič, 2009).

After more than 10 years of using *ThermoWood* products in a built environment the assessment results showed that colour changed to gray and that fibre erosion and surface shakes were quite common for *ThermoWood* products (Ala-Viikari, Mayes, 2009). Pigmented film- forming coating for decking had very short life span and required regular maintenance, although oil based finishes were a better option despite the fact that the colour would not be maintained. Miklečić et al. (2017) studied the interaction of thermally modified beech wood with nanoparticles-modified waterborne polyacrylate coating during outdoor and artificially exposure. The results showed that addition of TiO_2-rutil and ZnO nanoparticles to the coating improved the colour stability of thermally modified beech wood. However, nanosized ZnO increased peeling and cracking of coating, and caused a reduced adhesion of coating on thermally beech wood.

Acetylation

The acetylation of wood is a chemical modification of the wood cell wall using acetic anhydride. The reaction of acetic anhydride with wood polymers results in the etherification of the accessible hydroxyl groups in the cell wall with the formation of by-product, acetic acid (Rowell, 2006). This reduces the moisture sorption and improves the dimensional stability of the wood due to the reduction of free sites able to bind water through hydrogen bonds and bulking the cell wall back to its green volume (Rowell, 2016). The standard impregnation process basically consists of an impregnation of oven-dried wood with liquid phase acetic anhydride followed by conventional or microwave heating to initiate the chemical reaction with wood polymers (Rowell, 2006, Homan, Jorrisen, 2004). The reaction can be carried out with or without catalyst in a range of temperatures between 100 and 130 °C (Gerardin, 2016). After reaction, the mixture of acetic acid and acetic anhydride is removed from wood (Homan, Jorissen, 2004). Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization (Rowell, 2016). Acetylated wood consists only of carbon, hydrogen, and oxygen, and it contains absolutely of nontoxic constituents (Hill, 2006). Acetylated wood is presently commercialised by the company Accsys Technologies in Arnhem, The Netherlands (Mantanis, 2017) and is marked under commercial name Accoya for solid wood utilizing the radiate pine (*Pinus radiata*) and alder (*Alnus* spp.) (Sandberg et al., 2017). *Accoya´s* advantage over other modified wood materials is, in some applications, bright colour (Larrson Brelid, 2013).There is a slight wood colour change (usually darkening) upon acetylation with uncatalysed acetic anhydride (Rowell, 1983, Dong et al., 2016). It was found that acetylated wood had improved dimensional stability and decay resistance (Rowell, 1983, Rowell, 2006) and improved resistance to attack by termites and marine organisms

(Alexander et al., 2014, Jonson, Rowell, 1988). Studies performed with different wood species showed that equilibrium moisture content decreased as the degree of acetylation increased and that wood species had no significant effect on dimensional stabilisation as long as similar weight percent gain levels were obtained (Gerardin, 2016).

Weathering of Acetylated Wood

There are many researches related to the effects of acetylation on the resistance of wood to weathering.

Many researches have demonstrated that acetylation increases the weather resistance of wood.

(Plackett et al., 1992) reported that acetylation provided some protection to radiata pine (Pinus radiata) against accelerated weathering. Radiata pine veneers were more colour stable and resistant to surface checking than untreated veneers during accelerated weathering (Plackett et al., 1992). Dunningham et al. (1992) confirmed the results of improved checking resistance of acetylated veneers when compared with untreated veneers after 28 weeks natural weathering, but found that acetylated radiata pine veneer was only slightly less grey than untreated radiata pine veneer after 28 weeks of natural weathering. The degradation of lignin could be hindered due to acetylation and increased moisture resistance and dimensional stability could also restrain the photo degradation mechanism of wood. Immamura (1993) reported that erosion rate of earlywood and latewood and wood substance loss during weathering of acetylated spruce wood (*Picea jezoencis* Carr.) and sugi (*Cryptomeria japonica* D.Don) were significantly reduced compared to unmodified wood. Blocking accessible hydroxyl groups of lignin and holocellulose by using acetyl units reduced water uptake and retarded subsequent leaching of wood degradation products. Feist et al. (1991) established that acetylation of aspen wood helps protect wood from photochemical degradation during accelerated weathering. Erosion due accelerated weathering was reduced by 50 % compared to that of untreated wood. He found that acetylation protects the lignin component in wood to a small extent and the hemicelluloses component to a larger extent. The free radical process may be disrupted during weathering when these components are acetylated and the weathering process is then retarded.

However, Kalnins (1984) found that acetylated redwood was not resistant to photo degradation.

Anyway, it was found that the photo degradation of acetylated modified wood differs from unmodified wood but is not prevented (Hon 1995, Torr et al., 1996). Acetylated wood only shows initial stability against UV radiation and thereafter it begins to fade and grey.

Honn (1995) reported that acetylated southern yellow pine (*Pinus* spp.) wood exhibited a colour stabilization effect better than untreated wood after the initial 28 days of irradiation and after that this stabilization effect diminished steadily and discolouration started. Electron spin resonance (ESR) of photo irradiated acetylated wood revealed that active methyl and stable phenoxy radicals are generated. X-ray photoelectron spectroscopy (XPS) studies on acetylated Pinus radiata wood exposed to ultraviolet light have shown that de-acetylation occurs and that acetylation is ineffective in preventing photo-oxidation of wooden surfaces (Torr et al., 1996). Evans et al. (2000) found that depolymerisation of cellulose and erosion of the middle lamella still takes place after acetylation but mass loss is reduced and latewood cells maintained their structure. They also reported that acetylation of scots pine (*Pinus sylvestris* L.) veneers to low weight gains from 5 – 10 % increased the degradation of the modified veneers during natural weathering, but at a higher weight gain of 20 % the photostabilty of acetylated wood increased. The substitution of lignin phenolic hydroxyl groups, which occurs preferentially at low weight gains, appears to reduce the photo stability of wood. The substitution of hydroxyl groups on cellulose in wood, which occurs as a result of acetylation to high weight gains, appears to have beneficial effects on the photo stability of cellulose. However, photo protective effects of acetylation were reduced with a prolonged exposure of modified wood to weather because deacetylation of wood surface occurred (Evans, 2000).

Ohkoshi (2002) used Fourier transform infrared photoacustic spectroscopy analysis to characterize the surface changes in acetylated wood during light irradiation. He found that generation of carbonyl and lignin degradation diminished in the acetylated wood in comparison with unmodified wood, indicating that acetylation restrained the photochemical degradation of wood.

Temiz et al. (2006) also reported that acetylated scots pine wood (*Pinus sylvestris* L.) exhibited lower colour changes compared to unmodified, thermally modified and silicon modified wood. Acetylation possibly provides better colour resistance to wood surface by blocking the reactive sites of photo-induced degradation. The ability of acetylation to reduce checking and erosion of wood during weathering could be explained by the increased dimensional stability and hydrophobicity of the modified wood. (Evans, 2009). Lathela and Kärki (2015) reported that artificial weathering changed the colour of acetylated scots pine (*Accoya*) rapidly, after which the surfaces remained stable, as well as lighter and cleaner by visual review.

Acetylation of wood was shown to have positive effects on performance of coatings.

Reduced swelling and shrinkage of wood results in reduced stress in the coating, which enhances durability of the exterior wood coating system and thereby decreases the maintenance frequency (De Meijer, 2002).

This stability could be due to the higher checking resistance of acetylated wood when exposed outdoors which is result of the bulking of the cell wall of the modified wood by the acetyl substituents (Hill, 2006).

Schaller and Rogez (2007) studied light stabilization of acetylated wood and reported that acetylation partly protects lignin from photo degradation but there is still need to protect the acetylated wood with coating that has sufficient UV-VIS light protection with UV absorber and lignin stabilizer for better long term performance in terms of colour retention. The colour of acetylated Radiata pine (*Pinus radiata*) *Accoya* wood was bleached during artificial weathering. Mitsui (2010) stated that photo bleaching of acetylated wood was mainly caused by visible light. Scots pine (*Pinus sylvestris* L.) panels coated with an alkyd primer and two layers of acrylic top coats showed a considerably improved service life than unmodified coated panels after 13 years of outdoor exposure in Sweden (Larsson Brelid, Westin, 2007).The alkyd coating system (alkyd primer and alkyd topcoat) performed slightly poorer on the acetylated panels compared to unmodified panels indicating that the more acidic surface of the acetylated panels increased the aging of the alkyd coating making it more brittle (Larsson Brelid, Westin, 2007).

Bongers et al. (2005) were also reported that acetylated wood had a significantly better result with respect to long term coating performance compared to unmodified wood. Especially the acrylic white opaque coating was in good condition even after nine years of outdoor exposure.

It has been reported that acetylated hornbeam wood (*Carpinus betulus* L.) was less prone to crack during natural weathering and accelerating checking test (Fodor et al., 2017), but the modification did not hinder the fading and greying caused by ultraviolet light (Fodor, Nemeth, 2015). The photo degradation of lignin was confirmed by the FTIR spectra. Coating the samples with boiled linseed oil decreased the rate of colour change and checking (Fodor, Nemeth, 2015).

The development of staining fungi and mould on wooden surfaces is of great economic importance due to the loss of surface quality and a negative perception of wood (Gobakken et al., 2014). The results of the research concerning the resistance of acetylated wood surfaces to mould and blue stain fungi are very different (Bongers, De Meijer, 2012, Gobakken et al., 2014). It has been shown in several

studies that acetylated wood is not resistant against mould and blue stain fungi (Beckers et al., 1994, Wakeling et al., 1992, Gobakken, Lebow, 2010, Gobakken et al., 2010, Gobakken, Westin, 2008). The similar result was obtained by Gobakken et al. (2014) in an outdoor test, but in a laboratory test the result was completely different. Acetylated wood had the least growth of mould and staining fungi of the modified wood substrates in the laboratory test, but the opposite was recorded for the outdoor test. These differences in the results indicate the importance of testing both in laboratory and in outdoor conditions.

Furfurylation

Chemical modification of wood with furfuryl alcohol, known as furfurylation of wood, has been known for several decades (Goldstein, 1959, Stamm, 1977).

The process is based on in situ polymerisation of furfuryl alcohol which is a bio derived chemical (Gerardin, 2016). The acid catalyst reaction chemistry of furfuryl alcohol is very complex resulting in a highly branched and cross-linked furan polymer grafted to wood cell wall polymers (Homan, Jorissen, 2004, Xie et al., 2013, Mantanis, 2017). Furfuryl alcohol molecules penetrate into the wood cell wall and polymerize in situ. This results in a permanent swelling of the wood cell walls. It is unclear whether or not chemical bonds exist between the furfuryl alcohol polymer and the wood (Sandberg et al., 2017, Mantanis, 2017).

The properties of furfurylated wood depend on the retention of grafted/polymerised furfuryl alcohol in the wood (Gerardin, 2016). Wood modified with furfuryl alcohol to certain weight percent gains (WPGs) showed greatly improved dimensional stability, reduced water uptake and increased resistance to biological degradation (Lande et al., 2004, Epmeier et al., 2004, Treu et al., 2009) while leachates from furfurylated wood had low toxicity (Pilgard et al., 2010). The rich, brown colour of furfurylated wood is attractive and makes it possible for light-coloured woods to simulate dark, expensive wood. The advantage of dark colour is the ability to mask many blemishes and discolorations of native woods. Furfurylated wood is characterized by greater hardness, elastic and rupture moduli, as compared to untreated wood but, on the other hand, it is more brittle (Mantanis, 2017).

Nowadays, the industrial production of furfurylated wood is carried out by Kebony AS in Norway. The process is based on the full cell (vacuum/pressure) impregnation with a chemical solution followed by an intermediate vacuum drying step before steam curing and drying/post curing (Larrson Brelid, 2013). The impregnation liquid is a waterborne solution containing 40 % furfuryl alcohol, buffer agents,

maleic anhydride and citric acid catalysts (Pilgård et al., 2010). *Kebony Clear*, furfurylated wood is produced from radiata pine, southern yellow pine and maple and is used for flooring. *Kebony Character*, furfurylated wood is produced from Scots pine wood and is used for decking, siding, roofing and outdoor furniture. It has been established that wood species with more open pits and loose and ordered structures were best suited for furfurylation (Dong et al., 2016). Furfurylated *Kebony* wood is, like acetylated *Accoya* wood, also recommended for windows production by the German Association of Windows and Facades (VFF).

Weathering of furfurylated wood

It was shown that the modification of Scots pine (*Pinus silvestris* L.) wood with furfuryl alcohol was ineffective in reducing the discoloration and delignification of wood exposed to artificial accelerated weathering (Temiz et al, 2007). Furfurylated samples showed positive ΔL* values thus indicating that the wood surface became lighter after 800 hours of accelerated weathering.

A three-year outdoor weathering test of furfurylated (*Kebony*) wood decks of radiata pine (*Pinus radiata*), maple (*Acer* spp.) and southern yellow pine (*Pinus* spp.) was performed in order to evaluate physical and structural properties of modified wood decks and to compare with a control deck of Ipe wood (*Handroanthus* spp.) decks. The furfurylated radiata pine deck generally showed minor surface cracks, while the furfurylated maple decks presented the lowest degree of surface and end splitting. After three years of outdoor weathering the furfurylated wood decks tested exhibited extensive greying effects and showed no signs of black staining (except for southern yellow pine deck) and no fungal or mould decay (Mantanis, Lykids, 2015).

In the study of resistance to artificial weathering of three commercial modified wood products (*Accoya, Kebony* and *Q-Treat*) the total colour change was the largest with the *Kebony* specimens, the lightness of which increased the most. This is consistent with the results of Temiz et al. (2007).

Modification with DMDHEU

N-methylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) is widely used in the textile industry as an anti- wrinkling agent. It can react with hydroxyl groups of lignin and of hemicellulose, but it can also form complex pol-

ymers with itself as a cross linking agent (Homan, Jorissen, 2004). It is consequently expected to increase the resistance of wood to weathering due to cross-linking the cell wall and dimensionally stabilizing the wood. Although indications of cross linking with the cell wall polymers are found, the mechanisms of the reaction between DMDHEU and the wood cell wall are still unknown (Larson Brelid, 2013). The use of DMDHEU as an agent for modifying wood is reported for improving the dimensional stability, durability, coating properties and weathering resistance of wood (Militz, 1993, Xie et al., 2005, 2006, 2008, Xie et al., 2013, Tomažič, 2006). The improvement of wood properties as well as formaldehyde emissions of modified wood are positively correlated with the DMDHEU concentration applied. Experiments with ether-modified DMDHEU derivatives (mDMDHEU) reacted with methanol or diethylene glycol as formaldehyde scavengers exhibited good results in wood applications showing reduced formaldehyde emission and fixation and wood characteristics similar to DMDHEU treatment (Emmerich et al., 2017). The modification process includes the vacuum-pressure impregnation of wood with aqueous solutions of DMDHEU and catalysts such as magnesium chloride followed by curing step by polycondensation at a temperature of 100-120 °C under humid conditions, after which water is released (Xie et al., 2013). Molecular size of DMDHEU is small enough to penetrate cell walls. Modification of solid wood is limited to permeable wood species that are easy to impregnate (Emmarich et al., 2017). The modification process is developed and optimized for Scots pine (*Pinus sylvestris* L.), but investigations on other permeable wood species such as Rubber wood (Hevea brasiliensis Müll. Arg., Radiata pine (*Pinus radiata* D.Don), European beech (*Fagus sylvatica* L.), Sweetgum (*Liquidambar styraciflua* L.), Balsam poplar (*Populus ussuriensis*, Komarov) have also confirmed a high level improvement of durability and dimensional stability by DMDHEU modification (Emmerich et al., 2017). There is a need for optimization of curing processes for specific wood species. However, process development and optimization to industrial scale were limited to Scots pine until now, since modified beech showed increased crack formation (Emmarich et al., 2017). Commercial application of wood modification process with DMDHEU has been achieved in Germany and marketed by BASF Company under commercial name *Belmadur* (Sandberg et al., 2017). Key applications for DMDHEU modified *Belmadur* wood are decking and garden furniture and laminated Belmadur product has gain acceptance by the German association of Windows and Facades for use in exterior windows (Sandberg et al., 2017). The hygroscopic properties of DMDHEU-modified products are reduced (Larsson Brelid, 2013, Papadopoulos, Mantanis, 2012). Optical and haptic appearance of the modified wood was found to be almost unchanged besides slight darkening compared to unmodified wood (Emmerich et al., 2017). ASE values of 30 to 40 % are in range at 40 % WPG (Homan, Jorissen, 2004). However, brittleness may limit its use as load bearing structural elements (Xie et al., 2013). Other drawbacks are tendency to crack and high emission of formaldehyde from the products (Larrson Brelid, 2013).

Weathering of DMDHEU treated wood

DMDHEU was used to modify Scots pine veneers to different weight percent gains (WPG) and exposed to artificial weathering. Evidence from FT-IR spectra and weight losses of weathered veneers indicated that at higher weight gain (48 %) the treatment stabilized lignin to some extent. The lower percentage of strength loss observed for DMDHEU modified veneers in comparison to unmodified veneers suggested that DMDHEU modification reduced the degradation of cellulose during weathering. Electron microscopy revealed that DMDHEU modification was highly effective at preventing the degradation of the wood cell wall during weathering (Xie et al., 2005).

Several authors investigated the effects of wood modification with modified DMDHEU (mDMDHEU) on the performance of water- borne and solvent-borne stains and paints. The modified DMDHEU (mDMDHEU) Scots pine (*Pinus sylvestris*) sapwood was compatible with both water-borne and solvent-borne coating system and caused no significant change in wet-adhesion, blocking and drying rate (Xie et al., 2006). Natural and artificial weathering of uncoated and coated DMDHEU-modified sugi wood (*Cryptomeria japonica* D. Don) showed lower weight losses and less cracking than did the unmodified wood (Sudiyanni et al., 1996).

Although modification of the Scots pine wood with commercially available DMDHEU increased the hydrophobicity of the wood surface, it had no adverse effect on the wetting of the wood surface by the waterborne coating. Moreover, the modified surface exhibited much better wetting by exterior commercial waterborne coatings on modified substrates than on unmodified substrates (Tomažič, 2006, Petrič et al., 2007). Penetration of the coatings into DMDHEU-modified wood was deeper and consequently the dried coatings on DMDHEU modified wood exhibited increased adhesion. Coatings on DMDHEU modified wood showed increased performance after natural and artificial exposure in comparison with coatings on unmodified wood and therefore longer maintenance intervals of coatings could be expected on DMDHEU modified wood (Tomažič, 2006). However, water vapour permeability of the system DMDHEU modified wood – coatings was higher than in case of coatings on unmodified wood. It could be due to increased hygroscopicity due to remaining of the catalyst or due to unreacted free hydroxyl groups (Tomažič, 2006).

The results obtained after 18 months of natural weathering in Central Germany showed that the modification of Scots pine sapwood with modified 1,3-dimethylol-4,5-dihydroxyethyleneurea (mDMDHEU, received from BASF AG) enhanced the service life of wood used outdoors. Modified uncoated panels compared to unmodified exhibited reduced discoloration mainly caused by staining fungi. However, mDMDHEU treated panels couldn't prevent fungal staining of wood, but

did reduce colonization. Panels modified with mDMDHEU were also less deformed regarding to cupping and developed smaller cracks and reduced surface roughness and waviness compared to unmodified panels. Both acrylic and oil coatings displayed less discoloration and cracking on the mDMDHEU modified panels after 18 months of natural weathering compared to unmodified panels (Xie et al., 2008).

Colour measurements during 24 months of outdoor exposure of Scots pine sapwood (*Pinus sylvestris*) and beech wood (*Fagus sylvatica*) showed discoloration and lignin degradation of DMDHEU-modified wood (Pfeffer et al., 2011). FTIR spectroscopy revealed lignin degradation during initial exposure time (3-6 months). The surface discoloration was a combination of fungal growth and photo degradation of lignin. The fungal infestation was slowed down while lignin degradation was not, indicating that lignin degradation did not influence the initial fungal infestation of the modified wood surfaces. The DMDHEU modification also reduced the speed of liquid water uptake caused by the inclusion of the chemical in the ray cells, the mayor penetration pathways for water in unmodified wood (Pfeffer et al., 2011). However, the modified specimens exhibited cracks during and after outdoor exposure. The radial penetration of fungal hyphae was reduced in DMDHEU-modified wood which might be caused by blocking of the penetration pathways due to the inclusion of a chemical in the ray cells (Xie et al., 2008).

Conclusions

The test results of the weathering resistance of modified wood depend on many factors such as wood species, modification processes and parameters, type and conditions during outdoor or laboratory exposure. Therefore, the comparison of the results is very difficult. Based on the studied literature it can be summarized and concluded as follows:

- Weathering resistance of modified wood does not change largely when compared to unmodified wood, making a surface treatment advisable for protection and aesthetic appeal of wood. Commercially modified wood producers in their brochures recommend surface treatment materials for protection and retaining the original colour of modified wood without silver-gray patina.

- Thermally modified wood exposed to weathering conditions resulted in the formation of small cracks on the surface of uncoated wood and turned grey in colour. Unpigmented or low build stain did not protect the wood surface, but solvent-borne alkyds and water-borne acrylic paints exhibited better performance

than unmodified wood. Pigmented film-forming coating for decking showed to have a short life span during the natural exposure and required regular maintenance but oil based finishes were a better option despite the fact that the colour would not be maintained.

- Acetylated wood is also like any natural wood species susceptible to weathering in outdoor conditions. It only shows the initial stability against UV radiation and thereafter begins to fade and grey as other wood species. Acetylation of wood was shown to have positive effects on performance of coatings. It has been shown in several studies that acetylated wood is vulnerable to mould and blue stain fungi.

- Furfurylated wood decks after three years of outdoor exposure exhibited extensive greying effects and showed no signs of black staining or mould decay. Checking or small surface cracks also occurred. The original colour can be maintained using UV protection oils and water-based acrylic paints.

- DMDHEU-modified uncoated panels compared to unmodified exhibited reduced discoloration mainly caused by staining fungi. Panels were also less deformed regarding cupping and developed smaller cracks and reduced surface roughness and waviness compared to unmodified panels. Colour measurements during 24 months of outdoor exposure of DMDHEU-modified wood showed discoloration and lignin degradation, but both acrylic and oil coatings displayed less discoloration and cracking on the DMDHEU- modified panels after 18 months of natural weathering compared to unmodified panels.

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