The influence of melamine treatment in combination with thermal modification on the properties and performance of native hardwoods

Dissertation

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Summary

The objective of this study was to improve the properties of native hardwoods and find potential new applications in exposed environments that had previously been unsuitable for most of these species. Certain properties such as the aesthetics, hardness, impact bending strength, weathering resistance, and crack susceptibility are issues of the commercially available modified wood products. It was the aim of this study to prepare potential solutions for using the readily available resource beech wood (*Fagus sylvatica* L.) and other hardwoods (ash (*Fraxinus excelsior* L.), lime (*Tilia* spp.) and poplar (*Populus* spp.)) more efficiently and expand the knowledge about impregnation modification of hardwoods with melamine resin.

In this study, the curing process of melamine resin treatment was analyzed in depth first, because the properties of modified materials depend on the parameters of the treatment process. Then, thermal modification and melamine resin treatment were combined, and the resulting elasto-mechanical and weathering properties were assessed. The influence of the curing parameters of melamine resin treatment were analyzed to identify the determining factors for viable curing processes. It was also of interest if the control methods used would yield correct answers on how curing influences the material properties. Analyses with differential scanning calorimetry could be used to determine the minimum requirements of temperature and duration for complete resin curing in wood. The nitrogen content and fixation in the treated wood should give information about the quality of the incorporation of the resin in the wood matrix. The formaldehyde content and emissions should also provide information about whether the curing is complete and about the formed resin network. Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy could be used to locate the resin in the wood matrix and the cell walls. The influence of the curing variations on the mechanical properties such as hardness, bending strength, and impact bending strength were also investigated. Furthermore, it was of interest if the melamine resin treatment could be combined with thermal modification. The mechanical properties and the weathering performance were investigated.

The differential scanning calorimetry revealed to be well capable to determine the curing characteristics of melamine resin in solid beech wood. The curing reaction would onset at 110 °C and peak at 135 °C in a high-pressure crucible. The nitrogen fixation confirmed that higher temperatures and longer curing (>110 °C, 24 h) led to completely cured resin. High humidity while curing negatively influenced the fixation. The method to determine the fixation also had an effect: Leaching in cold water over a longer period gave more accurate results than extraction in hot water. Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy revealed an even nitrogen distribution across the cell walls of melamine-treated beech. There were more microcracks in dry-cured specimens than in steam-cured specimens. Steam curing led to slightly increased allocation of resin in the cell lumen, compared to dry curing. High humidity curing resulted in lower embrittlement and lower formaldehyde

emissions than dry curing. The bending strength and hardness, however, were not influenced by the curing conditions.

Treating thermally modified wood with melamine resin resulted in lower bulking after impregnation and curing. This depended on the thermal treatment intensity and was nonetheless able to increase the hardness, but not the impact bending strength. The weathering performance was positively influenced. Depending on the wood species, lesser or smaller surface cracks were observed. The embrittlement of the thermally modified wood was not influenced.

Some useful control methods for the curing of melamine resin in hardwoods were established. The test results of this study should be a basis to create a long-lasting product from non-durable native hardwoods.

Zusammenfassung

Das Ziel dieser Arbeit war es, die Eigenschaften einheimischer Laubhölzer zu verbessern und potenzielle neue Verwendungen in Außenanwendungen zu finden, die zuvor für die meisten dieser Arten ungeeignet waren. Bestimmte Eigenschaften wie die Ästhetik, die Härte, die Schlagbiegefestigkeit, die Witterungsbeständigkeit und die Rissanfälligkeit sind Probleme der im Handel erhältlichen modifizierten Holzprodukte. Ziel war es, mögliche Lösungen für eine effizientere Nutzung der gut verfügbaren Ressource Buchenholz (*Fagus sylvatica* L.) und anderer Laubhölzer (Esche (*Fraxinus excelsior* L.), Linde (*Tilia* spp.) und Pappel (*Populus* spp.)) zu erarbeiten und die Kenntnisse über die Imprägnierung von Laubhölzern mit Melaminharz zu erweitern.

In dieser Studie wurde zunächst der Aushärtungsprozess der Melaminharzbehandlung eingehend analysiert, da die Eigenschaften modifizierter Materialien von den Parametern des Behandlungsprozesses abhängen. Danach wurden die thermische Modifizierung mit Melaminharzbehandlung kombiniert und die resultierenden elastomechanischen und Bewitterungseigenschaften getestet. Der Einfluss der Härtungsparameter der Melaminharzbehandlung wurde analysiert, um die bestimmenden Faktoren für anwendbare Härtungsprozesse zu identifizieren. Ebenfalls von Interesse war, ob die verwendeten Kontrollmethoden korrekte Antworten darauf liefern, wie die Aushärtung die Materialeigenschaften beeinflusst. Eine Analyse mit dynamischer Differenzkalorimetrie könnte verwendet werden, um die Mindestanforderungen an Temperatur und Dauer für eine vollständige Aushärtung des Melaminharzes in Holz zu bestimmen. Der Stickstoffgehalt und die Stickstofffixierung des behandelten Holzes sollten Aufschluss über die Qualität der Aufnahme des Harzes in die Holzmatrix geben. Der Formaldehydgehalt und die Formaldehydemissionen sollten Auskunft über das gebildete Harznetzwerk geben und ob die Aushärtung abgeschlossen ist. Rasterelektronenmikroskopie in Kombination mit energiedispersiver Röntgenspektroskopie könnte verwendet werden, um das Harz in der Holzmatrix und den Zellwänden zu lokalisieren. Der Einfluss der Aushärtungsvariationen auf die mechanischen Eigenschaften wie Härte, Biegefestigkeit und Schlagbiegefestigkeit wurde ebenfalls untersucht. Weiterhin war es von Interesse, ob die Melaminharzbehandlung mit thermischer Modifizierung kombiniert werden kann. Die mechanischen Eigenschaften und die Witterungsbeständigkeit wurden untersucht.

Die dynamische Differenzkalorimetrie zeigte, dass sie die Aushärtungseigenschaften von Melaminharz in Buchenholz gut bestimmt werden kann. Die Aushärtungsreaktion im Hochdrucktiegel setzte bei 110 °C ein und erreichte bei 135 °C ihr Maximum. Die Stickstofffixierung bestätigte, dass höhere Temperaturen und eine längere Aushärtung (> 110 ° C, 24 h) zu vollständig ausgehärtetem Harz führten. Hohe Feuchtigkeit während der Aushärtung beeinflusste die Fixierung negativ. Die Methode zur Bestimmung der Fixierung wirkte sich ebenfalls aus: Das Auswaschen in kaltem Wasser über einen längeren Zeitraum ergab genauere Ergebnisse als die Extraktion in heißem Wasser. Rasterelektronenmikroskopie in Kombination mit energiedispersiver Röntgenspektroskopie zeigte eine

gleichmäßige Stickstoffverteilung über die Zellwandquerschnitte der mit Melamin behandelten Buche. In unter trockenen Bedingungen ausgehärteten Proben gab es mehr Mikrorisse als in unter Dampfatmosphäre ausgehärteten Proben. Die Aushärtung unter Dampfatmosphäre führte zu einem leicht erhöhten Harzanteil im Zelllumen im Vergleich zur Trockenhärtung. Die Härtung bei hoher Luftfeuchtigkeit führte des Weiteren zu einer geringeren Versprödung und zu geringeren Formaldehydemissionen als die trockene Aushärtung. Die Biegefestigkeit und die Härte wurden jedoch nicht durch die Aushärtungsbedingungen beeinflusst.

Die Behandlung von thermisch modifiziertem Holz mit Melaminharz hatte eine geringere permanente Quellung nach Imprägnierung und Aushärtung zur Folge. Dies hing von der Wärmebehandlungsintensität ab und konnte die Härte, aber nicht die Schlagbiegefestigkeit, erhöhen. Die Bewitterungsbeständigkeit wurde positiv beeinflusst. Je nach Holzart wurden weniger oder kleinere Oberflächenrisse beobachtet. Die Versprödung des thermisch modifizierten Holzes wurde nicht beeinflusst.

Einige nützliche Kontrollmethoden für die Aushärtung von Melaminharz in Harthölzern wurden etabliert. Die Testergebnisse dieser Studie sollten eine Grundlage für die Herstellung eines langlebigen Produkts aus nicht dauerhaften einheimischen Laubhölzern sein.

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Abbreviations

°C	Degree Celsius
ANOVA	Analysis of variance
ASE	Anti-swell-efficiency
bar	Bar pressure
BSF	Brilliant sulphoflavine
cps	Counts per second
DMDHEU	1,3-dimethylol-4,5-dihydroxyethyleneurea
DSC	Differential scanning calorimetry
EDX	Energy disperse X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EMC	Equilibrium moisture content
EMCR	Corrected equilibrium moisture content
FA	Formaldehyde
FA-C	Formaldehyde content
FA-E	Formaldehyde emission
g	Gram
h	Hour
H	Reaction enthalpy
HB	Brinell hardness
HWE	Hot water extraction
IB	Impact bending strength
kg	Kilogram
LM	Light microscopy
mbar	Millibar
ML	Middle lamellae
ml	Milliliter
mm	Millimeter
MMF	Methylated melamine formaldehyde resin
MOE	Modulus of elasticity
MOR	Modulus of rupture
MUF	Melamine urea formaldehyde resin
N	Nitrogen
Ne	Nitrogen content of extracted specimens
NF	Nitrogen fixation
NMM	N-methylol modified melamine resin

Nne	Nitrogen content of non-extracted specimens
OD	Oven-dry density
PF	Phenol formaldehyde resin
RH	Relative humidity
s	Second
S2	Secondary cell wall layer S2
S3	Secondary cell wall layer S3
SC	Solid content of impregnation solution
SEM	Scanning electron microscopy
SMA	Simple moving average
SR	Swell rate
SU	Solution uptake
TEA	Triethanolamine
UF	Urea formaldehyde resin
UMSP	UV microspectrophotometry
WB	Work in bending
WPG	Weight percent gain

1 Introduction

1.1 Motivation

The demand for renewable materials for building is increasing, while resources such as naturally durable wood are dwindling. Wood is a natural and renewable material. It is strong, lightweight, and aesthetically pleasing. It is also naturally degradable and can lack the required dimensional stability. That means that the integrity of the material is potentially shorter than the prospected service life. Thus, wood in outdoor applications requires protection.

Constructional wood protection is the traditional way of protecting wood from the elements and subsequent deterioration. Where constructional wood protection cannot be achieved, it can be typically provided by biologically active wood preservatives (DIN 68800-1 2011). The ingredients of wood preservatives are designed to specifically target fungi or insects but might leak over time and contaminate the surroundings. Their long-term influence on humans is not sufficiently clarified (Leisse 1992). Disposal of wood treated with preservatives is also an issue, as the extraction of the preservative is rather impossible, and the reuse of the material is difficult (Voss and Willeitner 1993). Developments in analytics, health issues and environmental concerns, and new regulations limit the use of preservatives (Militz 2008). There are novel alternatives to protect wood and prolong its service life. This protection and improvement of properties can be provided through physical alteration, called wood modification.

Wood modification changes the chemical and structural constitution and presents new properties to improve specific properties. Natural durability, dimensional stability, and resistance to weathering are some of those properties. The mechanisms of wood protection through wood modification of the already developed technologies have yet to be fully understood, and new ways might have to be found to establish further gains. The knowledge must also be expanded to include treating new resources such as new wood species or increasingly available species. This can occur when technology is expanded to different parts of the world (Hill 2011) or the composition of the domestic or available resources is modified.

For ecological and economic reasons, the forests in Germany will have more mixed stands and more hardwoods in the future. The goal is a more natural state of the managed forests with more biodiversity and a lower risk of calamities in mixed stands. The wood of broadleaved trees (hereafter named hardwoods) such as beech will be more abundant (BWI^3 2012). These species are often not durable or dimensionally stable enough to be used for construction materials or furniture, cladding, and decking in outdoor applications. On the other hand, they are readily available and easy to treat, making them ideal candidates for wood modification processes to improve their properties. European beech (*Fagus sylvatica* L.), common ash (*Fraxinus excelsior* L.), lime (*Tilia* spp.), and poplar (*Poplar* spp.) meet these requirements and are among the most abundant species in Germany now and will be throughout the next

decades. Beech is by far the most available species among them (BWI[3] 2012). To make use of the more available hardwood, some sort of wood protection must be applied. As those species have not been treated with the utilized processes before, existing processes have to be applied and adapted. The technologies might have to be combined to achieve the desired material properties.

This study further focused on understanding already developed technologies and combining technologies for new properties and potential applications, as described in depth in the next paragraphs.

1.2 Wood modification

Wood modification is a term describing chemical, biological, or physical techniques to positively alter the properties of wood and to prolong the service life using nontoxic agents or processes. The use, recycling or the disposal of the material at the end of the service life should not release any toxic substances. Protection against biological decay should be based on a nonbiocidal mode of action (Hill 2006). Ultimately, local, abundant, and renewable resources can be used to make products that subsidize endangered tropical hardwoods or petrochemical and unrecyclable choices. Biocidal wood preservatives and their potential impact on non-target species can also be avoided (Leisse 1992).

Wood modification methods employ different techniques to alter wood properties. Thermal modification alters the cell wall chemistry; chemical modification (e.g. treatment with acetic anhydride) is based on the covalent reaction of the modification agent with cell wall constituents. Other modifications are impregnation processes (wax, furfuryl alcohol, phenol formaldehyde resin, melamine formaldehyde resin). They can either fill the lumen and/or the cell wall cavities without the need of a covalent bond.

Chemical wood modification utilizes covalent bonding of agents to cell wall constituent's hydroxyl groups. One of the most researched and today also commercialized method is the acetylation with acetic anhydride (Rowell 1983; Hill 2006). In the case of high weight percent gain (WPG), the blockage of nearly all hydroxide groups in the cell walls is very effective at dimensional stabilization (Rowell 1983). One drawback was the strong smell of acetic acid of the early treatments. The process was further developed, and the commercialization was launched in the 2000s (Bongers *et al.* 2009).

Impregnation modification does not require the agent to covalently bond to the cell walls but must penetrate and be fixated in the wooden matrix to prevent leaching and ensure a consistent material performance (Hill 2006). Impregnation and curing of phenol formaldehyde resin (PF) resin in wood (Impreg and Compreg) was the first commercial solid wood impregnation modification to be widely used (Stamm 1964). Treatment with furfuryl alcohol is commercialized by Kebony ASA. It uses processed byproducts of the corn and sugar cane production and produces dimensionally stabilized, naturally durable and hardened wood products suitable for outdoor application (Lande *et al.* 2008). 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) has been used in the textile industry as a crease-

free agent for some time (Emmerich *et al.* 2019). Academic research about the use of DMDHEU as an impregnation agent for solid wood and wood products began in the 2000s and showed improved dimensional stability and durability against fungi (Krause 2006; Schaffert 2006; Wepner 2006; Bollmus 2011). Impregnation modification with wax products mostly only penetrated the cell lumen of wood but provided a certain level of mechanical wood protection and increased the durability and hardness (Scholz 2011).

Melamine formaldehyde resins (MF) were initially used as additives in the wood products industry to increase the water resistance of particleboards and overlay papers (Kohlmayr *et al.* 2014). The relatively high price of MF resins prevented developments of MF-treated solid wood products, although research showed the major improvements in dimensional stability and natural durability, surface hardness, bending strength, and fire retardancy (Lukowsky 1999; Rapp 1999). Because of the large potential of MF resins as wood modification agents, they will be discussed in more depth in the next chapter.

Thermal modification is very intuitive and one of the oldest methods of wood modification. Reports show that humans knew about increasing the durability of wood by heating it over a fire as early as the age of the Vikings. Fence posts in the Alps are still treated that way at the soil/air transition to increase the service life (Anonymous 2003). A comprehensive overview of the research during the 20th century is given by Hill (2006) and Esteves and Pereira (2009). Extensive research work was carried out in Finland in the 1990s (Anonymous 2003) and is still the country with the largest production of thermally modified wood (Scheiding 2018). The most intensive and comprehensive research work was conducted by VTT in Finland (Anonymous 2003).

Today, some modification processes are commercialized in Europe. Besides thermal modification (TM), furfurylation (F), and acetylation (AC), there is wax treatment and treatment with PF and UF resins. The most widely used method is TM with 400.000 m³/a (Militz 2015), followed by AC (40.000 m³/a) and F (25.000 m³/a) (Scheiding 2018). This is still a small number compared to the overall production of solid wood produced each year worldwide (400 m m³/a, (FAO 2011)), but that number is rising steadily (Scheiding 2018). High purchase costs compared to preservative treated wood or naturally durable tropical timber tend to keep modified wood in high quality niche applications.

1.3 Treatment with methylated melamine formaldehyde resin

Melamine resins are amino resins and were first synthesized in the 1940s and have been increasingly used since then. Today, there is a variety of uses, ranging from overlay papers (thin high-pressure laminates) used for kitchen countertops and laminate floorings, to wet strength for paper (in bills) and wood-based products (Hagstrand 1999), melamine tableware, camping tableware, fire retardants in airplane upholstery, and electrical insulation (Lukowsky 1999). From the 1950s onwards, melamine resin treatment of wood has been researched for dimensional stabilization. Stamm (1964) mentioned them as being “promising, but too expensive to be used for dimensional stabilization”. Further research

was conducted in the 80s and 90s, with Pittmann *et al.* (1994), Lukowsky (1999) and Rapp (1999) as examples for extensive testing regarding dimensional stability, decay resistance and weathering performance, and mechanical properties of many types of MF. The curing conditions were found to play a major role in the resulting properties of melamine-treated wood (Lukowsky 2002).

1.3.1 Process

Melamine formaldehyde resins (MF) are synthesized by the addition reaction (condensation) of melamine molecules with formaldehyde in water (Scheepers *et al.* 1995). Their shelf life is prolonged through the stabilization with alcohols, mainly methanol. The resulting type of MF, the methylated melamine formaldehyde resin (MMF), is the most common type of MF used today.

Wood modification with MF is a two-step process:

1) An aqueous solution of MF is used to impregnate wood

2) The treated wood is then dried, and the resin is cured under elevated temperatures.

Vacuum-pressure impregnation allows the impregnation solution to enter the lumens of the wooden matrix. A subsequent diffusion phase allows the impregnation solution and the including monomers to enter the cell wall cavities. The subsequent drying and curing usually takes place at elevated temperatures, but it can also be catalyzed by acids (Mizumachi and Fujino 1972; Scheepers *et al.* 1993). Water is allowed to evaporate during drying, whereas the resin remains in the cell walls. There, polycondensation-type crosslinking reactions occur during the curing, building a network (Jones *et al.* 1994). Melamine curing is temperature-dependent (Zeppenfeld 1991), as nearly all chemical reactions are. Becker (1968) stated 80 °C as a sufficient curing temperature. Typical curing temperatures ranged from 80 °C to 120 °C (Krause 2006), depending on the author, curing process, and type of resin (Lukowsky 1999; Krause 2006; Sint 2010). Another influential factor on the structure of the melamine resin network is the humidity during the curing process (Jones *et al.* 1994). The results of curing melamine formaldehyde resin depend on the conditions such as the temperature, pH value, and humidity. All of these influence the resin formation. When the resin network is formed, methanol and formaldehyde are split off (Lukowsky 1999). Especially industrial-scale processes of DMDHEU treatment had to account for conservative drying and curing and follow hot steam processes rather than conventional drying schemes (Schaffert 2006).

MF treatment of small specimens for specific tests was done at laboratory scale using drying ovens (Lukowsky 1999; Rapp 1999). When larger dimensions were treated, drying under dry conditions led to severe drying defects such as cell collapse and internal cracks (Lukowsky 1999). Dry processes can also lead to uneven distribution of the modification agent (Krause 2006). High-humidity or hot steam processes guarantee a lower moisture gradient between the wood surface and the surrounding atmosphere (Krause 2008; Mahnert 2013). Above 100 °C, water will boil and form vapor. The hot steam

process uses this principle to dry wood. Water will move and exit the wood in the gas phase and is thus not able to transport any impregnation agent across the wood cross section to the surface of the board. This migration effect has been described as a problem of dry curing processes (Schaffert 2006; Krause 2008).

Not many commercialized resin treatment processes have been implemented, rendering the real-world data rather small. Researchers have discussed pilot plant scale curing processes at various levels and different focusses. Wepner (2006) used a hot press to cure beech veneers treated with DMDHEU. Krause (2008) used hot steam processes to cure DMDHEU and melamine-treated pine. Different process conditions such as time and temperature affect the properties of modified wood. Indications of how the process conditions influence the properties were made (Krause 2006; Schaffert 2006; Wepner 2006) for DMDHEU treatment of wood. High temperature curing resulted in a more complete curing of the resin (Scheepers *et al.* 1993). Klüppel and Mai (2013) added to the discussion of this matter and found dry curing conditions leading to more complete curing than wet conditions. DMDHEU tended to migrate during drying and curing (Krause 2006). Using hot steam processes to cure wood treated with resins such as PF, DMDHEU or MMF yielded fewer drying defects. Krause (2006) conducted several iterations of full-sized impregnation and curing processes, analyzed the drying defects, nitrogen fixation, and mechanical properties. The results were incorporated in the next process to approach the best possible outcome. One verdict was that the resin treatment resulted in diffusion hindrance and made the treated wood behave like a difficult-to-dry species, such as oak (Rapp 1999). Lukowsky *et al.* (1998) and Lukowsky (2002) tested the influence of curing conditions on the formaldehyde emissions of melamine-treated pine specimens. Higher temperature and longer duration resulted in lower formaldehyde emissions.

1.3.2 Quality control of impregnation and curing processes

The most frequently used methods for quality control of impregnation modifications are based on the increased mass caused by the modification chemicals. The solution uptake (SU) is used to characterize the impregnation, and WPG is used to characterize the amount of cured modification agent in the wood after modification. Further methods, depending on type of resin and curing process parameters, were investigated during the last years. Such methods included the measurement of formaldehyde (FA) emissions and the nitrogen content, distribution, and fixation (NF). When resin formulations contain FA, emissions were measured to ensure they meet regulations (Lukowsky *et al.* 1998; Rapp 1999; Krause 2006; Wepner 2006). Curing specimens at higher temperatures for longer durations resulted in lower FA emissions (Lukowsky 1999). The degree of curing of nitrogen-containing resins such as DMDHEU or MMF can also be controlled by the nitrogen content and nitrogen fixation (NF) (Rapp 1999; Schaffert 2006; Krause 2008). Cured resin showed a higher resistance against leaching or extraction than uncured specimens, and thus showed a higher NF (Rapp 1999).

Microscopy techniques were used by several authors to detect the changes in wooden materials after gluing or wood modification. Kielmann *et al.* (2014) used light microscopy (LM) and UV microspectrophotometry (UMSP) to visualize MMF deposits in cell lumens. Biziks *et al.* (2015) visualized the penetration depth of different molecular weight phenol formaldehyde (PF) resins through the inability of safranin to stain the cross sections of modified beech wood. This method would be very useful if applicable for the investigation of the influence of curing processes on penetration and stainability of beech modified with melamine resin.

Leemann and Ruch (1972) used brilliant sulphoflavine (BSF) staining to quantify proteins in plant cells. Sernek *et al.* (1999) later used the same technique of BSF and safranin staining to detect the urea-formaldehyde resin (UF) bondline in beech plywood. Mahrdt *et al.* (2015) detected the UF bondline and UF penetration by combined dyeing and fluorescence microscopy imaging.

Numerous authors used electronic imagery to verify effects of wood modifications on the modified material. The most widely used methods were UMSP (Gindl *et al.* 2002; Mahnert 2013), electron energy loss spectroscopy (EELS) (Rapp *et al.* 1999), and scanning electron microscopy with energy disperse X-ray spectroscopy (SEM-EDX) (Rapp 1999).

UMSP and EELS require 100 nm thin cuts for the TEM. SEM-EDX requires small, smoothly cut wooden blocks, which is a less demanding sample preparation, and was used in this study. The SEM-EDX technique is particularly emphasized, as the specimen preparation for SEM analysis is simpler, and the EDX verification of nitrogen is a reliable method to localize melamine resin in cell walls.

Classified as an impregnation type modification (Hill 2006), melamine treatment does not need to covalently bond to wood cell walls. There have been disputed results about this in the literature. Devallencourt (2000) found co-condensation reactions between melamine and cellulose fibers. Lukowsky (1999) rendered only a small number of bonds possible. The three-dimensional network of melamine resin formed while curing is sterically locked (Lukowsky 1999) in the cell wall cavities (Devallencourt *et al.* 2000) and potentially does not need chemical bonds to exert the recorded changes to wood properties.

1.3.3 Properties

The properties of wood treated with melamine resin are altered in several ways. Melamine resin does not alter the original color of wood (Hagstrand 1999). It improves the surface hardness and dimensional stability (Inoue *et al.* 1993a; Rapp 1999) depending on resin uptake (Deka *et al.* 2007). Due to the incorporation of resin in wood cell walls, density and stiffness increase (Stamm 1964; Miroy *et al.* 1995; Gindl *et al.* 2003; Deka *et al.* 2007). The MOE was increased (Deka and Saikia 2000; Epmeier *et al.* 2004; Kielmann *et al.* 2013), reflecting the increased stiffness. The impact bending strength was reported to decrease (Epmeier *et al.* 2004; Kielmann *et al.* 2013), reflecting the increased stiffness. The bending

strength was reported to increase (Inoue *et al.* 1993a) or decrease (Epmeier *et al.* 2004; Lahtela and Kärki 2014), depending on low or high WPG, respectively.

The moisture properties of melamine-modified wood have been the focus of several investigations (Rapp and Peek 1995; Epmeier *et al.* 2004; Epmeier *et al.* 2007; Hosseinpourpia *et al.* 2016; Kielmann *et al.* 2016), but the influence of melamine resin treatment on the sorption behavior seemed benign. Rapp and Peek (1995) reported no change in EMC by melamine treatment, Epmeier *et al.* (2004) and Kielmann *et al.* (2016) showed a minor reduction of EMC through melamine treatment, and Epmeier *et al.* (2007) even recorded slightly increased EMCs after melamine treatment.

For outdoor application, besides dimensional stability, the appearance of the exposed surfaces is important, too. There were no significant color changes after artificial weathering of sugi specimens treated with MF (Inoue *et al.* 1993b). Pittmann *et al.* (1994) reported no deformation and no discoloration after weathering tests of Southern yellow pine samples treated with MF. An increased surface integrity and lower crack susceptibility were achieved by MF treatment of Scots pine (Rapp 1999). According to Hansmann *et al.* (2006), melamine treatment provided weathering protection. The reports about the crack susceptibility of melamine-treated wood are inconsistent. Hansmann *et al.* (2006) and Rapp and Peek (1995) stated an increased crack performance after melamine treatment, while Lukowsky (1999) reported no reduction in cracks after melamine treatment. Rapp (1999) reported a reduced crack performance during outdoor exposure above ground after melamine treatment.

1.4 Thermal modification

1.4.1 Process

Thermal modification is characterized by exposing wood to elevated temperatures, ranging from 160 °C to 240 °C under an oxygen-reduced atmosphere. The main goals of the processes are increased durability and dimensional stabilization (Militz and Altgen 2014). The processes differ mainly in the medium of heat transfer and the oxygen exclusion system. There are systems operated under either vacuum, atmospheric pressure steam, pressurized steam, oil or nitrogen. The principle of heat transfer and oxygen exclusion can be the same medium (e.g. steam or oil) or it can be separate (heated metal plates for heat transfer in a vacuum atmosphere). Steam as a medium of heat transfer and oxygen exclusion is the most widely used process in terms of quantity (Stellac, Finland). It is a relatively inexpensive and safe principle and can easily be scaled up (Scheiding 2018). The wood is firstly dried to near 0 % moisture content and then subjected to high temperatures in a second step while the steam excludes oxygen and prevents drying damages. The Plato process (Netherlands) also uses steam in a multi-stage process in a pressurized vessel. Recent advances with pressurized steam processes were made by FirmoLin in the Netherlands (Willems 2010). Oil was used by Menz Holz, Germany (Sailer *et al.* 2000). The wood is directly submerged and thus also gets hydrophobized surfaces. However, this process is currently not commercially available. Nitrogen is used as the inert atmosphere in the Retification process (France)

(Mitchell *et al.* 1953). Vacuum excludes the oxygen and heated metal plates provide the heat transfer in the Vacu³ process, used by the German company timura Holzmanufaktur GmbH and the Dutch company Lignius (New Polymeric Compound Industries BV). Some manual effort is required to alternatingly stack wood boards and metal plates containing the heated oil for this process. In return, this alternating pattern ensures even heat transfer and modification intensity throughout the stack and the boards. Downward pressure is exerted onto the stack to prevent cupping or warping of the boards (Wetzig *et al.* 2012).

1.4.2 Properties

The main wood components are affected by increased temperatures with increasing intensity in the order of: Lignin – Cellulose – Hemicellulose.

Hemicellulose has the least thermal stability and already undergoes major decomposition by depolymerization and hydrolysis at 170 °C (Rowell 2006). It is affected mostly by acidic hydrolysis, which works best under high humidity conditions, especially under high pressure, which prevents the acids from evaporating (Altgen *et al.* 2014). C-O bonds between the monomers of the hemicellulose are split off, and acetyl groups are eliminated. They further accelerate the acetic decomposition by creating acetic and formic acid (Sundqvist *et al.* 2006). The thermal degradation of pentoses is more severe than of hexoses. Softwoods have a higher degree of hexoses, and pentoses are more prevalent in hardwoods. Hardwoods therefore showed higher mass loss than softwoods in the same thermal treatments (Fengel 1993; Militz 2002).

Analog to hemicellulose, amorphous regions of cellulose are more susceptible to thermal degradation than crystalline regions. The degree of crystallinity increases through thermal modification (Fengel 1993). One reason for the increased hydrophobicity of TM is the hydrophobic nature of the crystalline regions (Wikberg and Liisa Maunu 2004; Boonstra and Tjeerdsma 2006).

Lignin is known to be less affected by thermal degradation. Nonetheless, there are changes to the lignin macromolecules. Lignin is softened at 70-80°C, and depolymerization occurs at 120 °C to 130 °C, which produces radicals. The molecules of lignin were found to undergo recombination at 140 °C to 200 °C (Windeisen and Wegener 2008).

The number of hydroxyl groups is significantly reduced. This causes a slower water uptake and less swelling, resulting in higher dimensional stability (Tjeerdsma *et al.* 1998). The increased durability of TM is in part ascribed to the reduction of OH groups. Other factors for the increased durability are the structural changes of cellulose and lignin and the formation of new chemical structures (Weiland and Guyonnet 2003).

Extractives are non-structural components of the wood matrix, ranging von 1 % to 10 % depending on the wood species. The total amount of natural extractives is reduced, the composition is altered (Fengel

1966), and new extractives are formed, depending on the type of process and intensity (Poncsak *et al.* 2009).

The property changes due to thermal modification are gradual and depend on the wood species, treatment temperature, and duration (Hill 2006). The longer the maximum temperature of the treatment is applied, the more severe the mass loss and overall change of properties (Kocaefe *et al.* 2008). All the different modification systems and processes generally result in the following changes in wood due to TM.

Due to thermal modification, the durability and dimensional stability are increased depending on wood species and treatment intensity (Militz and Altgen 2014). The equilibrium moisture content of wood is reduced through thermal modification by 50 %, depending on the process (Hill 2006; Esteves and Pereira 2009). Decreased EMCs can influence the mechanical properties; further, thermal modification is known to influence the mechanical properties of wood (Stamm 1964; Boonstra *et al.* 2007; Esteves and Pereira 2009). In the literature, there is contradictory information about the influence of thermal treatments on mechanical wood properties. Brinell hardness (HB), modulus of elasticity (MOE), and bending strength (MOR) were reported to increase or decrease depending on treatment intensity (Welzbacher 2007; Esteves and Pereira 2009). Light treatment was reported to increase hardness and bending strength, while more severe treatments decreased them. However, treatments intense enough to enhance the durability and the dimensional stability have the tendency to reduce the hardness and bending strength (Kubojima *et al.* 2000). Impact bending strength (dynamic) (Welzbacher 2007; Boonstra *et al.* 2007) and work in bending (static) (Kim *et al.* 1998; Wetzig *et al.* 2012; Rautkari *et al.* 2014) were decreased, and they were the most affected properties due to thermal modification.

Other changes to wood through thermal modification are a darker color (Niemz 2005), depending on treatment intensity, and a reduced density and higher porosity because of the decomposition of hemicelluloses (Andersson *et al.* 2005).

The weathering properties were subject of several studies, especially the development of checks and cracks. No improvement of crack susceptibility was reported for thermally modified wood by other authors (Feist and Sell 1987). In contrast, Rapp (2001) reported fewer cracks after heat treatment and weathering.

1.5 Double modification

Double modification of wood is a relatively new research topic. Wood modifications are rather expensive and new in themselves. They had to be established with commonly known material properties to see the full picture and make out potential weaknesses which should be compensated for in order to further promote this technology or product. From the market side: When target values for a potential application are known, the processes can be adjusted accordingly.

The combination of several wood modification systems involving either thermal and or melamine treatment has been covered to various extents (Epmeier *et al.* 2004; Hansmann *et al.* 2005; Mahnert 2013; Sun *et al.* 2013; Lahtela and Kärki 2014; Humar *et al.* 2016). The authors had different objectives and approaches, but their common theme was that they combined different modification methods for their unique properties and joint advantages.

1.5.1 Process

As mentioned above, the topic of combined wood modification was sparsely covered. No two papers were similar, and comparison and generalization were rather difficult. However, the found examples of double-modified wood were either two-step modification processes or some synergetic setups. E.g., when a resin treatment was combined with thermal modification, the impregnation was followed by a joint drying, curing, and thermal treatment step (Lahtela and Kärki 2014).

Epmeier *et al*. (2004) tested the feasibility to treat acetylated Scots pine, beech, and birch with melamine resin. Hansmann *et al.* (2005) similarly tested acetylation in combination with melamine treatment. Both studies subsequently used two modification methods without further process adaption. Mahnert (2013) used melamine treatment as a secondary modification to improve properties of several thermally modified hardwood species. An adjusted thermal process was used, and a melamine treatment process had to be developed. Sun *et al.* (2013) thermally modified melamine-urea-formaldehyde-treated eucalyptus. The resin treatment was fixed, but the thermal treatment was variable. Lahtela and Kärki (2014) also used a subsequent thermal modification of melamine-treated Scots pine. They also used a fixed resin treatment procedure and varied the thermal treatment. Humar *et al.* (2016) thermally modified Norway spruce treated with different wax suspensions.

The possibilities of combining different modification methods were shown. It was also shown that the order of modifications can be changed (whereas to what effect cannot be answered). The effects of the treatment intensities were addressed by Hansmann *et al.* (2005) (melamine resin soaking time) and Lahtela and Kärki (2014) (thermal modification temperature).

1.5.2 Properties

The properties of double-modified wood are the result of the combination of treatments and their intensities. The order of modification will potentially influence the outcoming properties, though no reports were found to address that issue. Generally speaking, the hardness of (double) modified wood was increased when melamine treatment was involved. Further, all modifications and combinations showed reduced impact bending strength values. The target values for the intended properties are relevant to decide what combination of modifications could achieve that goal.

Epmeier *et al.* (2004) reported that the combination of acetylation and melamine treatment showed improved dimensional stability, reduced EMC, and slightly improved bending strength.

Melamine-treated thermally modified hardwoods (Mahnert 2013) showed improved hardness and dimensional stability, excellent durability, and adequate weathering resistance while showcasing the aesthetics of a high-end solid wood product. The impact bending strength was reduced.

Lahtela and Kärki (2014) showed that mild rather than strong thermal modification in combination with melamine treatment could increase the bending strength. It also increased the dimensional stability and decreased the water uptake but also the impact bending strength.

1.6 Objectives of this study

The mentioned studies show the possibilities to improve the properties of native hardwoods and potential new applications in exposed environments that were previously unsuitable for most of these species. Certain properties such as aesthetics, hardness, bending strength, weathering resistance, and low crack susceptibility are still issues in available modified wood products such as thermally modified wood.

It is the aim of this study to prepare potential solutions for using the available resource hardwood more effectively. The species chosen to investigate the curing influence was beech (*Fagus sylvatica* L.), as it is the most available hardwood species in Germany. Common ash (*Fraxinus excelsior* L.), lime (*Tilia* spp.) and poplar (*Populus* spp.) were also included. They exhibit the same ideal preconditions for wood modification as beech: They show a low natural durability, are readily available and potentially permeable enough to be impregnated. This study aims at expanding the knowledge about impregnation modification of hardwoods with melamine resin. Potential applications of such modified wood products are outdoor usage without ground contact (use class 3), e.g. decking for terraces, pool areas, cladding of private and commercial buildings, and outdoor furniture. The core questions were:

1. What are the effects of the curing conditions on the microstructure, chemical composition and resin distribution in the wooden matrix, and the cell wall components and the resulting material properties? **Paper (I, II, III, IV)**

2. Can the interactions of the curing conditions and the material properties be exploited as curing control mechanisms? **Paper (I, II, III, IV)**

3. Is melamine treatment suitable to positively alter the mechanical, water-related, and weathering properties of thermally modified hardwoods? **Paper (V, VI, VII, VIII)**

1.7 List of papers

Paper I: “Determining the N-Fixation – A reliable method to verify the curing quality of wood modification with melamine resin?”

Georg Behr, Antje Gellerich, Susanne Bollmus, Holger Militz

Presented at: the European Conference on Wood Modification 7 - 2014

Paper II: “Different Methods of Nitrogen Analysis and their Suitability to Control the Curing Quality of Wood Modification with Melamine Resin”

Georg Behr, Antje Gellerich, Susanne Bollmus, Holger Militz

Presented at: European Conference on Wood Modification 8 - 2015

Paper III: “Influence of curing conditions on properties of melamine modified wood”

Georg Behr, Antje Gellerich, Susanne Bollmus, Sascha Brinker, Holger Militz

Published in: European Journal of Wood and Wood Products 76 (4) - 2018

Paper IV: “The influence of curing conditions on the properties of European beech (Fagus sylvatica) modified with melamine resin assessed by light microscopy and SEM-EDX”

Georg Behr, Susanne Bollmus, Antje Gellerich, Holger Militz

Published in: International Wood Products Journal 9 (1) - 2018

Paper V: “Improving dimensional stability of thermally treated wood by secondary modification”

Georg Behr, Karl-Christian Mahnert, Susanne Bollmus, Holger Militz

Published in: holztechnologie 58 (2) - 2017

Paper VI: “Improvement of mechanical properties of thermally modified hardwood through melamine treatment”

Georg Behr, Susanne Bollmus, Antje Gellerich, Holger Militz

Published in: Wood Material Science & Engineering 13 (5) - 2018

Paper VII: “Weathering protection of European hardwoods through double modification”

Georg Behr, Antje Gellerich, Susanne Bollmus, Holger Militz

Presented at: International Research Group on Wood Protection (IRG/WP 17-30715) - 2017

Paper VIII: “Accelerated weathering – Performance of beech and poplar after double modification”

Georg Behr

Unpublished

2 Paper I: Determining the N-Fixation – A reliable method to verify the curing quality of wood modification with melamine resin?

(published at the European Conference on Wood Modification 7 - 2014)

Abstract

As a thermosetting resin, melamine should show a higher fixation after hot curing than after drying at room temperature. The nitrogen (N) fixation rates are used to control the curing quality of wood modification with DMDHEU and melamine. A melamine solution with 19 % solid content was used to impregnate beech samples of two groups: One was cured at 103 °C and one air dried at room temperature (20 °C). The nitrogen analysis after a hot water extraction resulted in an N fixation of 77 % for both groups. The anti-swell-efficiency (ASE) test was used to investigate differences in dimensional stability. It was modified (freeze drying instead of oven drying) to avoid further curing due to high temperatures during the drying step. Both groups had a positive ASE at the first cycle. The initially higher ASE of the air-dried samples was greatly reduced and roughly corresponded to the ASE of the cured specimen from cycle two onwards. The air-dried samples showed a severe mass loss due to uncured melamine leaching out of the samples, whereas the cured samples lost as little as the untreated references. This suggests a more thorough fixation of the melamine resin in the cured samples in contrast to the very similar nitrogen fixation. Based on the results of both the fixation and the ASE, it can be concluded that determining the N-fixation is rather applicable for controlling the impregnation process than the curing quality of wood modification with melamine.

2.1 Introduction

Wood modification such as the treatment with methylated N-methylol melamine (NMM, referred to as melamine) can be used to improve the performance of non-durable native hardwoods e.g. beech (*Fagus sylvatica* L.) and expand the use to outdoor applications. Melamine treatment consists of two steps: Impregnation and curing. Different methods can be used to control the quality of melamine treatments: The determination of the weight percent gain (WPG) and the nitrogen fixation (NF) besides testing the improvement of relevant properties directly. The WPG is the weight of the chemical retaining in the product after impregnation and curing (based on dry weight). As the curing reaction of melamine resins is temperature sensitive (Rapp 1999) high temperatures are applied to ensure proper curing. Melamine contains a high percentage of nitrogen, whereas untreated wood is almost nitrogen free (Keller and Nussbaumer 1993). Within the last years, testing the N-content and -fixation were successfully utilized for quality control purposes for nitrogen containing wood modifications such as DMDHEU (Krause 2006; Bollmus 2011) and melamine (Mahnert *et al.* 2013). The N-fixation compares the N-content before and after extraction to determine the content of fixed melamine in the sample. Besides the durability, the dimensional stability is another key property for materials used in Use Class 3 conditions

such as decking and cladding. Melamine is known for enhancing the ASE up to 30 % (Lukowsky 1999). The dimensional changes of modified material between dry and wet state are measured and compared to those of untreated material. The drying step commonly utilizes a drying oven. As the behavior of uncured melamine should be examined, high temperatures had to be avoided to stop further curing. Freeze drying is a careful method to dry e.g. perishable, high quality foods such as coffee ('instant coffee') and aromatic herbs (Ratti 2001). It can also be applied for drying sawn timber, but never exceeded the experimental state due to high energy costs (Trübswetter 2006). Freeze drying takes advantage of the fact that water sublimes from ice directly to gas below a pressure of 6.11 mbar. Freeze drying is a convenient method to dry wood on a laboratory scale: It is quick and gives very similar dry weights compared to conventional oven drying at 103 °C (Larnøy 2008).

2.2 Material and Methods

In this study a melamine solution with 19 % solid content (INEOS Melamines Madurit MW840 75WA) was used to impregnate twenty beech wood samples (25 x 25 x 10 mm^3) for each of two treatment groups: One was cured at 103 °C in a drying oven with adjustable temperature and humidity levels and one air dried at room temperature. Ten samples of each group were ground in a cutting mill (SM 100 by RETSCH Haan Germany with a 2 mm sieve) after curing. One part of the wood flour was subjected directly to the nitrogen analysis (Kjeldahl method in a FoodALYT system by OMNILAB Bremen Germany: Block digestion system SBS 850, steam distillation D 1000 and back titration TS 10). Another part underwent a hot water extraction (86 °C, 24 h), was then dried and also analyzed for nitrogen. The calculated nitrogen fixation is the ratio between the nitrogen content of extracted (Ne) and non-extracted (Nne) samples [NF = (Ne / Nne)*100].

The remaining ten samples underwent a modified ASE test to check the dimensional stability. The adapted ASE contained the following steps: Freezing (-25 °C) and freeze drying (1 mbar, -20 °C, 24 h and 0.06 mbar, 4 h), water impregnation (30 min, 60 mbar), water storage (20 °C, 24 h) and storage at normal climate (20 °C, 65 %RH, 5 days). The used freeze dryer was an ALPHA 1-2 LD plus, Martin Christ Gefriertrocknungsanlagen GmbH Osterode Germany. Dimensions and weight were measured after the steps water storage and freeze drying. A leaching test did not take place before the test. In order to calculate the anti-swell-efficiency [ASE=(SR_ref–SR_mel)/SR_ref*100], the dimensional changes [(swell rate; SR=(area_wet–area_dry)/area_dry*100)] of the treated samples are referenced to those of the untreated samples going through the same procedure.

2.3 Results and Discussion

In this work the results of two different treatments with very similar nitrogen fixations are presented and discussed. The WPG and the nitrogen content of both groups determined with the Kjeldahl method was similar after impregnation and curing /air-drying (non-extracted) and also after extraction in hot water, no difference in fixation was detectable (Table.1). The nitrogen fixation rates are used to control the

curing quality of wood modifications. As melamine is a thermosetting resin, it is expected that hot curing should give a higher fixation than drying at room temperature (Rapp 1999). The hot water extraction is conducted using ground wood. By grinding wood, the cured and uncured melamine in the cell lumens presumably become accessible to extraction. In the N fixation test only the mass of N is considered.

Table.1: WPG, nitrogen content, N-fixation and weight loss of melamine treated beech and references

Curing treatment	WPG [%]	N content non-extracted [%]	N content extracted [%]	N fixation [%]	N loss by extraction [%]	Weight loss during ASE [%]
Cured (103 °C / 25 %RH 24 h)	17	7.1	5.5	77.5	1.6	0.8
Air dried (20 °C / 65 %RH 168 h)	17	7.0	5.4	77.1	1.6	10.4
Untreated references	-	0.13	0.12	(98.4)	-	1.3

To verify the dimensional stability, the modified ASE test was used. The dimensional changes of the samples of both treated groups were less than those of the untreated samples at the first cycle (Figure 1). The initially higher ASE of the air-dried samples is greatly reduced and roughly corresponds to the ASE of the cured specimen from cycle two onwards.

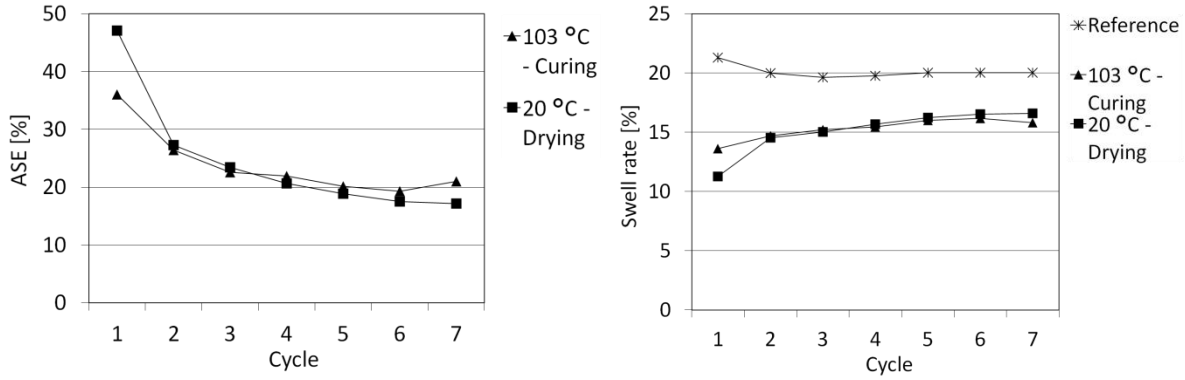

Figure 1; left: Anti-swell-efficiency (ASE) of beech treated with melamine resin and cured (103 °C) and air dried (20 °C); right: Swell rate of beech treated with melamine resin and cured (103 °C) and air dried (20 °C)

The ASE is a relative value and referenced to the swell rate of the untreated samples of the current cycle. Changes of either the swelling of the treated samples or the references have a great influence on the ASE. The decreasing ASE is a combination of an increasing swelling of the treated samples and the lesser swell rate of the references (Figure 1).

Uncured melamine is not properly cross-linked and can leach out of the solid wood samples, whereas the cured melamine is immobile. The ASE starts to decline after the first cycle. The dry mass of the

20 °C - drying samples also decreases significantly (10 %), whereas the 103 °C - curing samples and the references only lose about 1 % mass (Figure 2).

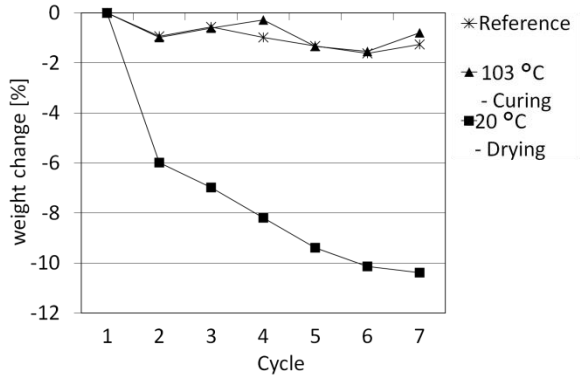

Figure 2: Weight change during ASE: Beech treated with melamine resin and cured (103 °C), air dried (20 °C); Untreated beech as reference

The decreasing ASE and the mass loss of the air-dried samples correspond strongly. This compliance is not apparent in the cured samples and suggests a more thorough fixation of the melamine resin in contrast to the results of the nitrogen fixation. The mass loss during the ASE test is composed of all substances leached out of the treated wood (Table.1).

The temperature and the pH value are the two main factors for the reaction speed of curing of melamine resins (Lukowsky 1999). In this case the acidity of beech wood (pH 5.4; (Fengel and Wegener 1989)) probably caused the melamine to react and precipitate. It was immobile to the extraction with hot water and thus showed high fixation rates. But the repeated water impregnation, water storage and drying during the ASE caused severe leaching of uncured melamine.

2.4 Conclusions

The study shows that freeze drying, as an alternative to oven drying, can be utilized to dry temperature sensitive samples in tests such as the ASE. Based on the results of both, the nitrogen fixation and the ASE, it can be concluded that determining the nitrogen fixation is rather applicable for controlling the impregnation process than the curing quality of wood modification with melamine. The hot water extraction does not show the true fixation of melamine in this study. The cured and air-dried melamine showed a high nitrogen fixation but only the air-dried melamine was severely leached out by cyclic watering during the ASE test.

3 Paper II: Different methods of nitrogen analysis and their suitability to control the curing quality of wood modification with melamine resin

(P*ublished at the European Conference on Wood Modification 8 - 2015*)

Abstract

To ensure the quality of wood modifications it is important to test the material properties. Moreover, measures of quality control have to assure how the process parameters influence the material properties. A melamine solution was used to impregnate beech wood samples divided into different curing variations including air drying at room temperature. The content of fixed nitrogen after wood modification with melamine resin was tested following two different extraction methods: hot water extraction and leaching (based on DIN EN 84 (1997)). The fixation after hot water extraction did not show differences between air drying and curing variations. In contrast, leaching the samples did show the influence of different curing temperatures and durations. High fixation rates after leaching ensured proper curing and can be a tool for quality control of wood modification agents containing nitrogen, such as melamine resin.

3.1 Introduction

Wood modification such as the treatment with methylated N-methylol melamine formaldehyde resin (NMM or MMF, referred to as melamine) can be used to improve the performance of non-durable native hardwoods e.g. beech (*Fagus sylvatica* L.) in outdoor applications. A proper melamine treatment consists of two steps: Impregnation and curing. To ensure the quality it is important to test the altered material properties for the desired improvements. Moreover, measures of quality control have to be taken to assess how the process parameters influence the material properties. Such methods can be: The determination of the solution uptake (SU), weight percent gain (WPG) and the nitrogen fixation (NF). Melamine contains a high percentage of nitrogen, whereas untreated wood is almost nitrogen free (Keller and Nussbaumer 1993). Within the last years, the N-fixation after hot water extraction (HWE) was applied as a quality control for wood modifications, for example with DMDHEU (Krause 2006; Wepner 2006; Bollmus 2011) and MMF (Krause 2008; Mahnert *et al.* 2013). The N-fixation compares the N-content before and after extraction to determine the content of fixed melamine in the sample. The curing reaction of melamine resins is temperature sensitive (Rapp 1999). Proper curing is thus ensured by high temperatures and long curing durations. However, lower temperatures and shorter curing durations are desirable considering economical aspects.

Previously, the authors used the NF after HWE to assess the curing quality of a melamine treatment and produced contradictory results: The high fixation after proper curing as well as the low fixation after just air drying were not depicted correctly (2.3, p. 14). Against this background, a new test was set up to further investigate this matter. The focus of this study was to evaluate if leaching the samples in cold

water can be combined with nitrogen fixation to control, and later predict, the curing quality. This method is then applied to evaluate the minimum requirements regarding temperature and duration for a complete curing of melamine resin for the modification of wood.

3.2 Material and Methods

In this study a melamine solution with 19 % solid content (INEOS Melamines GmbH, Madurit MW840 75WA) was used to impregnate beech wood samples (25 x 25 x 10 mm³) divided into seven curing varieties: Cured at 103 °C and 120 °C for 4 h, 24 h and 48 h in drying ovens and one was air dried at room temperature until equilibrium moisture content (EMC) was reached (Table 2).

Table 2: Curing parameters of the melamine treated beech

Temperature [°C]	Duration [h]
120	4, 24, 48
103	4, 24, 48
20 (air drying)	500 (until EMC)

A schematic sequence of the sample preparation is given in Table 3. Samples of group A were ground in a cutting mill (SM 100 by RETSCH Haan Germany with a 2 mm sieve) and subsequently fed to the nitrogen analysis (Kjeldahl method in a FoodALYT system by OMNILAB Bremen Germany: Block digestion system SBS 850, steam distillation D 1000 and back titration TS 10) to determine the N-content directly after curing. Entire samples of group B were leached based on DIN EN 84 (1997) (tap water instead of demineralized water), dried and afterwards ground up and analyzed for nitrogen. Group C underwent hot water extraction (86 °C, 16 h), before being dried, ground and analyzed. The calculated nitrogen fixation is the ratio between the nitrogen content of extracted (Ne) and non-extracted (Nne) samples [NF = (Ne/Nne)*100]. The samples of each group were mixed together after grinding. Slight deviations in WPG and therefore nitrogen content between the groups can occur.

Table 3: Sample preparation for N analysis

Group	A (N-content)	B (HWE)	C (Leaching)
Treatment sequence	Impregnation and curing		Leaching
⇩		Cutting mill	
		Extraction	
		Nitrogen analysis	

3.3 Results and Discussion

After impregnation and curing, the solution uptake (SU) and the weight percent gain (WPG) were similar in all groups. The resulting nitrogen contents were also similar after curing/drying (Table 4).

Table 4: Process parameters and results of impregnation (SU), curing (WPG) and nitrogen analysis (N-content and fixation after hot water extraction and leaching)

Max temperature [°C]	Duration [h]	Weight percent gain [%]	(A) Nitrogen content [%]	(B) N-fixation after hot water extraction [%]	(C) N-fixation after leaching [%]
120	4	18.7 (1.8)	7.3	83	91
120	24	18.5 (0.8)	7.5	80	98
120	48	17.6 (0.9)	7.6	78	102*
103	4	19.1 (1.5)	6.9	76	84
103	24	18.6 (0.9)	7.7	77	83
103	48	16.5 (1.2)	7.3	80	98
20 (Air drying)	500	17.9 (1.2)	7.3	81	60
Untreated	-	-	0.15	-	-

* Higher WPG and therefore higher nitrogen content of group C than group A.

The first part of the study was to test the nitrogen fixation (NF) after two different extraction methods for their accuracy and applicability as a tool to control the curing quality. Two extreme curing variations were selected for this comparison: Curing at 120 °C for 48 h and air drying at room temperature. After hot water extraction (HWE) they had the same fixation, after leaching the cured samples had a high and the air dried samples a low fixation (Table 4). After HWE it was not possible to distinguish between well fixed and unfixed samples. Leaching, on the other hand, did show distinct differences. Therefore, the fixation after leaching will be used to evaluate the curing quality.

The second part was to assess the curing parameters on their influence on the nitrogen fixation (Figure 3). The results are consistent with the literature: Higher temperatures and longer durations lead to a higher degree of curing.

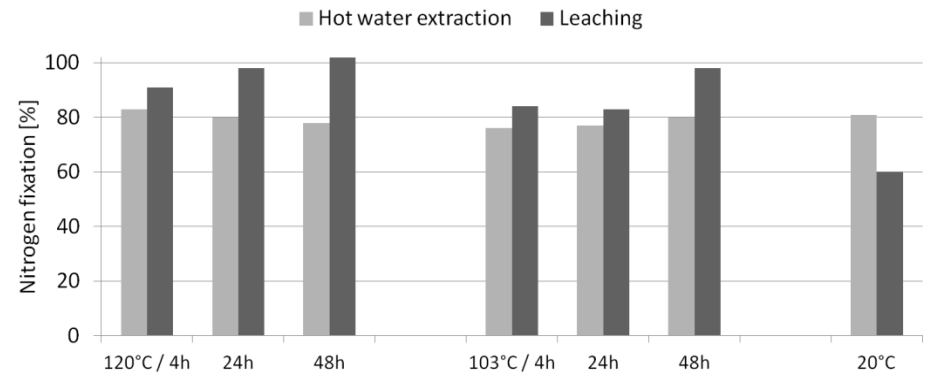

Figure 3: Nitrogen fixation of differently cured and air-dried specimen and varied extraction methods

3.4 Conclusions

The nitrogen analysis after hot water extraction did not show distinct differences between varying curing conditions or air drying. Based on these results the authors see this method as not suitable to

assess the curing quality. In contrast, leaching the samples did show the influence of curing temperatures and durations. This method is adequate and can be seen as a suitable analysis for controlling the curing quality of modified wood treated with resin containing nitrogen such as melamine. High fixation rates after leaching ensured proper curing of the samples in the examined curing variations in this study. For a better understanding of the curing mechanisms, further testing should also include other methods such as formaldehyde emission and -content and work in bending and more curing parameters.

4 Paper III: Influence of curing conditions on properties of melamine modified wood

(Published in the European Journal of Wood and Wood Products 76 (4) - 2018)

Abstract

The curing conditions influence the material properties of wood modified with melamine resin. To identify the most influential parameters, the process conditions were varied separately. The degree of conversion (differential scanning calorimetry; DSC), work in bending (WB), nitrogen fixation, formaldehyde emission, formaldehyde content and content of free formaldehyde were measured to verify the influence of the curing conditions on the material properties. The temperature and duration positively influenced the curing of melamine resin as the DSC results indicate. However, the humidity was the greatest influence on the material properties: The formaldehyde properties and the WB differed most between dry and high humidity processes with the latter producing material being less brittle and having lower formaldehyde emissions. It can be derived that DSC measurements, formaldehyde emission and -content are valuable methods to characterize the influence of curing conditions on the material properties. The FA content in combination with the emission revealed a different FA release factor for dry and high humidity processes. The conditions for future curing processes will vary depending on the desired material properties: Dry processes at high temperatures favor more complete resin networks, whereas hot steam processes can be used for material with low formaldehyde emission and less embrittlement.

4.1 Introduction

Wood in outdoor application is exposed to moisture conditions leading to dimensional changes and fungal attack. Improvements in dimensional stability, hardness and decay resistance through wood modification would not only expand the field of application but also create new markets for native wood as a renewable and sustainable resource (Hill 2006). Treatment with thermosetting resins is among other wood modification systems such as thermal modification and acetylation. MMF resins have a wide range of application in the wood products industry (Kohlmayr *et al.* 2014). They are used as adhesives, binder material, for finishing surfaces and as impregnation agents. Decking and cladding made of modified wood would be located in a high-price market sector. Therefore, a control of the modification process and the properties of the modified material is essential when homogenous products are demanded. Wood modification with thermosetting resins including melamine resin alter the mechanical properties of the wood modified therewith; The compression strength and the hardness are increased (Miroy *et al.* 1995), impact bending and work in bending (WB) are reduced (Kielmann *et al.* 2013; Mahnert 2013).

This study deals with three main topics: Identification of the minimum requirements to cure melamine resin in wood, the influence of the process parameters temperature, duration and RH on the material

properties of MMF resin treated wood and which test method will give correct results about the altered material properties.

Other scientists have applied various methods to characterize the curing process. The influence of temperature on the curing reaction of a condensation type resin was first published by Mizumachi (1973). The degree of curing (degree of conversion) of melamine urea formaldehyde resin (MUF) was examined using the differential thermal analysis and the differential scanning calorimetry (DSC). The influence of wood on the degree of curing of MUF was investigated by Pizzi and Panamgama (1995). The same methods were used to study the curing reaction of MMF impregnated papers and the resulting properties (Kandelbauer *et al.* 2009a; Kohlmayr *et al.* 2014). The most frequently used methods for quality control of impregnation modifications are based on the increased mass caused by the modification chemicals. The solution uptake (SU) is used to characterize the impregnation and the weight percent gain (WPG) to characterize the amount of cured modification agent in the wood. Different methods depending on type of resin and curing process parameters were investigated during the last years. Such methods include the measurement of formaldehyde (FA) emissions and the nitrogen content and – fixation (NF). When resin formulations contain FA, emissions were measured to ensure they meet regulations (Lukowsky *et al.* 1998; Rapp 1999; Krause 2006; Wepner 2006). Curing specimens at higher temperatures for longer durations resulted in lower FA emissions (Lukowsky 1999). Curing of nitrogen containing resins such as DMDHEU or MMF can also be controlled by the nitrogen content and – fixation (NF) (Rapp 1999; Schaffert 2006). Thorough curing of MMF resulted in the fixation of the nitrogen containing resin (Rapp 1999). Different process conditions such as time and temperature affect the properties of modified wood. Indications of how the process conditions influence the properties were made by Krause (2006), Schaffert (2006) and Wepner (2006) for DMDHEU treatment of wood. High temperature curing resulted in a more complete curing of the resin (Scheepers *et al.* 1993). Klüppel and Mai (2013) further discussed this matter and found dry curing conditions leading to more complete curing than wet conditions.

The minimum requirements for curing were examined using differential scanning calorimetry (DSC). To investigate the curing process, the parameters temperature, time and RH were varied separately to verify their influences on the material properties. After the modification processes, different methods such as NF, FA content and - emission and WB were applied to determine the altered material properties. Cross referencing the test results with the process parameters ought to show the validity of the test result and the influence of the process parameters on the material properties.

4.2 Material and Methods

Clear specimens of beech wood (*Fagus sylvatica* L.) were oven dried and impregnated (Vacuum 100 mbar for 1 h; Diffusion phase at atmospheric pressure for 2.5 h) with different solutions of methylated melamine formaldehyde resin (MMF). The solid content (SC) of the impregnation solution

was dependent on the experimental setup. (Table 5). Based on the stock solution of the MMF resin (Madurit MW 840, INEOS Melamines GmbH, Frankfurt Germany), 1 % Triethanolamine (Th. Geyer GmbH & Co. KG, Renningen Germany) was added to the impregnation solution as pH buffer.

Table 5: Overview of the solid content (SC) of the impregnation solution [%], size of the specimens for treatment (mm^3), and type of specimens (solid specimens or wood particles) for analysis of the different curing series. List of the applied tests for each curing series.

Series	Applied tests	SC [%]	Size of specimens for treatment (rad x tan x lon) [mm^3]	Specimen type for analysis
Minimum thermal requirements	DSC	50	4 x 10 x 65 (impregnation); 4 x 4.5 (curing, DSC)	Solid specimens
Material properties	3-point bending	19	10 x 10 x 180	Solid specimens
	Nitrogen fixation		25 x 25 x 10	Wood particles
	FA emission			Solid specimens
Formaldehyde properties	FA content	19	25 x 25 x 10	Wood particles
	FA emission			Solid specimens
	Content of free FA			Solid specimens
	Nitrogen fixation			Wood particles

4.2.1 Determination of minimum curing time and temperature

The analysis with DSC (200 F3 Maia, NETZSCH GmbH, Selb Germany) was used to record the dependency of the degree of conversion (degree of curing) on temperature and time of the curing process. Oven-dry beech wood specimens were impregnated and weighed directly after impregnation to determine the solution uptake (SU). Afterwards cylindrical specimens were die-cut, weighed and stored at -18 °C until curing and subsequent testing.

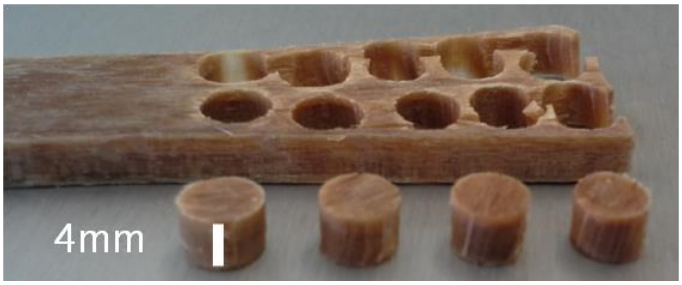

Figure 4: Preparation of melamine treated beech specimens for DSC analysis

The specimens (Figure 4) of MMF treated beech wood were cured in a laboratory drying oven at set temperatures for specific durations (Table 6).

Table 6: Parameters of the curing processes for the determination of the minimum thermal requirements via DSC: Curing temperature [°C] and - duration [h]. Subsequent analysis of the residual reactivity via DSC.

Temperature [°C]	Duration [h]
90	0.1, 0.2, 0.4, 0.8, 1.7, 3.3, 6.7, 27, 48, 107
90	0.1, 0.2, 0.4, 0.8, 1.7, 3.3, 6.3, 13, 19, 91
105	0.1, 0.2, 0.4, 0.8, 1.7, 3.3, 6.7
110	0.1, 0.2, 0.4, 0.8, 1.7
120	0.1, 0.2, 0.4, 0.8

The specimens consisted of wood, water and resin but only the resin released measurable reaction energy. Therefore, the mass of the specimens was corrected to only account for the mass of the resin (Eq. 1).

$$M_i - M_0 - M_w = M_r \quad (1)$$

M_r = Mass of resin [g]

M_i = Mass after impregnation and die-cut [g]

M_0 = Dry mass before treatment [g]

M_w = Mass of water [g]

After curing the specimens were placed in high pressure, gold plated steel crucibles (30 µl) which were sealed and subjected to a temperature gradient ranging from 20 °C to 180 °C at a heating rate of 10 °C/min. The enthalpy changes were recorded and analyzed for the onset- and peak temperature and enthalpy integral (H) with the NETZSCH Proteus Thermal Analysis 5.2.0 program. Onset - and peak temperature were used to describe the reaction. The onset temperature is defined as the intersection of the tangents of the peak and the extrapolated baseline. It is defined as the temperature at which the reaction starts to accelerate and subsequently proceeds without external energy input. The peak temperature is defined by the maximum thermal activity (heat flow) of the reaction. Uncured specimens were analyzed in the DSC to determine the full reaction enthalpy. As described by Kandelbauer *et al*. (2009b) the calculated degree of conversion is the ratio of the enthalpy of the cured and uncured specimens (Eq. 2). To determine the influence of wood on the curing reaction of MMF, the reaction kinetics of the pure stock solution (75 % SC) of the resin was analyzed in the DSC with the same temperature program as mentioned above.

$$H\alpha\ [\%] = (H_{uncured} - H_{cured}) / H_{uncured} * 100 \quad (2)$$

H_α = Degree of conversion [%]

$H_{uncured}$ = Enthalpy integral of the uncured specimen [kJ/g]

H_{cured} = Enthalpy integral of the cured specimen [kJ/g]

The information about the reaction time and temperature derived from the DSC measurements was used to lay out the following curing series.

4.2.2 The influence of curing time, temperature and relative humidity on work in bending, nitrogen fixation and formaldehyde emission

To determine the influence of the curing parameters on the material properties, the process parameters were varied individually. Curing took place in a laboratory oven (XVC305 UNOX S.p.A., Padova Italy) with the capability to control the temperature as well as the relative humidity (RH). Based on the DSC results, the applied curing parameters were 90 °C, 105 °C and 120 °C for 4, 24 and 48 hours. The RH (% steam) during curing was varied between 0 %, 40 %, 80 % and 100 %. The percentage of steam resulted in different RH levels at different temperatures. For economic reasons, this was only applied to curing processes lasting 24 h (Table 7).

Table 7: Parameters of the curing processes for the determination of the material properties and the formaldehyde properties. Temperature [°C], duration of curing [h] and the relative humidity of the curing process [% steam]

Series	Treatment	Temperature [°C]	Duration [h]	Relative humidity [% steam]
Material properties	untreated	-	-	-
	uncured	20	-	-
	cured	105	4, 24, 48	0
			24	80
		120	4, 24, 48	0
			24	40, 80, 100
Formaldehyde properties	cured	90	24	0, 100
		105	24	0, 100
		120	24	0, 100

4.2.2.1 Determination of work in bending

The work in bending was measured in a three-point bending test DIN 52 186 (1978) on a universal testing machine (Z010 Zwick/Roell, Ulm Germany). The results were analyzed with testXpert II (Zwick/Roell, Ulm Germany). 15 replicates per group were used, for the dimensions and solid content of the impregnation solution see Table 5.

4.2.2.2 Determination of nitrogen fixation

The results of curing nitrogen containing resins such as MMF can be controlled by the nitrogen fixation (NF). The content of nitrogen remaining in the sample after an extraction method is considered to be fixated. The extraction method in this study was leaching of the specimens based on DIN EN 84 (1997).

Entire specimens were leached and afterwards ground up in a cutting mill with a 2 mm sieve (SM 100 by RETSCH, Haan Germany) for subsequent nitrogen content analysis. The Kjeldahl method (1883) was used to determine the nitrogen content of the sample. The wood particles were subjected to the nitrogen analysis (block digestion system SBS 850, steam distillation D 1000 and back titration TS 10, FoodALYT system OMNILAB, Bremen Germany). The NF was calculated as the ratio of nitrogen content of leached and unleached samples (Eq. 3).

$$Fix_N\ [\%] = (N_{unleached} - N_{leached}) / N_{unleached} * 100 \quad (3)$$

Fix_N = Nitrogen fixation [%]

$N_{unleached}$ = Nitrogen content unleached sample [%]

$N_{leached}$ = Nitrogen content leached sample [%]

4.2.2.3 Determination of formaldehyde emission

The FA emissions of the specimens after curing were measured based on the EN 717-3 (1996). Four specimens were placed in each flask containing 50 ml demineralized water. Three flasks per curing process were placed in an oven at 40 °C for 24 h. The formaldehyde concentration of the solution was photometrically determined (Specord 205, Analytik Jena AG, Jena Germany) using the acetyl acetone method.

4.2.3 The influence of curing temperature and relative humidity on formaldehyde content, formaldehyde emission, content of free formaldehyde and nitrogen fixation

The FA emission was determined as mentioned above.

Two 0.5 g samples from the differently cured treatment groups were analyzed for their FA content by hot steam distillation in half concentrated phosphoric acid for 33 min (FoodALYT D 1000 OMNILAB, Bremen Germany). The FA concentration of the solution of was then measured photometrically as mentioned above. To put the FA content and the resulting FA emissions in relation to each other, their ratio was calculated (Eq. 4).

$$Factor_{E/C} = FA_{emission} / FA_{content}) \quad (4)$$

$Factor_{E/C}$ = Ratio of formaldehyde emission and formaldehyde content

$FA_{emission}$ = Formaldehyde emission [mg/kg]

$FA_{content}$ = Formaldehyde emission [g/kg]

The content of free FA of the specimens after curing was photometrically determined according to DIN EN 120 (1992) in a perforator apparatus.

4.3 Results and Discussion

4.3.1 Minimum thermal requirements for curing melamine resin

4.3.1.1 Minimum curing temperature and duration of melamine resin curing in the presence of wood

The differential scanning calorimetry (DSC) analysis revealed a temperature and time dependency of the degree of conversion. Reported curing temperatures for MMF range from 80 °C to 140 °C (Lukowsky 1999; Rapp 1999). Wood components start to degrade at 140 °C. The temperature for the curing experiments was therefore limited to 120 °C. The results of this study revealed that there was less residual reactivity of methylated melamine formaldehyde resin (MMF) at higher temperatures and longer curing times. Bergmann *et al.* (2006) used the DSC analysis to show the influence of wood and wood constituents on the curing temperature of several MMFs with different degrees of methylation. Partially methylated resins (such as the resin used in this study) were more temperature sensitive than fully methylated resins. DSC was used to characterize the curing reaction of MMF and the influence of the presence of wood. The results showed that the presence of wood lowered the reaction temperature considerably (Table 8).

Table 8: DSC analysis of melamine resin and melamine treated beech wood. Onset and peak temperatures; Group mean values and standard deviation in parenthesis

Specimens/Group		Onset [°C]	Peak [°C]
Melamine (20 %)	(n=2)	164.3 (1.0)	180.2 (0.5)
Melamine (50 %)	(n=2)	165.7 (0.4)	179.4 (1.4)
Beech and melamine (50 %)	(n=12)	110.4 (2.2)	135.4 (1.8)

Kandelbauer *et al.* (2009b) calculated a temperature and time dependency of the curing reaction of MMF via DSC measurements (without the presence of wood). The presence of wood lowered the crosslinking temperature significantly. The difference in reactivity presented in this study were comparable to Bergmann *et al.* (2006). When MMF was cured in wood the onset and peak temperature were distinctly lower: The onset temperature was reduced by 54 °C (from 164 °C to 110 °C) and the peak temperature by 45 °C (from 180 °C to 135 °C). The curing reaction of MMF can be catalyzed by the acidity of wood (Mizumachi and Fujino 1972; Scheepers *et al.* 1993). This would lead to lower reaction temperatures as observed in this study.

Different resins react differently to the presence of wood. MUF seemed to have the same reaction towards the presence of wood as MMF. Experiments by Pizzi and Panamgama (1995) with melamine

urea formaldehyde resin (MUF) and wood showed similar effects: the activation energy was lower for wood/MUF mixtures than for MUF alone. The curing of urea formaldehyde resin (UF) can be retarded or catalyzed by wood: Mizumachi (1973) showed an increase in activation energy of UF in the presence of wood. Xing *et al.* (2005) characterized the curing of UF resin reaction via DSC and found several effects of the wood on the curing reaction: Here, the presence of wood lowered the activation energy, but it also led to a lower degree of conversion of the resin by a diffusion effect. Popovic *et al.* (2011) reported that crosslinking of UF resin took place at above 100 °C in the presence of wood. Wood had a retarding effect on curing reaction as the peak temperature rose higher compared to resin alone being cured.

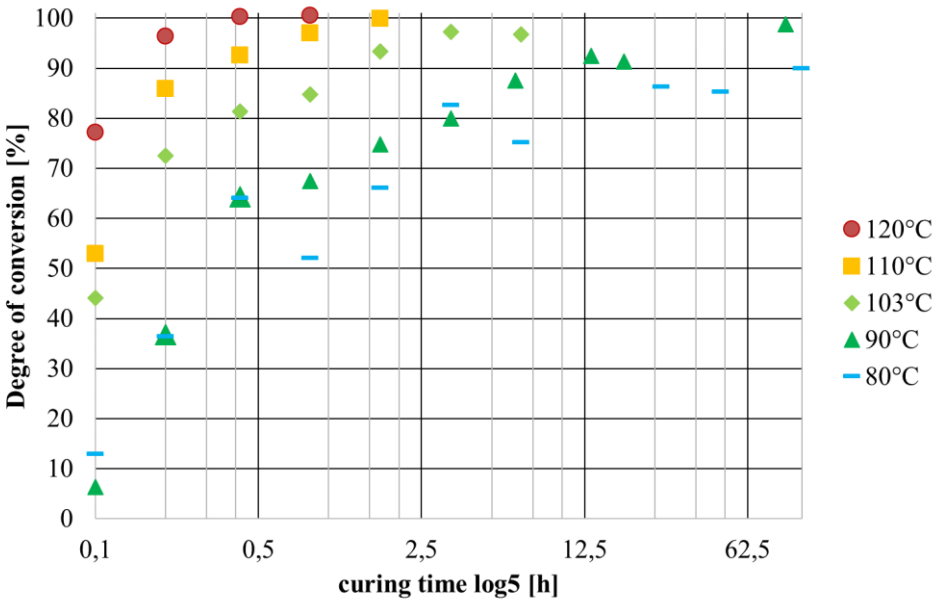

Figure 5: The degree of conversion of melamine treated beech calculated from the DSC results. A logarithmic scale (log5) was chosen to show the curing progress after different curing times (6 min – 110 h and different temperatures; 80 °C – 120 °C)

The curing reaction of MMF started at temperatures as low as 80 °C but could never be completed at this temperature (Figure 5). Even after 107 hours, the curing was not finished, and a residual reactivity could be measured at 80 °C. With curing temperatures above 100 °C, the curing was completed in less than 3 hours. Specimens cured at 120 °C only needed minutes to show a distinct progress of the curing reaction. After 30 min, there was no reactivity left at all to be measured.

4.3.1.2 Suitability of the method

The DSC specimens showed how the temperature affected the curing of MMF in wood. They represent the compare temperature of a board being cured and thus could simulate the minimum requirements of a complete curing. The DSC data is suitable used to depict the curing behavior of MMF resin alone and of impregnated wooden specimens.

4.3.2 Work in bending, nitrogen content and - fixation and formaldehyde emission

The work in bending (WB), nitrogen fixation (NF) and formaldehyde (FA) emission were used to investigate the influence of the curing temperature, duration and relative humidity (RH) on the material properties. The results are displayed in Table 9.

Table 9: Results of the curing series to determine the influence of the curing temperature, duration and relative humidity (RH). Weight percent gain (WPG), work in bending (WB) [N/mm²], nitrogen fixation (NF) after EN 84 [%] and formaldehyde (FA) emission. Group mean values with standard deviation in parenthesis

Treatment	Temperature [°C]	Curing time [h]	RH [% Steam]	WPG [%]	WB [N/mm²]	NF [%]	FA emission [mg/kg]
untreated	-	-	-	-	26.3 (4.8)	-	3.2 (1.1)
uncured	20	-	-	-	22.6 (3.8)	60.2	559.2 (18.3)
cured	105	4	0	16.2 (1.4)	13.6 (3.9)	84.5	239.4 (5.4)
		24	0	16.5 (1.0)	13.3 (2.7)	82.2	226.7 (18.3)
			80	15.1 (1.0)	13.3 (2.9)	102.3*	63.0 (5.5)
		48	0	15.4 (1.4)	13.6 (3.1)	97.7	194.5 (3.8)
	120	4	0	16.5 (1.6)	12.7 (3.0)	90.9	223.6 (13.1)
		24	0	17.2 (0.7)	14.6 (3.5)	98.1	129.0 (4.8)
			40	17.1 (0.4)	12.5 (3.2)	102.0*	94.0 (7.6)
			80	13.4 (0.9)	19.3 (3.2)	91.0	28.7 (3.4)
			100	14.8 (0.8)	18.3 (4.4)	81.2	12.0 (1.0)
		48	0	17.0 (0.8)	12.0 (3.8)	101.5*	89.2 (7.5)

The weight percent gain (WPG) was recorded to ensure a uniform treatment. The WPG for the specimens for the determination of NF could only be calculated theoretically to prevent post curing when recording the oven dry weight. A consistent WPG was considered when the specimens were chosen. The average WPG varied from 13.4 % to 17.2 % with an overall average of 15.4 %.

4.3.2.1 Influence of the curing temperature, duration and relative humidity on the work in bending

The WB was tested in a three-point bending test. The impregnated but uncured specimens showed the least reduction in WB, but the mere presence of uncured resin in wood already decreased the WB. WB showed generally reduced values to about 50 % of the reference's strength for most curing processes (Table 5). Curing temperature and duration of the dry processes did not affect the WB, whereas the high RH processes at 120 °C had less reduced strength values. However, high RH at 105 °C curing did not show a difference to dry curing. A higher degree of modification causes more embrittlement (Lukowsky 1999; Bollmus 2011; Kielmann *et al.* 2013). The WB could show the influence of the curing process: Less embrittlement and thus a less reduced WB could indicate a less completely cross-linked resin network.

4.3.2.2 Influence of the curing temperature, duration and relative humidity on the nitrogen content and - fixation

Solution uptake and responding WPG varied between groups and between individual specimens. The differences in WPG resulted in slightly different nitrogen contents. If the WPG was higher in leached specimens than in unleached specimens, NF values above 100 % were calculated. The NF was used to evaluate the influence of the curing processes on the degree of curing. The recorded NF rates in this study varied between 60 % and 100 %. In general, the NF was higher at higher temperatures and longer curing durations. The influence of the RH on the NF was dependent on the temperature: Lower NF values of at high RH were recorded at 120 °C compared to the dry processes. Higher fixation was recorded for curing at 105 °C and high RH compared to the dry process. 105 °C and 120 °C seemed to be sufficiently high temperatures to polymerize MMF to an un-leachable state. The DSC measurements, on the other hand, indicated a minimum temperature of 110 °C for complete resin curing. Air drying without curing led to the lowest NF; however, 60 % of the nitrogen was fixed in the sample. The influence of the curing temperature and duration on the NF was consistent with the literature, describing the curing of resins as thermo-sensitive (Rapp 1999). The presence of moisture can have a strong influence on NF (Klüppel and Mai 2013) but the influence of RH on NF could not be clarified in this study. Krause (2006) measured the influence of curing process parameters of DMDHEU treated Scots pine and beech wood on the material properties where the NF rates were considerably lower: 50 % NF were recorded when the specimens were cured at high temperatures under dry conditions and 25 % fixation when cured under wet conditions (specimens were wrapped in plastic bags to retain moisture). However, it is scarcely reported how hot steam processes influence the degree of curing analyzed via NF. Wepner (2006) found the nitrogen content to be suitable to calculate the amount of modification agent brought into the wood specimens (WPG), he did not use the NF to evaluate the influence of process parameters on the degree of curing. Schaffert (2006) reported that the NF of different DMDHEU modifiers was high (87 % - 97 %) after hot steam processes and stated that hot steam processes are sufficient for complete curing of the resin. It has to be considered, that water is a product of condensation reactions such as the polymerization of MMF (Jones *et al.* 1994). High moisture contents while curing shift the chemical equilibrium towards the educts, potentially obstructing a complete curing reaction. The lower NF values of processes with high RH at 120 °C compared to the fixation values of the dry process at 120 °C are an indication of this chemical mechanism.

4.3.2.3 Influence of the curing temperature, duration and relative humidity on the formaldehyde emission

The formaldehyde (FA) emission was negatively correlated to temperature. The same was recorded for the duration of the processes. There was a positive correlation of RH while curing at 120 °C and the reduction of the FA emission. Air drying and no curing led to the highest FA emission. The literature suggests that more complete curing causes less emission of FA (Lukowsky *et al.* 1998; Lukowsky 2002).

High temperatures and long durations should thus lead to lower emissions. For the dry processes this is in accordance to the literature (Lukowsky *et al.* 1998; Schaffert 2006; Wepner 2006): The FA-emissions measured with the flask method were lower at higher temperatures and longer curing durations. The high RH processes showed very low FA emissions even at lower temperatures. This was published for wood modified with DMDHEU (Krause 2006; Schaffert 2006): Hot steam processes led to the lowest FA-emissions. The FA-emission was highly influence by the availability of water while curing (Petersen 1971). A potential explanation is the fact that FA is highly soluble in water. The hot steam present in the curing oven could absorb the FA. This could lead to a considerably lower FA content of the specimens after treatment.

4.3.3 The influence of curing temperature and relative humidity on the formaldehyde properties and nitrogen fixation

The influence of the curing process parameters on the material properties were measured by work in bending, NF and the formaldehyde emission. Further investigations of the formaldehyde properties, especially regarding the influence of RH during curing on the FA-content were conducted. The selected temperatures were 90 °C, 105 °C and 120 °C. The curing time was kept at 24 h and 0 % and 100 % steam were used. The results of the second curing series are displayed in Table 6. NF and FA-emission were recorded as reference to the first curing series investigating the material properties.

4.3.3.1 Influence of curing temperature and relative humidity on the formaldehyde content

The formaldehyde (FA) content decreased slightly at higher temperatures in dry processes. The high RH curing showed significantly lower FA contents than the dry processes. No temperature dependency could be seen at high RH curing. No literature about the remaining FA content after curing MMF resin in wood could be found. The difference of the amount of FA present in the specimens after curing and the resulting FA emissions is compared in the following paragraph.

4.3.3.2 Interdependency of the formaldehyde content and the formaldehyde emission

When comparing the FA emission with the measured FA content in this study, it supports the hypothesis that low emissions are caused by low contents (Figure 6).

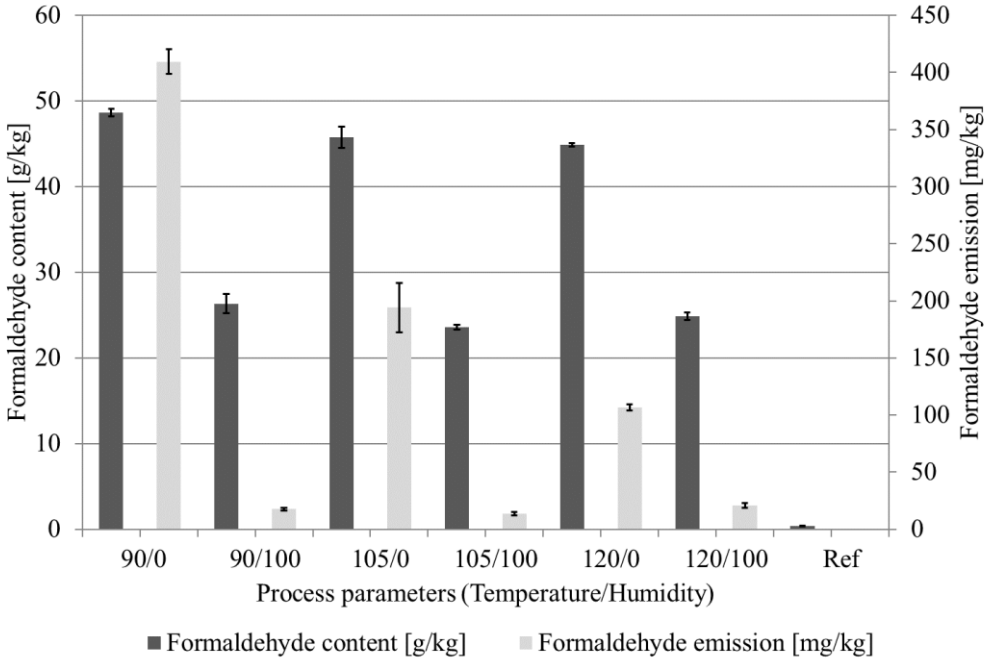

Figure 6: Formaldehyde content and formaldehyde emission of beech modified with melamine resin under different curing conditions

It can be derived that steam in high RH processes is the potential vector to extract FA from the specimens while curing. Our results showed that this was the case regardless of the temperature. The specimens cured at high RH had the same low FA content and emitted similar amounts of FA independent of the curing temperature. The dry cured specimens had a higher FA content and a much higher FA emission than the specimens cured at high RH. If the FA content and the FA emission are compared via the $factor_{E/C}$ it can be seen that for the dry processes the factor is temperature sensitive and that the factor is constant for the high RH processes (Table 10).

Table 10: Results of the curing series to determine the influence of the curing temperature and relative humidity (RH) on FA content, FA emission, Factor FA emission/FA content, content of free FA and nitrogen fixation (NF). Group mean values with standard deviation in parenthesis

Treatment	Temp [°C]	RH [% Steam]	FA content [g/kg]	FA emission [mg/kg]	Factor E/C	Free FA [mg/kg]	NF [%]
untreated	-	-	0.36 (0.02)	7.2 (0.6)	-	1.3 (0.9)	-
cured	90	0	48.6 (0.4)	409.4 (10.8)	0.0084	641.5 (8.1)	71.2
		100	26.3 (1.1)	17.7 (1.2)	0.0007	42.1 (2.5)	94.5
	105	0	45.8 (1.2)	194.0 (21.7)	0.0042	327.0 (3.4)	95.3
		100	23.6 (0.3)	13.6 (1.4)	0.0006	15.2 (1.3)	93.5
	120	0	44.8 (0.2)	106.6 (2.7)	0.0024	205.6 (5)	98.7
		100	24.9 (0.4)	20.7 (1.9)	0.0008	11.3 (1.4)	93.7

Different bridges between MMF molecules occur when cured in different conditions: Methylene-ether bridges are transformed to methylene bridges at high temperatures. The first being more susceptible to hydrolysis and thus less stable (Scheepers *et al.* 1993).

4.3.3.3 Influence of curing temperature and relative humidity on the content of free formaldehyde

The results of the content of free formaldehyde had the same pattern as the results of the emission test and thus yielded no further information but confirmed the results of the latter.

4.3.3.4 Influence of curing temperature and relative humidity on the nitrogen fixation

The results of the NF of the high RH processes at 120 °C were not uniform. At first the fixation of high RH curing was lower than that of the dry process, when repeated, there was no difference in fixation of humid and dry processes. The specimens of the process 90 °C/0 %RH had a low NF (71 %), all others showed high NF (94 % - 98 %). Curing processes with high RH could not be differentiated from dry curing via NF.

4.3.4 Comparing the results of the test methods – DSC and the curing processes

This study was conducted to gain knowledge about the minimum thermal requirements for curing MMF in wood, the influence of process parameters on the material properties of MMF treated beech wood and the accuracy of the applied test methods. Temperature, duration and RH of the curing processes were the variable parameters. The applied tests were differential scanning calorimetry (DSC), work in bending (WB), formaldehyde (FA) emission, FA content, content of free FA and NF after leaching.

The DSC analysis showed promising results regarding the influence of wood on the curing reaction of MMF resin by lowering the respective onset temperatures and peak temperatures when in contact with wood. It was possible to distinguish partially and completely cured specimens, as the degree of conversion can be calculated by the residual reaction enthalpy. A higher degree of conversion was recorded after higher curing temperatures and longer curing durations. The Q10 temperature coefficient (Holleman *et al.* 1995) describes the general influence of time and temperature on chemical reactions as a doubling in reaction speed for every 10 K the temperature is increased. The minimum curing conditions for complete MMF curing in beech wood are 1 to 5 hours at above 110 °C to 120 °C as suggested by the DSC results.

The WB was sensitive enough to distinguish between untreated and treated groups. Curing temperature and duration did not affect WB, whereas the high RH processes at 120 °C had less reduced WB values than the dry process. However, high RH at 105 °C curing did not show a difference to dry curing. It became evident that the RH was the most influential parameter regarding WB. Different curing conditions in themselves can cause different resin network formations. Jones *et al.* (1994) described the influence of different amounts of water present while curing producing different structures of the resin networks. Lukowsky (2002) investigated the influence of different FA contents of resin formulations on properties of modified wood. High FA contents led to increased cell wall penetration and thus more

embrittlement compared to lower FA contents. If the high RH curing leads to lower FA contents, the less reduced WB can be explained by a lower degree of modification.

The FA emissions responded directly to the temperature and the duration of curing process. The RH of the curing process seemed to be a crucial factor for the FA emission. High RH while curing led to lower emissions, independent of the curing temperature. It was thus difficult to assign the FA emissions to certain process parameters. Content of free FA was influenced by the process parameters the same way and contains the same information as FA emission. FA content showed similar responses to the curing parameters temperature and RH but on a different scale. Higher temperatures led to lower FA contents in dry processes. High RH led to reduced FA contents, regardless of the temperature. The quotient of FA content and emissions changes strongly between dry and high RH processes: High RH while curing led to reduced FA contents but led to very low emissions.

The NF showed a high variability. There is no conclusive explanation for the differences in fixation at high RH levels from the first to the second curing series. The authors have reported about the validity of NF as a mean of curing control (Behr *et al.* 2014), see 2.3 p. 14, (Behr *et al.* 2015), see 3.3 p. 18. The preferred method of leaching specimens in cold water instead of extraction of wood particles in hot water seemed to be a valid method. Hence, NF itself is questionable as a reliable test method because it is unclear whether the fixation values can be attributed to material properties. Nevertheless, NF values above 90 % assured a stable fixation of MMF in wood.

Varying the curing process parameters led to the following test results: If the curing temperature was increased, DSC showed a higher degree of conversion, FA emission and FA content were reduced, and WB and NF were unchanged. If the curing duration is extended, DSC showed a higher degree of conversion, FA emission was reduced, and WB and NF were unchanged. If the RH is increased, FA emission and FA content were severely reduced, NF was unchanged, and WB was less reduced.

4.4 Conclusions

Beech wood was treated with a methylated melamine formaldehyde resin (MMF) to determine the minimum requirements for curing, the influence of the curing process parameters (temperature, duration and relative humidity (RH)) on the material properties (work in bending (WB), formaldehyde (FA) emission, FA content, content of free FA and nitrogen fixation (NF) after leaching) and to survey the applied test methods on their accuracy to represent the material properties.

The minimum curing conditions for complete curing of MMF in beech wood are 1 to 5 hours at above 110 °C to 120 °C as suggested by the DSC results. DSC is a very useful tool to examine the curing reaction of MMF regarding curing temperature and duration.

The process conditions for curing MMF vary depending on the application of the modified material: Dry curing conditions result in a more complete resin curing, preferably at high temperatures as shown

by the NF. However, the results of the NF were not uniform; it might not be trusted as a sole test method. The FA emission showed a positive influence of temperature and curing duration.

Hot steam processes can be used to achieve even lower FA emissions and potentially less reduced WB. The FA content is mostly influenced by the RH of the curing processes. The FA content in combination with the emission revealed a different FA release factor for dry and high RH processes. The WB of beech wood is reduced by MMF treatment. Different temperatures and curing durations did not affect the WB. However, high RH while curing showed the least reduction in WB.

4.5 Addendum

The following supplemental data has been added to this paper for the discussion of the thesis:

Table 8 has been expanded to include the curing temperatures without 1 % pH buffer triethanolamine (TEA), see Table 11.

Table 11: DSC analysis of melamine resin and melamine treated beech wood. Onset and peak temperatures of the curing process in high pressure crucibles; Group mean values and standard deviation in parenthesis

Specimens/Group		Onset [°C]	Peak [°C]
Melamine (20 %)*	(n=2)	164.3 (1.0)	180.2 (0.5)
Melamine (20 % without TEA)	(n=2)	162.5 (0.9)	178.2 (1.2)
Melamine (50 %)*	(n=2)	165.7 (0.4)	179.4 (1.4)
Beech and melamine (50 %)*	(n=12)	110.4 (2.2)	135.4 (1.8)
Beech and melamine (50 %, without TEA)	(n=8)	100.2 (1.6)	125.9 (1.7)

* All impregnation solutions in this thesis were conducted using 1 % TEA as pH buffer

Table 9 has been expanded to include the bulking values, nitrogen content and the modulus of rupture, see Table 12.

Table 12: Results of the curing series to determine the influence of the curing temperature, duration and relative humidity (RH). Weight percent gain (WPG), bulking (volumetric, after curing and storage at 20 °C/65 % RH until EMC), work in bending (WB) [N/mm²], modulus of rupture [N/mm²], nitrogen content [%], nitrogen fixation (NF) after EN 84 [%] and formaldehyde (FA) emission. Group mean values with standard deviation in parenthesis

Treatment	Temp. [°C]	Curing time [h]	RH [% Steam]	Bulking [%]	WPG [%]	WB [N/mm²]	MOR [N/mm²]	NC [%]	NF [%]	FA emission [mg/kg]
untreated	-	-	-	-	-	26.3 (4.8)	134.2 (11.1)	0.20	-	3.2 (1.1)
uncured	20	-	-	-	-	22.6 (3.8)	144.6 (11.6)	7.30	60.2	559.2 (18.3)
cured	105	4	0	9.4 (0.4)	16.2 (1.4)	13.6 (3.9)	137.2 (15.2)	6.90	84.5	239.4 (5.4)
		24	0	**9.2 (0.9)**	**16.5 (1.0)**	13.3 (2.7)	127.8 (17.6)	**7.73**	82.2	226.7 (18.3)
			80	**6.6 (0.9)**	**15.1 (1.0)**	13.3 (2.9)	132.1 (16.3)	**7.63**	102.3*	63.0 (5.5)
		48	0	8.0 (1.2)	15.4 (1.4)	13.6 (3.1)	135.4 (16.1)	7.35	97.7	194.5 (3.8)
	120	4	0	8.5 (0.5)	16.5 (1.6)	12.7 (3.0)	135.8 (14.0)	7.29	90.9	223.6 (13.1)
		24	0	**9.5 (1.1)**	**17.2 (0.7)**	14.6 (3.5)	143.3 (11.9)	**7.45**	98.1	129.0 (4.8)
			40	8.9 (0.6)	17.1 (0.4)	12.5 (3.2)	139.4 (20.3)	7.41	102.0*	94.0 (7.6)
			80	5.9 (1.5)	13.4 (0.9)	19.3 (3.2)	149.3 (13.2)	7.27	91.0	28.7 (3.4)
			100	**4.1 (0.8)**	**14.8 (0.8)**	18.3 (4.4)	153.5 (20.3)	**7.98**	81.2	12.0 (1.0)
		48	0	10.2 (0.6)	17.0 (0.8)	12.0 (3.8)	130.9 (23.6)	7.58	101.5*	89.2 (7.5)

* Higher WPG and therefore higher nitrogen content of the extracted specimens than the non-extracted specimens led to the calculation of theoretical fixation rates above 100 %

5 Paper IV: The influence of curing conditions on the properties of European beech (Fagus sylvatica) modified with melamine resin assessed by light microscopy and SEM-EDX

(Published in the International Wood Products Journal 9 (1) – 2018b)

Abstract

The curing conditions influence the material properties of wood modified with melamine resin. Beech was impregnated with melamine resin and cured under dry and wet conditions to investigate the influence of humidity while curing. The topochemistry of modified wood was assessed by light microscopy and SEM-EDX to visualize physical changes on cell wall level. Light microscopy in combination with staining did not show differences between the processes. EDX line scans showed an even distribution of resin across the cell wall. The SEM micrographs revealed that dry processes had a more severe impact on the structural integrity of the material. Dry cured resin modified wood might not only show brittleness because of the resin itself but also because of micro cracks developed during curing.

5.1 Introduction

Wood in outdoor applications is exposed to moisture conditions leading to dimensional changes and fungal attack. Improvements of the mechanical and chemical properties through wood modification would not only expand the field of application but also create new markets for native wood as a renewable and sustainable resource (Hill 2006). Modification with thermosetting resins such as methylated melamine formaldehyde resin (MMF) is one of the established wood modification systems besides thermal modification, acetylation and furfurylation. MMF resins have a wide range of applications in the wood industry (Kohlmayr *et al.* 2014). They are used as adhesives, binder material, for finishing surfaces and as impregnation agents. If MMF was applied as a wood modification agent, decking and cladding made of modified wood would be located in a high-price market sector. Therefore, a control of the modification process and the modified material is essential when homogenous products are demanded.

Process conditions such as time and temperature affect the properties of modified wood. High temperature curing resulted in a more complete curing of the resin (Scheepers *et al.* 1993). Klüppel and Mai (2013) further discussed this matter and found that dry curing conditions lead to more complete curing than wet conditions. Wet conditions led to resin precipitation in the cell lumens and consequently higher resin content compared to the cell walls.

Microscopy techniques were used by several authors to detect the changes in wooden materials after gluing or wood modification. Kielmann *et al.* (2014) used light microscopy (LM) and UV

microspectrophotometry (UMSP) to visualize MMF deposits in cell lumens. Biziks *et al.* (2015) visualized the penetration depth of different molecular weight phenol formaldehyde (PF) resins through the inability of safranin to stain the cross sections of modified beech wood. This method would be very useful if applicable for the investigation of the influence of curing processes on penetration and stainability of beech modified with melamine resin.

Sernek *et al*. (1999) used brilliant sulphoflavine (BSF) and safranin staining to detect the urea-formaldehyde resin (UF) bondline in beech plywood. Mahrdt *et al.* (2015) detected the UF bondline and UF penetration by combined dyeing and fluorescence microscopy imaging. This technique was first established by Leemann and Ruch (1972). BSF was here used to quantify proteins in plant cells.

Numerous authors used electronic imagery to verify effects of wood modifications on the modified material. The most widely used methods were UMSP (Gindl *et al.* 2003; Mahnert *et al.* 2013), electron energy loss spectroscopy (EELS) (Rapp *et al.* 1999), and scanning electron microscopy with energy disperse X-ray spectroscopy (SEM-EDX) (Rapp 1999).

UMSP and EELS require demanding sample preparation, whereas SEM-EDX only requires small smoothly cut wooden blocks. The SEM-EDX technique is particularly emphasized as the specimen preparation for SEM analysis is rather simple and the EDX verification of nitrogen is a reliable method to localize melamine resin in cell walls.

The aim of this study was to analyze the influence of the curing conditions on melamine treated wood through light and electron microscopy. In particular, there were three topics: The impact of the curing conditions on staining specimens in light microscopy imaging, the micro structural changes of the melamine modified cell wall matrix through SEM and the resin distribution across the wooden matrix and the cell wall layers as analyzed by EDX.

5.2 Material and Methods

5.2.1 Material

Beech wood (*Fagus sylvatica* L.) was cut to specimens free of defects (Table 13). The methylated melamine formaldehyde resin used in this study was supplied by INEOS Melamines GmbH, Frankfurt Germany.

Table 13: Specimen sizes for light microscopy and scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM/EDX)

Applied tests	Specimen size for curing (rad x tan x long) [mm]	Specimen size for microscopy (rad x tan x long) [mm]
Light microscopy	10 x 10 x 180	3 x 3 x 0.02
SEM EDX		3 x 3 x 10

5.2.2 Methods

5.2.2.1 Impregnation and curing

Oven-dry specimens were impregnated (vacuum 100 mbar for 1 h; diffusion phase at atmospheric pressure for 2.5 h) with MMF resin (solid content 19 %) and 1 % Triethanolamine as buffer. The curing took place in a laboratory oven with the capability to control the temperature as well as the humidity (XVC305 UNOX S.p.A., Padova Italy). Two curing processes were set up, each lasted 24 h at 120 °C and differed in humidity: 0 % and 100 % steam (0 % and 52 % RH respectively) were used. The specimens were allowed to dry at room temperature for 24 h prior to curing. Solution uptake and weight percent gain (WPG) were recorded to ensure a uniform treatment. The WPG for the specimens for leaching could only be calculated theoretically in order to prevent post curing when recording the oven dry weight. Slides and specimens for light microscopy and SEM-EDX were cut from specimens after the different curing processes.

5.2.2.2 Light microscopy

The specimens for light microscopy were prepared from small specimens as mentioned above. Sections of 20 µm thickness were prepared using a sliding microtome with disposable blades. One series of sections of all treatment groups was stained in a safranin solution (0.5 %) for ten minutes. Another series of sections was stained with brilliant sulphoflavine (BSF), washed out for two weeks in demineralized water, rinsed in 50 % and 96 % ethanol (1 h each) and finally embedded in Euparal, dried at 60 °C overnight and fixed on microscopic slides.

5.2.2.3 Scanning electron microscopy and energy dispersive X-ray spectroscopy

The samples for scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) were prepared using fine hand tools and a sliding microtome with disposable blades. The specimens were placed on sample holders and carbon sputter coated. SEM micrographs were taken with an EVO LS 15 (Carl Zeiss Microscopy GmbH Jena Germany), 8.5 mm working distance, 10 kV acceleration voltage and 430 pA spot size. The EDX images were recorded using an X-MAX 50 mm² detector (Oxford Instruments GmbH, Wiesbaden Germany) in combination with the AzTecEnergy program, a recording time of 300 s, and a scan size of 1024 px. Line scans were placed to span the distance across two cell walls. The recording time was 300 s. Nitrogen and carbon data were recorded and used for the analysis of the nitrogen distribution. Comparison and thus quantification of elemental distribution on wood is challenging as the surface is rough. In order to improve and compare the data of several line scans and specimens, the nitrogen data were normalized using the carbon data. Under the supposition that the carbon content is uniform throughout the cell wall layers (Blazej 1979), the recorded carbon data (counts per second; cps) of an even, horizontal area were defined as the normalization constant. Then the nitrogen cps of every spot of the line were normalized over the mean carbon cps of that defined area (Eq. 5).

$$Ncps_n = Ncps_x / (Ccps_x / Ccps_N) \quad (5)$$

$Ncps_n$ = Normalized nitrogen count per second

$Ncps_x$ = Nitrogen count per second

$Ccps_x$ = Carbon count per second

$Ccps_N$ = Normalization constant; carbon count per second

The simple moving average (20 SMA; Microsoft Excel 2016) was used to facilitate the line scan graphs of the nitrogen distribution across the cell wall

5.3 Results and Discussion

5.3.1 Impregnation and curing

Specimens with uniform WPGs were chosen for the analysis. The average WPG varied between 13.4 % and 17.2 % with an overall average of 15.4 %.

5.3.2 Light microscopy

Transverse sections of the specimens treated with MMF resin and stained with safranin and brilliant sulphoflavine (BSF) are shown in Figure 7.

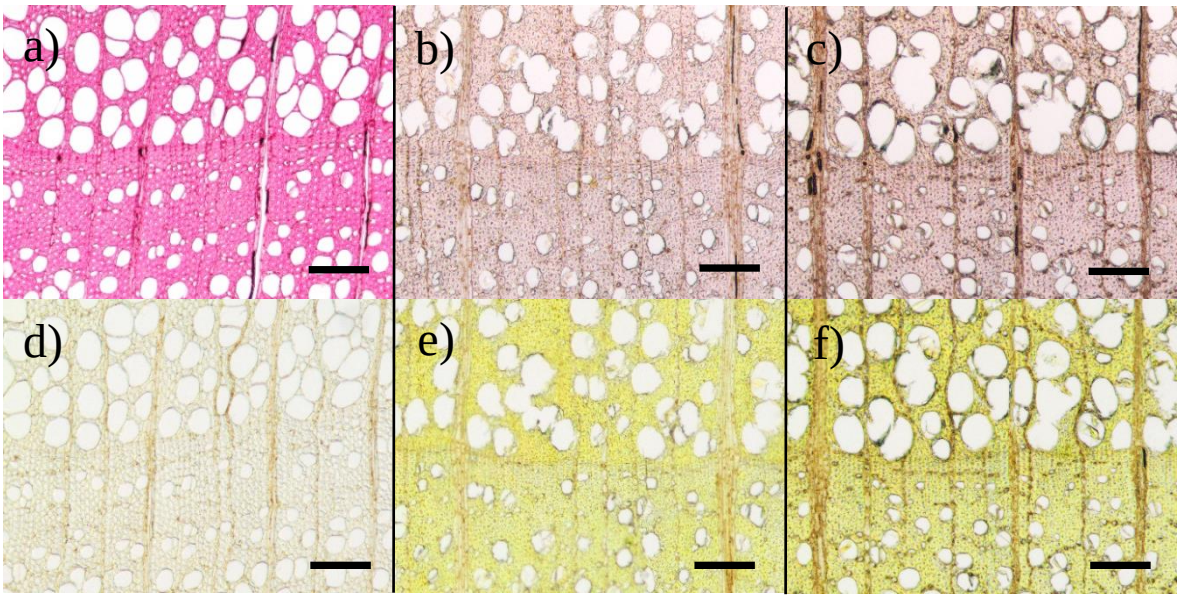

Figure 7: Top row: Light micrographs (100x) of 0.5 % safranin stained beech sections, a) untreated beech b) dry cured melamine treated beech c) steam cured melamine treated beech cured. Bottom row: Light micrographs (100x) of brilliant sulphoflavine (BSF) stained sections. d) untreated beech e) dry cured melamine treated beech f) steam cured melamine treated beech cured. Scale bar 100 µm

The untreated references showed a saturated coloration by the safranin, whereas the melamine treated specimens were barely stained. Biziks *et al.* (2015) visualized the difference in penetration depth of different molecular weight phenol formaldehyde (PF) resins through the inability of safranin to stain the cross sections of modified beech wood compared to untreated beech. In this study, there was only one resin used and therefore no drastically different penetrations depths were to be seen. The effect of the different curing conditions became not visible in thin sections after staining. BSF staining led to brightly colored melamine treated sections. The untreated sections remained unstained. There were no apparent differences between the dry and steam cured sections. Different curing regimes can result in different resin distributions as demonstrated by Klüppel and Mai (2013). Therefore, we assume that differences in cell wall penetration in the present study were not pronounced enough to distinguish between the processes by staining and light microscopy. It can be concluded that the staining methods for UF resin (Sernek *et al.* 1999; Mahrdt *et al.* 2015) proved to be highly efficient for the general detection of melamine resin in wood but not for the differentiation between the dry and high relative humidity process.

5.3.3 Scanning electron microscopy and energy disperse X-ray spectroscopy

5.3.3.1 Scanning electron microscopy

SEM images of transverse surfaces of small blocks of MMF treated beech specimens cut by microtome are shown in Figure 8 a), b).

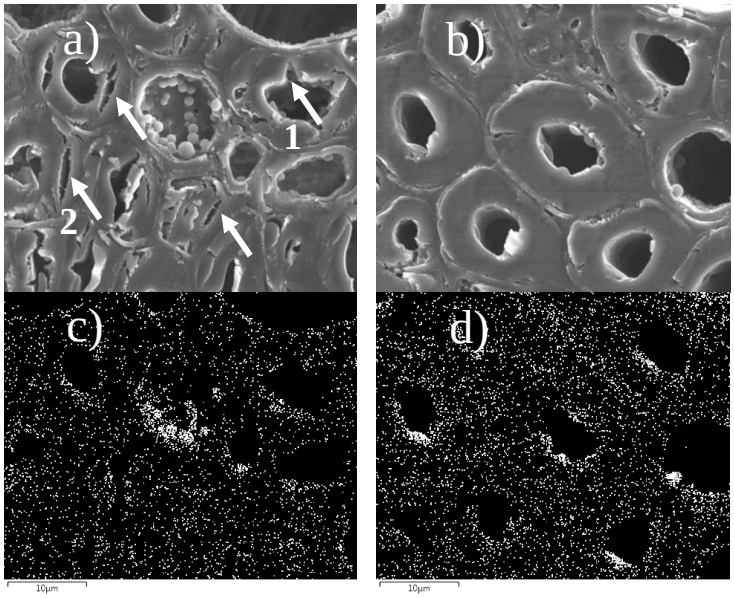

Figure 8: SEM images 2500x of a) dry cured melamine treated beech and b) steam cured melamine treated beech and c)/d) the respective EDX mapping of the nitrogen distribution. The arrows indicate micro cracks in the cell walls. 1: cell wall rupture across a single cell wall from the lumen to the middle lamellae. 2: internal cell wall rupture parallel to the cell wall located in the S2.

SEM images were used to evaluate the structure and condition of the cut surface of the specimens. Micro cracks were detected in both dry and steam cured specimens with substantially more cracks in the dry cured material. The micro cracks in the dry cured material were found across single cell walls from lumens to the middle lamellae (arrow 1) and internal cell wall ruptures parallel to the cell wall located in the S2 (arrow 2). The influence of resin modification on the structural integrity of beech assessed by electron micrographs was reported by Bollmus (2011). The propagation of macro cracks was monitored but no micro cracks were reported. Mahnert *et al.* (2013) investigated the resin distribution in MMF treated koto (*Pterygota macrocarpa* K. Schum.) and limba (*Terminalia superba* Engl. & Diels) with UMSP but did not detect any micro cracks. To the best knowledge of the authors the effect of curing conditions on the microstructure of resin treated wood had not been examined yet. It is known that drying conditions greatly influence the quality of dried wood. Fast drying with large drying rates leads to steep moisture gradients causing stress to the wooden matrix (Klüppel and Mai 2013). Data about the influence of high temperature drying conditions (115 °C) on the microstructure and the mechanical properties of Scots pine (*Pinus sylvestris* L.) suggested that high temperature drying caused micro cracks, but the mechanical properties were unaffected (Terziev and Daniel 2002). A similar temperature (120 °C) was applied during resin curing in this study. A potential reason for the formation of the cracks might be the drying conditions rather than the resin modification. Bollmus (2011) also found that the curing conditions affected the structure of ray parenchyma cells, but there was no difference between dry and hot steam curing and resin, or water impregnated specimens. Applying high temperatures between 120 °C and 130 °C while curing led to the recorded damages (Bollmus 2011).

5.3.3.2 Energy disperse X-ray spectroscopy

5.3.3.2.1 EDX mapping of elemental nitrogen

The energy dispersive X-ray spectroscopy (EDX) mapping of nitrogen showed the distribution of the resin (Figure 8 c), d)). Both processes showed a rather even distribution across the scanned surface and across the cell walls. Li *et al.* (2012) also recorded an even distribution of the modification agents maleic anhydride and methacrylate across the cell wall matrix via their respective content. There was excess resin visible in the lumens, forming granules (‘bubbles’). More granules were visible in the steam cured specimens than in the dry cured specimens. Mahnert *et al.* (2013) reported about granules in MMF modified wood, cured under wet conditions. Furuno *et al.* (2004) described the granules to form above a certain solid content/resin concentration (PF), below this concentration all the resin was located in the cell walls. Granules might indicate a saturated cell wall under the given curing conditions. Saturated cell walls might occur at high resin concentrations but also under high relative humidity curing conditions. The steam cured specimens showed lower nitrogen concentrations in the cell walls in combination with more frequent granules in the lumens. This might be an indication of a difference in resin concentration between the cell wall and lumen of the steam cured specimens and the dry cured specimens. Klüppel

and Mai (2013) reasoned that the higher diffusion potential of dry curing led to higher resin concentrations in dry cured specimens.

5.3.3.2.2 EDX line scans

SEM images of two representative cross section areas of dry and steam cured beech with the respective EDX line scans and nitrogen cps (counts per second) can be seen in Figure 9.

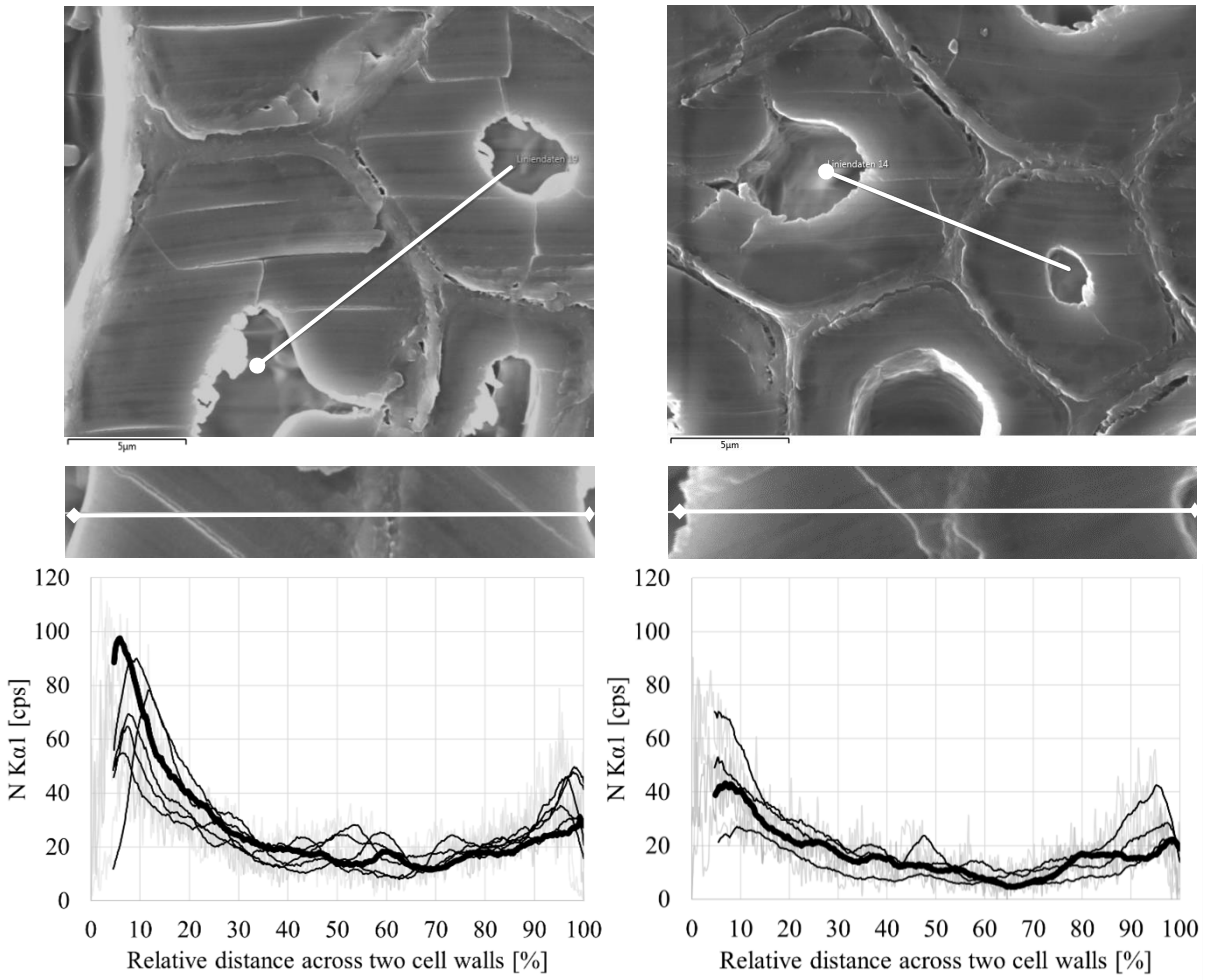

Figure 9: SEM micrographs (5000x) of dry cured beech (left) and steam cured beech (right) with the position of the line scan (thick black line, below). Line scans with nitrogen counts per second (cps) across two cell walls of dry cured (left; n = 6) and steam cured (right; n = 4) melamine modified beech. Thin black lines: Moving average (20 SMA) of the normalized nitrogen counts per second (cps) of several line scans on different specimens.

The line scans revealed the resin distribution across the cell walls of MMF treated beech with generally lower MMF concentrations towards the middle lamella (ML) than in the outer S2 and S3. Measurements from other authors revealed different concentration gradients from S2 to the ML. Higher MMF concentrations in beech towards the ML were reported by Kielmann *et al.* (2014) as analyzed by UMSP. Mahnert *et al.* (2013) also reported higher resin concentrations in the ML than in the S2 of MMF treated

koto and limba via UMSP measurements. In contrast, Rapp (1999) used SEM-EDX and recorded a slightly higher nitrogen concentration in the ML than in the S2 and a steeply rising gradient in the S3 towards the lumens, similar to the results in this study. Rapp (1999) explained the findings with the higher accessibility of lignin rich areas like the S3 and ML over the cellulose rich S2 and a resin diffusion gradient from the lumen towards the ML. Furuno and Goto (1973) found lower resin concentrations in the S2 than in the ML. Gindl *et al.* (2003) recorded higher MMF concentrations in the S2 than the ML. The behavior is explained by the higher affinity of the hydrophilic MMF resin towards the S2 as a less lignified cell wall region.

Generally, lower a nitrogen cps was attributed to the steam cured specimens. The distribution of nitrogen across the cell wall itself did not seem to be affected by the curing conditions and showed a similar pattern.

5.4 Conclusions

Beech wood was treated with a methylated melamine formaldehyde resin (MMF) and cured under differently humid conditions to determine the influence of the curing process on the distribution of the chemical on a microscopic level. There were more micro cracks in the dry cured than in the steam cured material. Further on, the steam cured specimens showed lower nitrogen concentrations in the cell walls in combination with more frequent granules in the lumens. Light microscopy in combination with two staining methods was a suitable method to distinguish between MMF treated and untreated specimens. There was, however, no difference between the different curing processes detectable. Scanning electron microscopy in combination with energy dispersive X-ray spectroscopy (SEM-EDX) was a valuable tool to visualize the structural changes induced by the curing processes. The line scan function in SEM-EDX was suitable to detect the elemental nitrogen of the MMF resin and can be used to detect the resin distribution across cell walls. SEM-EDX could be very useful method for future analysis of the influence of curing processes on the material properties of resin modified wood.

6 Paper V: Improving dimensional stability of thermally treated wood by secondary modification

(Published in holztechnologie 58 (2) - 2017)

Abstract

The potential of treating thermally modified wood with melamine resin to improve the dimensional stabilization is investigated in this study. One half of two poplar (*Populus* spp.) boards were thermally modified (T1: 210 °C; T2: 230 °C) in a commercial process, the other two halves were used as untreated reference material. Ten specimens of each material were impregnated with a solution of a commercially available methylolated melamine resin and dry-cured in a laboratory oven. The anti-swell-efficiency (ASE) based on the swell rate was measured during ten cycles of repeated drying and wetting. The melamine treatment caused a higher bulking in the references than in thermally modified wood. The ASE of T1 was improved by secondary modification, whereas the ASE of T2 was higher than that of the secondary modified material. Reasons for the low bulking may be found in the same mechanisms providing good dimensional stability of thermally modified wood in the first place. The cell walls are hydrophobized by the thermal modification and thus less accessible for melamine oligomers.

6.1 Introduction

Wood in outdoor applications is exposed to severe changes in temperature, humidity and thus dimensional changes. A fundamental improvement in dimensional stabilization through wood modification would not only expand the field of application but also create new markets for native wood as a renewable and sustainable resource.

Thermal modification is the most common method of wood modification. It is commercialized in a variety of processes which differ in terms of treatment intensity (peak temperature and duration of treatment), treatment atmosphere and medium of heat transfer. During thermal modification, the dimensional stability and durability of wood are improved by treatment between 160 ºC and 260 ºC (Militz 2002). Thermal modification is classified as active wood modification since the chemical composition of the wood is altered and cell wall polymers are degraded. The thermal stability of the cell wall polymers increases in the order hemicelluloses, cellulose and lignin. Thermal modification is known to influence the swelling of wood (Burmester 1975). The anti-swell-efficiency (ASE) of wood modified at commercially relevant temperatures is ascribed to the reduced number of OH-groups due to degradation of cell wall polymers. In the literature, an ASE between 24 % and 68 % is reported for thermally modified wood (Santos 2000; Koch 2005). One reason for this high variation is the variety of wood species, modification processes and measurement techniques.

The impregnation modification of wood with methylolated melamine formaldehyde resin (MMF) has been scientifically investigated by various researchers during the last decades (Stamm 1964; Pittman *et al.* 1994; Lukowsky 1999). MMF-resin does not alter the original color of the wood (Hagstrand 1999). It improves the surface hardness and dimensional stability of wood (Inoue *et al.* 1993a; Miroy *et al.* 1995; Rapp 1999; Gindl *et al.* 2003). The dimensional stability of wood through MMF-modification is increased due to diffusion of the MMF-oligomers into the cell wall and hardening which results in bulking of the cell walls and blocking of OH-groups, excluding these for attachment of water molecules. The literature suggests an ASE between 17 % and 26 % for wood modified with an impregnation solution containing 10 % melamine oligomers (Lukowsky 1999; Krause 2008).

Aim of this study was the combination of thermal modification (primary modification) and MMF-modification (secondary modification) to further improve the dimensional stability of the modified wood. The alteration of ASE of the modified wood by different intensities of thermal modification and secondary modification was investigated.

6.2 Material and Methods

6.2.1 Specimen preparation

Two poplar (*Populus* spp.) boards from the same batch (1 and 2; with a dry density of 540 - 420 kg/m³) were cut into two halves. One half of each board was thermally modified (T1 and T2) in a commercial process, the other half was used as untreated reference material (R1 and R2; Figure 10).

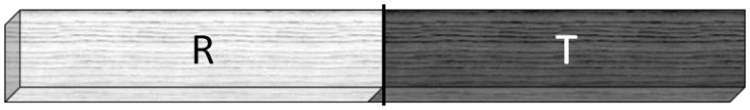

Figure 10: Material allocation for references (R) and thermal modification (T) from one board

A series of 20 defect free adjacent small specimens (Table 14) with perpendicularly oriented annual rings was produced from both halves of each board. The oven dry mass of the modified specimens was determined after drying at 103 °C for 24 h. Ten specimens of each series were modified with MMF resin (M1 and M2).

Table 14:Characteristics of specimens and modifications: Oven-dry density (OD), specimen size, modification temperature and solid content (SC) for the impregnation solution. Mean values (SD)

Label	Treatment	OD [kg/m³]	Specimens size (r x t x l) [mm³]	Modification temperature [°C]	SC impregnation solution [%]
R1	Reference Board 1	540 (1)	20 x 20 x 10	-	-
M1	Melamine treatment 1	560 (2)	20 x 20 x 10	-	10
T1	Thermal modification 1	500 (2)	20 x 20 x 10	210	-
TM1	Thermal modification 1 and Melamine treatment 1	540 (2)	20 x 20 x 10	210	10
R2	Reference Board 2	420 (5)	25 x 25 x 10	-	-
M2	Melamine treatment 2	433 (9)	25 x 25 x 10	-	7.5
T2	Thermal modification 2	400 (6)	25 x 25 x 10	230	-
TM2	Thermal modification 2 and Melamine treatment 2	437 (5)	25 x 25 x 10	230	7.5

6.2.1.1 Thermal modification

The material was thermally modified using the vacu³® process at Timura Holzmanufaktur GmbH, Germany. Operated under vacuum, heated steel plates serve as medium of heat transfer. The treatment duration at maximum temperatures 210 °C (T1) and 230 °C (T2) was 7.5 h.

6.2.1.2 Melamine modification

The specimens were impregnated with a solution of the MMF Madurit MW840/75WA (Ineos Melamines GmbH, Germany). The solid content (SC) of the MMF used for the MMF-modification of P2 was adjusted to meet the lower density of poplar board 2 and obtain the same uptake of resin (weight percent gain; WPG). SCs of the impregnation solutions are given in table 1. A full cell impregnation process (vacuum of 60 mbar for 0.5 h followed by a pressure phase of 2 h at 12 bar) was applied. Specimens were dried and cured in a laboratory oven at a maximum temperature of 120 °C for 24 h. The oven dry mass of the modified specimens was determined after drying at 103 °C for 24 h. Subsequently solution uptake (SU; Eq. 6), increased dry mass due to resin incorporated into the specimens (WPG; Eq. 7) and bulking as percentage increase in dry volume due to modification were calculated. The calculations were based on 10 replicates per modification intensity.

$$SU\ [\%] = (Mi - M) / M \times 100 \quad (6)$$

$$WPG\ [\%] = (M2 - M1) / M1 \times 100 \quad (7)$$

M = Mass before impregnation [g]

Mi = Mass after impregnation [g]

M1 = Dry mass before impregnation [g]

M2 = Dry mass after curing [g]

6.2.2 Determination of the anti-swell-efficiency

The ASE (Eq. 9) based on the swell rate (SR; Eq. 8) was tested during ten cycles of repeated drying and wetting without prior leaching. First, mass and dimensions of the specimens were recorded after careful oven-drying. Afterwards, the specimens were vacuum impregnated with tap water at 60 mbar for 0.5 h and left submerged for 16 h. Then, mass and dimensions were recorded, and the SR was calculated. The calculation of the swell rate follows Hill and Jones (1996) but is based on the cross-section area (radial x tangential) of the specimens according to Schaffert (2006) and Bollmus (2011). The measurements were conducted with an accuracy of 0.001 g and 0.01 mm.

$$SR\ [\%] = (Aw - Ad) / Ad \times 100 \quad (8)$$

$$ASE\ [\%] = (SRt - SRu) / SRu \times 100 \quad (9)$$

Ad = Dry area of the specimens [mm²]

Aw = Wet area of the specimens [mm²]

SRu = Maximum swelling of the untreated specimens [%]

SRt = Maximum swelling of the treated specimens [%]

6.3 Results and Discussion

6.3.1 Thermal modification

The thermal modification caused a mass loss depending on the modification intensity. The higher temperature caused more degradation and thus more mass loss (T1 and T2; 8 % and 10 %). Thermal modification of wood is usually carried out at 160 °C to 250 °C (Militz 2002; Hill 2006); the applied temperatures (210 °C and 230 °C) are considered medium and high treatment intensities.

6.3.2 Melamine modification

After melamine modification, differences between bulking of M1/M2 and TM1/TM2 (4.3 %; 4.8 % and 1.4 %; -0.5 %) were observed (Table 15).

Table 15: Results (N=10) of the modifications: Oven-dry density (OD), bulking, solution uptake (SU) and weight percent gain (WPG). Mean values (SD)

Label	OD [kg/m³]	Bulking [%]	SU [%]	WPG [%]
R1	540 (1)	-	-	-
T1	500 (2)	-	-	-8*
M1	560 (2)	4.3 (1.1)	147 (6)	12.2 (0.6)
TM1	540 (2)	1.4 (2.4)	145 (10)	11.6 (0.7)
R2	420 (5)	-	-	-
T2	400 (6)	-	-	-10*
M2	433 (9)	4.8 (1.0)	177 (4)	11.2 (0.4)
TM2	437 (5)	-0.5 (0.7)	177 (4)	9.7 (0.5)

Reasons for that could be anatomical and chemical properties of thermally modified wood. Thermal modification blocks diffusion pathways by sealing the cell wall due to hydrophobation of hemicelluloses and increased condensation of lignin (Tjeerdsma *et al.* 1998; Windeisen and Wegener 2008). It also reduces the number of OH-groups, leaving less potential binding sites for melamine (Weiland and Guyonnet 2003). Nevertheless, similar SU and WPG, potentially because of increased porosity (Pfriem *et al.* 2009), were observed. Pfriem (2011) reported the effect of increased porosity after thermal modification: less water absorption in radial and tangential direction and more water uptake in longitudinal direction was recorded.

6.3.3 Anti-swell-efficiency

The swelling and the ASE of R2, M2, T2 and TM2 can be seen in Figure 11. The ASE is a relative value referring to the swelling of the untreated specimens. The swelling of all treatments increased slightly with progressing ASE-cycle number. The result was a decrease of ASE over the course of the ASE test. A potential reason for this development could be cracking of the specimens during the test. Since the specimens remained free of cracks throughout the test, the increasing swell rate cannot be explained based on the current results.

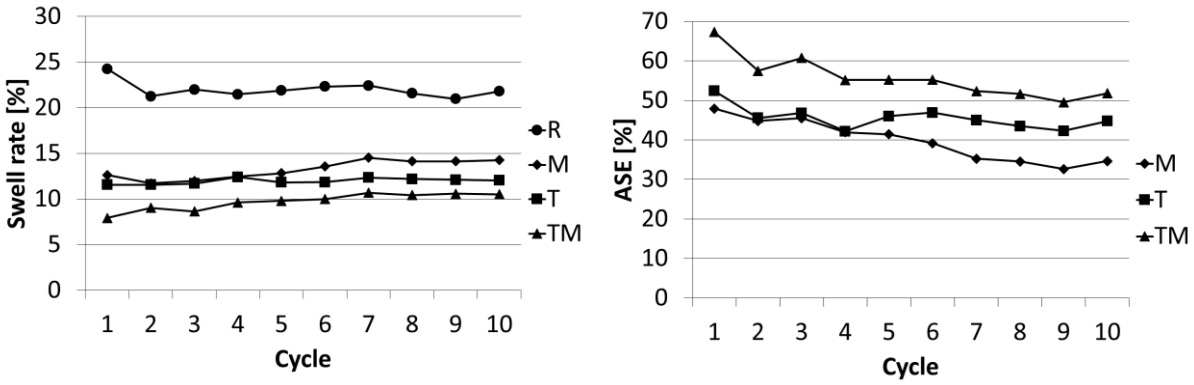

Figure 11: Results (N=10) of the anti-swell-efficiency test: Swell rate (left) of R2, M2, T2 and TM2 and ASE (right) of M2, T2 and TM2 over the course of 10 cycles of repeated drying and soaking.

The different densities of poplar board 1 and 2 caused different absolute swelling rates (Table 16). The ASE increased with increasing intensity of thermal modification: After the 10th cycle T1 and T2 retained an ASE of 45 % and 52 %.

Table 16: Results (N=10) of the swell rate (SR) and anti-swell-efficiency (ASE) after cycle 2 and 10 of materials P1 and P2 untreated and after modifications.

Label	SR^2 [%]	SR^{10} [%]	ASE^2 [%]	ASE^{10} [%]
R1	21	22	-	-
M1	12	14	45	35
T1	12	12	46	45
TM1	9	11	57	52
R2	16	16	-	-
M2	12	13	28	20
T2	7	8	59	52
TM2	7	8	56	50

The results are in accordance to Welzbacher (2007) as the ASE increases with rising modification temperatures. Higher modification temperatures lead to increasing hydrophobation of hemicelluloses and cellulose due to cleavage of OH-groups (Weiland and Guyonnet 2003), and a higher degree of polymerization (Bhuiyan *et al.* 2000). This reduces the water sorption of the cell wall and leads to less swelling.

M1 and M2 have similar WPGs and the resulting ASE ranges from 35 % to 20 % respectively. Melamine treatment enhances the dimensional stabilization of wood (Stamm 1964; Rapp 1999). The literature suggests an ASE between 17 % and 26 % for Scots pine modified with an impregnation solution containing 10 % melamine oligomers (Lukowsky 1999; Krause 2008). Sint, (2010) reported 19 % to 35 % WPG in *Bombax* spp. impregnated with 10 % Madurit MW840 resin. The melamine treatment of TM1 further improved the dimensional stability compared with T1 (52 % and 45 % ASE). The initially higher ASE of T2 (52 %) was not improved but slightly decreased by melamine treatment (TM2: 50 % ASE). The hindered bulking may account for the reduced or negative ASE. Bulking of the cell wall allows easier penetration of the cell wall by the melamine oligomers to penetrate bulked cell walls (Hill 2006). With a decreased bulking, the ability of the melamine oligomers to penetrate the cell wall is greatly reduced. This can explain that no further dimensional stabilization of the wood can be obtained.

For further studies, the influence of density in unmodified timber and the WPG on the improvement of dimensional stability should be investigated.

6.4 Conclusions

In this study the potential of secondary modification as a tool for further improvement of dimensional stability of thermally modified wood was assessed. Poplar was thermally modified at two different temperatures (T1: 210 °C and T2: 230 °C). Ten specimens of thermally modified and unmodified poplar

(R) were subsequently modified with methylolated melamine formaldehyde resin (MMF). The dimensional changes of melamine treated (M), thermally modified wood (T) and melamine treated thermally modified wood (TM) were compared to those of R in an anti-swell-efficiency test (ASE). The melamine treatment caused a different bulking in M (4.3 % - 4.8 %) and TM (1.4 % - -0.5 %). The specimens of T1 and T2 had a high ASE (45 % and 52 %). The ASE of T1 was improved by secondary modification (ASE TM1: 52 %), whereas the ASE of T2 remained higher than that of TM2 (50 %). The melamine treatment of thermally modified poplar yielded good results for solution uptake and weight percent gain, but the bulking was lower than expected. Reasons may be found in the same mechanisms providing good dimensional stability of thermally modified wood in the first place: The cell walls are less accessible for melamine oligomers due to hydrophobation resulting from thermal modification. The mechanisms responsible for the hydrophobation are the degradation of hemicelluloses (Tjeerdsma *et al.* 1998) including a reduction of OH-groups (Weiland and Guyonnet 2003) and the increased crystallinity of the cellulose (Bhuiyan *et al.* 2000). The hydrophobation of the cell wall due to thermal modification might hinder impregnation modification with water-based solutions thereof. However, impregnation modification of thermally modified wood aiming for mainly filling lumens will be unaffected.

6.5 Addendum

In addition to poplar, the dimensional stability (ASE) of beech, ash and lime were also investigated. The thermal modification and melamine treatment were the same as in paper VI. For the specifics of impregnation and curing see chapter 7.2, p.55, the results of the curing can be seen in Table 17.

Table 17: Characteristics and results of the melamine treatment (N=40): Solid content (SC) [%] of the impregnation solution, solution uptake (SU) [%], bulking [%] and weight percent gain (WPG) [%]. Mean values with standard deviations in parenthesis

Species	Treatment	SC [%]	SU [%]	Bulking [%]	WPG [%]
Beech	Melamine treatment	20	88 (7)	2.8 (1.3)	13.7 (1.1)
	Double modification	25	78 (4)	-1.4 (0.5)	14.2 (0.8)
Ash	Melamine treatment	19	100 (5)	3.6 (1.1)	12.8 (1.2)
	Double modification	20	96 (14)	-1.6 (0.4)	14.2 (1.2)
Lime	Melamine treatment	13	129 (11)	2.7 (1.7)	12.9 (3.9)
	Double modification	13	139 (21)	-2.6 (0.9)	13.3 (1.4)

The results of 10 cycles of ASE test are displayed in Table 18.

Table 18: Oven dry density (OD) [kg/m³] and results of the anti-swell-efficiency test (N=40): Swell rate (SR) [%] and anti-swell-efficiency (ASE) [%] after 10 cycles. Mean values and standard deviation in parenthesis

Species	Treatment	OD [kg/m³]	SR_{10} [%]	ASE_{10} [%]
Beech	Untreated	737 (08)	18.7 (0.2)	-
	Melamine treatment	804 (12)	16.6 (0.9)	11.2 (4.7)
	Thermal modification	660 (07)	10.2 (0.2)	45.6 (0.9)
	Double modification	763 (15)	11.0 (0.4)	41.1 (2.3)
Ash	untreated	624 (32)	16.4 (1.8)	-
	Melamine treatment	676 (34)	13.5 (1.2)	13.8 (2.9)
	Thermal modification	562 (38)	8.3 (2.3)	49.3 (15.3)
	Double modification	650 (35)	9.6 (0.3)	40.6 (1.9)
Lime	untreated	569 (44)	18.5 (2.3)	-
	Melamine treatment	618 (38)	14.6 (2.2)	20.9 (4.8)
	Thermal modification	498 (43)	9.9 (2.1)	46.6 (7.2)
	Double modification	576 (44)	10.5 (1.4)	42.6 (6.1)

7 Paper VI: Improvement of mechanical properties of thermally modified hardwood through melamine treatment

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Abstract

Specimens of beech, ash, lime and poplar were thermally modified (T) and treated with an aqueous solution of melamine (M) resin to investigate the mechanical changes after combined (double) modification (TM). Density, solution uptake, weight percent gain, bulking and equilibrium moisture content were recorded to ensure proper treatment. Samples for Brinell hardness and three-point bending were cured at 120 °C under dry conditions. The WPGs of the two treatment groups M and TM were similar but bulking of TM specimens was negative. This might indicate an incomplete penetration into the thermally modified cell wall in combination with a potential leaching of soluble hemicellulose components by the alkaline impregnation solution. The decreased hardness of heat-treated wood was substantially increased by melamine treatment (combined modification). Both modifications and their combination slightly increased the modulus of elasticity. The modulus of rupture was increased after melamine treatment, decreased after thermal modification and combined modification. The work in bending was severely reduced for all treatments. Melamine treatment of thermally modified wood was carried out successfully and some mechanical properties were improved. Double-modified wood with increased bending strength and extraordinary surface hardness would be suitable for non-structural outdoor applications such as decking and cladding.

7.1 Introduction

Thermal modification is the most widely used wood modification system today (Militz 2015). It is commercialized in a variety of processes that differ in terms of treatment intensity (peak temperature and duration of treatment), treatment atmosphere and medium of heat transfer. During thermal modification, the chemical composition of the wood is altered, and cell wall polymers are degraded. Due to thermal modification, durability and dimensional stability are increased depending on wood species and treatment intensity (Militz and Altgen 2014). The thermal stability of the cell wall polymers increases in the order of hemicelluloses, cellulose and lignin. The equilibrium moisture content of wood is reduced through thermal modification by 50%, depending on the process (Hill 2006; Esteves and Pereira 2009). Decreased EMCs can influence the mechanical properties, further, thermal modification is known to influence the mechanical properties of wood (Stamm 1964; Boonstra *et al.* 2007; Esteves and Pereira 2009). In the literature, there is contradictory information about the influence of thermal treatments on mechanical wood properties. Brinell hardness (HB), modulus of elasticity (MOE) and bending strength (MOR) were reported to increase or decrease depending on treatment intensity (Welzbacher 2007; Esteves and Pereira 2009). Impact bending strength (dynamic) (Welzbacher 2007;

Boonstra *et al.* 2007) and work in bending (static) (Kim *et al.* 1998; Wetzig *et al.* 2012; Rautkari *et al.* 2014) are affected most by thermal modification. A reduction of mechanical properties limits the range of applications for heat treated wood.

The impregnation modification of wood with methylated melamine formaldehyde resin (MMF, referred to as melamine) has been scientifically investigated by various researchers during the last decades (e.g. (Stamm 1964; Pittman *et al.* 1994; Lukowsky 1999; Rapp 1999). Focus of the investigations were dimensional stability (Stamm 1964), durability against wood destroying fungi in laboratory tests (Sailer 1995; Rapp and Peek 1996) and outdoor tests (Rapp 1999), as well as fire retardancy (Pittman *et al.* 1994). Numerous formulations of melamine were tested in the literature, often without stating the chemical composition. The resins vary in formaldehyde content and degree of methylation which results in different effects on wood properties (Lukowsky 1999), (Lukowsky 2002). This should be considered when results are compared. Melamine resin does not alter the original color of wood (Hagstrand 1999). It improves the surface hardness and dimensional stability (Inoue *et al.* 1993a; Rapp 1999). Due to the incorporation of resin in wood cell walls, density and stiffness increases (Stamm 1964; Miroy *et al.* 1995; Gindl *et al.* 2003; Deka *et al.* 2007) and impact bending strength decreases (Kielmann *et al.* 2013). The MOE was increased (Deka and Saikia 2000; Epmeier *et al.* 2004; Kielmann *et al.* 2013), the MOR increased (Inoue *et al.* 1993b) or decreased (Epmeier *et al.* 2004; Lahtela and Kärki 2014), depending on WPG. The moisture properties of melamine modified wood have been the focus of several investigations (Rapp and Peek 1995; Epmeier *et al.* 2004; Epmeier *et al.* 2007; Hosseinpourpia *et al.* 2016; Kielmann *et al.* 2016), but the results are inconclusive. Rapp and Peek (1995) reported no change in EMC by melamine treatment, Epmeier *et al.* (2004) and Kielmann *et al.* (2016) showed a minor reduction of EMC through melamine treatment and Epmeier *et al.* (2007) recorded increased EMCs.

The combination of several wood modification systems including melamine resins has been covered by some authors to various extends (Epmeier *et al.* 2004; Hansmann *et al.* 2005; Mahnert 2013; Sun *et al.* 2013; Lahtela and Kärki 2014). The combination of thermal modification and thermosetting resins was investigated by Sun *et al.* (2013). Eucalyptus was impregnated with melamine-urea-formaldehyde resin and the specimens were heat treated to improve dimensional stability and mechanical properties. The authors concluded that the combined treatment had the potential to increase the material quality of solid wood products. Lahtela and Kärki (2014) treated Scots pine with melamine resin and subsequently thermally modified the material to improve the physical and mechanical properties. The authors described that moderate heat treatment enhanced the wood properties. Mahnert (2013) investigated thermally modified koto (*Pterygota macrocarpa* K. Schum.) and limba (*Terminalia superba* Engl. & Diels) treated with melamine resin as a substitute for teak wood in maritime applications. He reported on superior hardness, durability and dimensional stability of the material and found decreased MOE, MOR and work in bending values. The results for the mechanical properties of double modified material

which was tested by Mahnert (2013), Sun *et al.* (2013), Lahtela and Kärki (2014) are summarized in Table 25.

The low hardness and work in bending are drawbacks of thermally modified wood and can presumably be compensated by melamine treatment. Improvements of the mechanical properties through combined wood modification would not only expand the field of application but also create new markets for native wood as a renewable and sustainable resource. Therefore, the aim of this study was to improve mechanical properties of thermally modified hardwoods through melamine treatment. The treatment performance was assessed via solution uptake, WPG and bulking. The altered properties by modification were evaluated through Brinell hardness and modulus of elasticity, bending strength and work in bending in a static three-point bending test setup. This will provide an extensive profile of the mechanical properties of double modified native hardwood species.

7.2 Material and Methods

7.2.1 Specimen preparation

The hardwood species used in this study were beech (Fagus sylvatica L.), ash (Fraxinus excelsior L.), lime (*Tilia* spp.) and poplar (*Populus* spp.). Four boards of each species were cut into halves. One half of each board was thermally modified (T) in a commercial process, the other halves were used for melamine treatment (M) and as untreated reference material (R). The oven dry mass of the modified specimens was determined after drying at 103 °C for 24 h. Specimens of untreated and thermally modified material for recording density, solution uptake, weight percent gain, bulking and equilibrium moisture content and performing Brinell hardness as well as three point-bending tests were modified with MMF resin (generating materials M and TM) (Table 19).

Table 19: Experimental specifications, number of specimens and specimen size of the used materials in this study

Test	Number of specimens of each treatment group	Specimen size (rad x tan x lon; mm³)
Density, solution uptake, weight percent gain, bulking	40	20 x 20 x 10
Hardness	12	25 x 50 x 50
Three-point bending	25 - 40	10 x 10 x 180

7.2.2 Thermal modification

The material was thermally modified at Timura Holzmanufaktur GmbH (Rottleberode, Germany) using the Vacu³-process. Operated under vacuum, heated steel plates served as a medium of heat transfer. The treatment duration at a maximum temperature of 230 °C was 7.5 h.

7.2.3 Melamine modification

The specimens were impregnated with a solution of a methylated melamine formaldehyde resin (MMF) Madurit MW840/75WA (Ineos Melamines GmbH, Frankfurt, Germany). The solid content (SC) of the impregnation solution was adjusted for each wood species (according to pre-trials; data not shown) to meet the density and obtain about the same uptake of resin (weight percent gain; WPG). SCs of the impregnation solutions are given (Table 20). 1 % Triethanolamine (referred to resin stock solution) was added as buffer.

Table 20: Wood species, treatment and solid content (SC) of impregnation solution for melamine treatment of the material in this study. Mean values with standard deviation in parenthesis

Wood species	Treatment	Solid content of melamine resin in impregnation solution [%]
Beech	Untreated	20
	Thermo	25
Ash	Untreated	19
	Thermo	20
Lime	Untreated	13
	Thermo	13
Poplar	Untreated	8
	Thermo	7

A full cell impregnation process (vacuum of 60 mbar for 0.5 h followed by a pressure phase of 2 h at 12 bar) was applied. Specimens were air dried (24 h) and subsequently cured in a laboratory oven. The temperature was raised from 20 °C by 20 °C every 24 h before the specimens were cured at 120 °C for additional 24 h. The oven dry mass of the modified specimens was determined after cooling in a desiccator. Eq. 10 shows the solution uptake (SU).

$$SU\ [\%] = \frac{(Mi-M)}{M} * 100 \qquad (10)$$

M = Mass before impregnation [g]

Mi = Mass after impregnation [g]

Eq. 11 shows the percentage increase in dry mass due to resin incorporated into the specimens (WPG).

$$WPG\ [\%] = \frac{(M2-M1)}{M1} * 100 \qquad (11)$$

M1 = Dry mass before impregnation [g]

M2 = Dry mass after curing [g]

Eq. 12 shows the bulking as percentage increase in dry area due to modification.

$$\text{Bulking [\%]} = \frac{(A2-A1)}{A1} * 100 \quad (12)$$

A1 = Dry area before impregnation [mm²]

A2 = Dry area after curing [mm²]

The equilibrium moisture content (EMC) at 20 °C and 65 % RH of the specimens was calculated. To minimize the influence of the additional weight due to the chemical modification (Akitsu *et al.* 1993), the reduced equilibrium moisture content (EMC_R) was calculated based on the dry weight of the specimens before modification (Eq. 4).

$$EMC_R = \frac{(Me-M2)}{(M2-WPG)} * 100 \quad (13)$$

Me = Equilibrium mass at 20 °C / 65 %RH [g]

M2 = Dry mass after curing [g]

WPG = Weight percent gain [%]

7.2.4 Brinell hardness

Brinell hardness testing was conducted on a Zwick/Roell (Ulm, Germany) universal testing machine with a 10 kN load cell. The test was adopted to EN 1534 (2000), the specimens measured 25 x 50 x 50 mm³ (rad x tan x long). The test force was adapted to the density of the species (Table 21).

Table 21: Test force of Brinell hardness [N] for treatment groups

Wood species	Treatment	Test force [N]
Beech	Untreated	1000
	Melamine	1000
	Thermo	1000
	Thermo-melamine	1000
Ash	Untreated	1000
	Melamine	1000
	Thermo	1000
	Thermo-melamine	1000
Lime	Untreated	500
	Melamine	1000
	Thermo	500
	Thermo-melamine	500
Poplar	Untreated	500
	Melamine	500
	Thermo	200
	Thermo-melamine	200

7.2.5 Three-point bending test

The three-point bending test was performed to obtain data about the changing physical properties regarding modulus of elasticity (MOE), bending strength (MOR) and work in bending (WB) in a static test design. The specimens were tested on a Zwick/Roell (Ulm, Germany) universal testing machine with a 10 kN load cell according to EN 52 186 (1978). The test speed was 4 mm/min and the MOE was measured at 10 % to 40 % of MOR with an external strain sensor. MOE, MOR and WB were calculated by the control program testXpert II V3.5. WB is closely related to impact bending strength (IB) (Kollmann 1951), thus indicating the material properties regarding dynamic load. Aside from varying absolute values, IB and WB correlate positively.

7.2.6 Statistical analysis

To test the different groups for significant differences with a parametric one factor ANOVA (Analysis of Variance), the data must fulfil the normality assumption, the assumption of homogeneity of variances and the assumption of balanced sample group sizes. The data was analyzed for the assumption of normality using the Shapiro-Wilk test separately for each species and treatment group for the data of hardness, MOE, MOR and WB. The Levene/Brown-Forsythe test for the assumption of homogeneity of variances was performed. The normality assumption and the assumption of homogeneity were rejected at an error level (p-value) beyond 0.05. Both tests revealed several treatment groups that did not fulfil the assumptions. Therefore, the nonparametric Kruskal-Wallis test was selected to perform the ANOVA. The Dunnett's test was performed using a nonparametric multi comparison packet (Konietschke 2015) to compare each of the treatment groups with the reference group in RStudio (R Development Core Team 2011). They were regarded as significantly different when below a p-value of 0.05.

7.3 Results and Discussion

7.3.1 Melamine treatment

Melamine treatment of thermal modified wood altered the material properties. Basic data about the melamine treatment (density, solution uptake, WPG, bulking, EMC, EMC_R) of both untreated and thermally modified wood can be seen in Table 22.

Table 22: Results of the treatment of beech, ash, lime and poplar with melamine resin: Oven dry density (OD), solution uptake (SU), weight percent gain (WPG), bulking and equilibrium moisture content (EMC) and reduced equilibrium moisture content (EMC_R). Mean values with standard deviation in parenthesis

Wood species	Treatment	OD [kg/m³]	Solution uptake [%]	WPG [%]	Bulking [%]	EMC_R [%]
Beech	Untreated reference	737 (38)	-	-	-	11.9 (0.1)*
	Melamine	804 (30)	88 (7)	13.7 (1.1)	2.8 (1.3)	11.4 (0.2)
	Thermo	660 (18)	-	-	-	5.1 (0.1)*
	Thermo melamine	763 (14)	78 (4)	14.2 (0.8)	-1.4 (0.5)	8.4 (0.3)
Ash	Untreated reference	624 (32)	-	-	-	11.7 (0.1)
	Melamine	676 (34)	100 (5)	12.8 (1.2)	3.6 (1.1)	11.4 (0.2)
	Thermo	562 (38)	-	-	-	4.9 (0.3)
	Thermo melamine	650 (35)	96 (14)	14.2 (1.2)	-1.6 (0.4)	7.9 (0.1)
Lime	Untreated reference	569 (44)	-	-	-	10.4 (0.2)
	Melamine	618 (38)	129 (11)	12.9 (3.9)	2.7 (1.7)	10.5 (0.1)
	Thermo	498 (43)	-	-	-	4.9 (0.3)
	Thermo melamine	576 (44)	139 (21)	13.3 (1.4)	-2.6 (0.9)	7.7 (0.2)
Poplar	Untreated reference	346 (47)	-	-	-	11.6 (0.1)
	Melamine	367 (41)	234 (36)	13.4 (3.7)	3.9 (1.1)	11.9 (0.1)
	Thermo	308 (54)	-	-	-	5.5 (0.3)
	Thermo melamine	361 (46)	252 (46)	13.7 (2.5)	-3.6 (2.8)	9.3 (0.1)

*= EMC_R of R and T equals EMC: These treatment groups have not been modified with melamine resin.

The solid content of the impregnation solution was adjusted to the density of the different wood species; similar weight percent gains (WPG) throughout all treated materials were achieved. Poplar and lime were more heterogeneous in density and treatability than beech and ash. Thus, resulted in a higher variability for solution uptake and respectively WPG. The melamine treatment of unmodified wood as well as thermally modified wood was similar regarding SU and WPG but there were major differences related to the resulting bulking (Table 22). The bulking of all four thermally modified wood species was negative after melamine treatment. Behr *et al*. (2017b) (see 6.3.3, p. 49) also showed negative bulking in treated thermally modified poplar with melamine resin: The higher the modification temperature, the lower the bulking after melamine treatment. The resulting hydrophobation of the cell wall due to thermal modification might hinder impregnation modification with water-based solutions thereof. Bulking is regarded as an indicator of modification intensity (Lukowsky 1999; Hill 2006). Low bulking of the thermally modified wood indicates a low level of cell wall penetration. This could be shown by SEM/EDX images (to be published). If not in the cell wall, a major proportion of the resin is potentially located on the S3 layer in the cell lumens which are visible in microscopic analysis, rather forming a coating and 'bubbles' (Mahnert *et al.* 2013).

There could be another reason for negative bulking after melamine treatment of thermally modified wood. Alkaline impregnation agents might be able to remove degraded cell wall components such as hemicellulose constituents as used in Kraft pulping for cellulose production. The leaching can be more pronounced for hardwoods than for softwoods (Alén *et al.* 2002) as hardwood hemicelluloses are mainly

pentoses which degrade faster under the influence of heat treatment than hexoses (Zaman *et al.* 2000). Melamine resin formulations are alkaline (pH 9 to 10) and might not be strong enough to degrade cell wall components but might be able to solve and leach the thermally degraded hemicelluloses. Melamine resin treatment might have separate effects: Cell wall bulking due to incorporation and leaching thermally degraded hemicellulose components, which leads to shrinkage. When thermally modified wood is impregnated with melamine resin, the two effects are combined: As the swelling of thermally modified wood is limited, the alkaline, leaching-induced shrinkage becomes apparent.

The EMC of thermally modified wood was reduced to about 5 % compared to 11 % - 12 % of unmodified wood. The melamine treated thermally modified wood showed an increased EMC_R: The combined modification raised the EMC from 5 % - 6 % to 8 % - 9 %, depending on the wood species. The reason for the increased EMC_R of melamine treated thermally modified wood could be that the resin itself is hydrophilic and contributes to moisture sorption (Hosseinpourpia *et al.* 2016).

Melamine treatment of unmodified wood did not alter the EMC_R in this study. Melamine treatment is often reported to reduce the EMC (Epmeier *et al.* 2004), (Kielmann *et al.* 2013). When calculating the moisture content of modified wood, the denominator is changed by the mass of the modification agent. Just by the difference in mass, the EMC calculation would show reduced moisture values. The EMC_R is based on the dry mass [g] after modification, subtracting WPG [g] and therefore excludes the influence of the increased mass.

7.3.2 Brinell Hardness

The results for the Brinell hardness are shown in Table 23. The Brinell hardness (HB) results can be divided into three main findings:

(1) Thermal modification led to a significantly decreased hardness except for lime.

(2) Treatment with melamine resin led to a significantly increased hardness of untreated wood and thermally modified wood.

(3) The hardness after combined modification was significantly higher than that of untreated wood, except for poplar.

Table 23: Results of Brinell hardness (HB) Mean values with standard deviation in parenthesis

Wood species	Treatment	HB [N/mm²]
Beech	Untreated reference	41 (4)
	Melamine	65 (8)
	Thermo	34 (11)
	Thermo melamine	53 (13)
Ash	Untreated reference	36 (4)
	Melamine	48 (6)
	Thermo	30 (5)
	Thermo melamine	45 (8)
Lime	Untreated reference	19 (4)
	Melamine	25 (3)
	Thermo	18 (3)
	Thermo melamine	24 (4)
Poplar	Untreated reference	10 (4)
	Melamine	12 (3)
	Thermo	7 (3)
	Thermo melamine	10 (2)

The hardness of untreated wood is strongly dependent on the density (Kollmann 1951). Thermal modification reduced the density of the material (see 6.2.1) and could have led to decreased hardness. The reports about the hardness of thermally modified wood are contradictory: The hardness was increased after short treatment durations even at high temperatures, but longer treatment durations decrease the hardness (Sundqvist *et al.* 2006). The applied treatment time in this study was 7.5 h at the maximum temperature of 230 °C. (Wetzig *et al.* 2012) reported this process to alter the hardness of beech, ash and poplar as following: mild treatments increased hardness, more severe treatments decreased hardness. High temperature thermal modification as in this study can be regarded as a severe treatment and the EMC was reduced to less than half of the value for unmodified wood. In unmodified wood the reduction of EMC leads to increased hardness (Kollmann 1951). In thermally modified wood the mass loss induced hardness decrease has a stronger influence than the reduced EMC.

The melamine treatment increased the hardness of thermally modified wood to levels higher than that of unmodified references. Literature about the hardness values after combined wood modification is scarce. Mahnert (2013) reported that a melamine treatment of thermally modified koto and limba wood increased the hardness significantly. The changed EMC_R of TM might have influenced the hardness of TM as discussed for thermally modified wood. Nevertheless, this effect is very small and is largely outweighed by the increase of hardness due to the incorporated resin.

Treatment with melamine resin increased the hardness, potentially by increasing the density of the materials and because of the polymeric network (Table 23). It increased the hardness of untreated as well as thermally modified wood treated therewith. The WPGs were adjusted to the densities to create even resin loads per weight. This led to higher resin uptake per wood volume for high-density wood species: Melamine treatment led to a higher absolute increase of hardness with wood species of higher

densities. Melamine treatment on its own was often found to increase the hardness (Inoue *et al.* 1993a; Epmeier *et al.* 2004), dependent on the WPG. Rapp (1999) reported the hardness of the modification agent itself has great influence on the hardness of the modified material. He found melamine treated wood of the same density as untreated wood being substantially harder. The high increase in hardness of beech in comparison to poplar supports, that the polymeric network more than the density is the reason for the increased hardness.

7.3.3 Three-point bending

The multiple results of the three-point bending test (see Table 24) are shown and discussed as follows: Modulus of elasticity (MOE), Modulus of rupture (MOR) and work in bending (WB).

Table 24: Results of three-point bending test: Modulus of elasticity (MOE), Modulus of rupture (MOR) and work in bending (WB) Mean values with standard deviation in parenthesis

Wood species	Treatment	MOE [N/mm²]	MOR [N/mm²]	WB [N/mm²]
Beech	Untreated reference	11500 (650)	109 (7)	20.7 (4.4)
	Melamine	12780 (720)	114 (13)	9.5 (2.5)
	Thermo	12300 (900)	86 (13)	5.8 (1.6)
	Thermo melamine	13830 (680)	99 (11)	6.5 (1.3)
Ash	Untreated reference	12750 (1850)	121 (16)	27.3 (8.3)
	Melamine	12740 (1270)	125 (19)	14.3 (4.2)
	Thermo	13380 (2580)	86 (12)	5.4 (1.4)
	Thermo melamine	12000 (2360)	89 (16)	6.3 (1.8)
Lime	Untreated reference	9940 (2590)	77 (16)	13.2 (4.4)
	Melamine	11430 (2420)	97 (24)	8.5 (3.6)
	Thermo	11930 (1990)	75 (19)	5.7 (2.6)
	Thermo melamine	10930 (2590)	73 (27)	4.8 (3.1)
Poplar	Untreated reference	7900 (1140)	59 (9)	9.7 (2.1)
	Melamine	8320 (960)	70 (11)	6.8 (2.2)
	Thermo	7950 (2450)	56 (17)	5.1 (2.4)
	Thermo melamine	6900 (1660)	50 (9)	3.7 (1.2)

7.3.3.1 Modulus of elasticity (MOE)

The MOE of thermally modified beech was increased. In contrast, the MOE of thermally modified ash, lime and poplar were slightly decreased (1 % for poplar and up to 20 % for lime; Table 24). Boonstra *et al.* (2007) described the MOE of thermally modified wood as being higher at 165 °C and the same as the reference at 185 °C treatment temperature. Esteves and Pereira (2009) reported the same behavior, as the MOE increased for less intense thermal treatments and decreased for more severe treatments. Rautkari *et al.* (2014) reported the MOE of thermally modified wood being unchanged compared to unmodified Scots pine, when treated under high pressure and saturated steam at 180 °C. Wetzig *et al*. (2012) found only minor changes in static MOE after thermal modification at different temperatures of beech, ash and poplar.

There was no uniform influence of double modification on the MOE of the investigated wood species in this study: The MOE of double modified beech and ash was increased and that of lime and poplar decreased, resulting in levels ±10 % of the unmodified material. (Sun *et al.* 2013) described the MOE to decrease after thermal modification of MUF treatment of high-density eucalyptus, whereas in this study the MOE of the high-density species beech and ash was decreased.

The melamine treatment led to slightly increased MOE values of all unmodified wood species. This is backed by the literature: Deka and Saikia (2000) also found a slight increase in MOE after treatment of a softwood (*Anthocephalus cadamba* Miq.) with melamine resin.

The influence of the EMC on the MOE of wood is known to be linear (Kollmann 1951). Bollmus (2011) found the same behavior of DMDHEU modified beech and untreated beech. The resin modification did not change the moisture dependency of MOE.

The MOE did not change as much as other material properties e.g. MOR and WB. A stress-strain curve (Figure 12) of unmodified and modified wood shows that the elastic limit of modified wood seemed to be unchanged followed by abrupt rupture without the wood-typical plastic deformation, where most of the energy will be absorbed as shown by Mahnert (2013) for tropical double modified wood. The minor MOE changes do not represent the overall material characteristics.

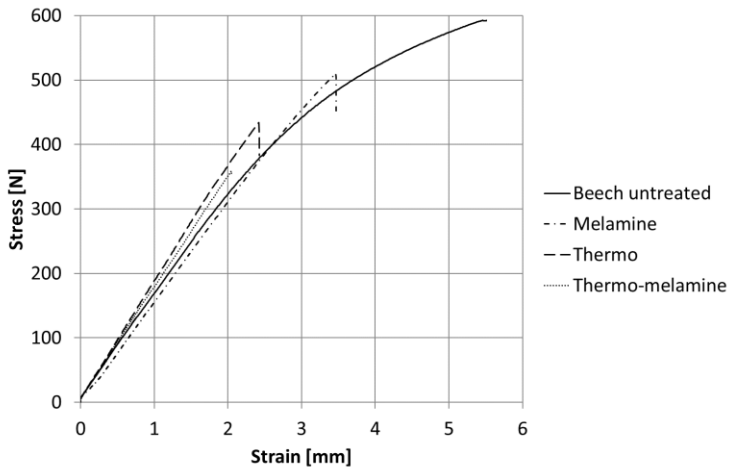

Figure 12: Exemplary stress-strain curve of untreated and modified beech specimens of this study

7.3.3.2 Modulus of rupture (MOR)

Thermal modification decreased the MOR of all four wood species. The melamine treatment did not improve the MOR of thermally modified wood. The MOR was increased after melamine treatment of unmodified wood except for beech.

Thermal modification led to decreased MOR values of all tested wood species. The MOR of beech and ash were more reduced compared to that of lime and poplar. This confirms the results of Wetzig *et al.* (2012). Lahtela and Kärki (2014) also found that the MOR of thermally modified pine decreased with increasing treatment temperature. Boonstra *et al*. (2007) correlated the reduced bending strength of thermally modified wood to degraded hemicelluloses. The reduction of sorption properties of thermally modified wood was shown (Tiemann 1915). Kollmann (1951) investigated the influence of EMC on mechanical properties of wood: Reducing the EMC from 10 % to 5 % increased the MOR of beech and ash. Esteves and Pereira (2009) qualify the positive influence of low EMC values on the strength of thermally modified wood by the greater negative influence of lowered density (see Table 24) caused by the degraded hemicelluloses.

The double modification did not alter MOR significantly compared to thermally modification: It was slightly increased in beech, unchanged in ash and lime and was slightly decreased in poplar (Table 24). Lahtela and Kärki (2014) investigated thermally modified melamine treated Scots pine: The MOR after combined treatment was only slightly reduced compared to melamine treatment, whereas the sole thermal treatment decreased the MOR more than double modification. It should be considered that they used an impregnation solution with a high solid content (47 %). The results are still comparable to those in the present study. Sun *et al.* (2013) recorded no change in MOR between sole thermal treatment and MUF and subsequent thermal treatment.

The MOR of melamine treated wood was slightly increased. Epmeier *et al*. (2004) also found a slight increase of the MOR of pine wood after melamine modification. The MOR of small defect free wood specimens is density dependent (Kollmann 1951). As the density of melamine treated wood was increased it might have contributed to increase MOR values. Inoue *et al*. (1993a) treated sugi (Cryptomeria japonica D. Don) and produced comparable results with 25 % melamine formaldehyde resin the MOR increased by 18 %. The bending strength in three-point bending depended on the compression and tensile strength of the specimens (Kollmann 1951). Tensile strength was reported to decrease after wood modification with thermosetting resins (Bollmus 2011; Leitch 2016), while transverse compression strength was increased (Gindl *et al.* 2003). The MOR was influenced by both tensile and compression strength.

According to Kollmann (1951) the mechanical properties of wood and wood products are moisture dependent. The EMC_R was not altered by melamine treatment. Rapp and Peek (1995) recorded un-altered EMC_R values of melamine treated wood. As the moisture content is unchanged, it can be ruled out as an influence on the mechanical properties of melamine treated wood. The EMC_R of all four double modified wood species increased at the same rate, whereas the MOR changed differently for each wood species. There was no clear influence of the changed EMC_R on MOR.

7.3.3.3 Work in bending (WB)

The work in bending (WB) was changed severely by all applied modifications. Thermal modification strongly reduced the WB (-64 % overall; up to -80 % in ash). Thermal modification was often described to reduce the WB or impact bending significantly. Boonstra *et al.* (2007) reported about 50 % reduction in impact bending after thermal modification. Welzbacher (2007) found thermal modification processes to affect the impact bending negatively (-50 %). Wetzig *et al.* (2012) recorded reduction of impact bending up to 59 %, only mildly treated ash showed an increased impact bending strength (+10 %). They suggest the high density of ash to be the critical factor for this behavior. Lahtela and Kärki (2014) reported 45 % reduction of impact strength after thermal modification at high temperature.

Double modification slightly decreased WB in lime and poplar and increased the WB in beech and ash compared to thermal modification. Comparable results were obtained by Mahnert (2013) and Lahtela and Kärki (2014). Mahnert (2013) reported about combined thermo and melamine modification of tropical hardwoods koto and limba. He found only minor changes in WB and IB after the melamine treatment of thermally modified wood (Table 25). Lahtela and Kärki (2014) reported the impact strength of thermally modified, melamine treated and double modified wood to be similarly reduced to less than 50 % of the reference's strength.

Table 25 : Results of Brinell hardness and three-point bending test: Brinell Hardness, Modulus of elasticity (MOE), Modulus of rupture (MOR) and impact bending (IB). Mean relative changes of the treatment groups compared to the control group in percent.
* In MAHNERT the values are partially referenced to the thermally modified specimens

Authors	Wood species	Treatment	Δ Brinell Hardness [%]	Δ MOE [%]	Δ MOR [%]	Δ IB [%]
Sun *et al.* (2013)	Eucalyptus	Thermo (220 °C)	-	-20	-50	-
		MUF	-	+11	+10	-
		MUF + Thermo (220 °C)	-	-10	-50	-
Lahtela and Kärki (2014)	Pine	Thermo (212 °C)	-	-	-40	-52
		Melamine	-	-	-22	-52
		Melamine + Thermo (212 °C)	-	-	-26	-59
Mahnert (2013)	Koto	Thermo	-27	+10	-25	-36
		Thermo + Melamine	+5	-	-	-48
	Limba	Thermo + Melamine	+60*	-	-	+8*
	Pine	Thermo + Melamine	-	(-15 / -20)*	(-10 / -15)*	-

The reduction of WB after melamine treatment was 42 % over all wood species. Stamm (1964) reported a strong reduction of impact strength for melamine modified solid wood. Lukowsky (1999) and Epmeier *et al*. (2004) also recorded reduced impact strength after melamine modification.

In accordance with Kollmann (1951), the EMC does not influence the impact bending or work in bending until fiber saturation, whereas water saturated samples have a strongly increased impact bending strength. Nevertheless, minor changes in EMC do not change the WB measurably and can be excluded as a reason for the altered WB. The EMC_R of double modified wood is higher than that of all four

thermally modified wood species. As the WB changed depending on species there seemed to be no apparent influence of EMC_R on WB. The Brinell hardness, Modulus of elasticity (MOE), Modulus of rupture (MOR) and work in bending (WB) of the treatments as relative change to the untreated references are shown in Table 26.

Table 26: Results of Brinell hardness and three-point bending test: Brinell Hardness, Modulus of elasticity (MOE), Modulus of rupture (MOR) and work in bending (WB). Mean relative changes of the treatment groups compared to untreated wood in percent and significance indicator: * = significant differences of treatment group to untreated reference; - = not significantly different

Wood species	Treatment	Δ Brinell Hardness [%]		Δ MOE [%]		Δ MOR [%]		Δ WB [%]	
Beech	Untreated reference	-	-	-	-	-	-	-	-
	Melamine	57	*	11	*	5	-	-54	*
	Thermo	-17	*	7	-	-21	*	-72	*
	Thermo melamine	29	*	20	*	-9	*	-69	*
Ash	Untreated reference	-	-	-	-	-	-	-	-
	Melamine	35	*	0	*	3	*	-48	*
	Thermo	-15	*	5	*	-29	*	-80	*
	Thermo melamine	27	*	-6	-	-26	*	-77	*
Lime	Untreated reference	-	-	-	-	-	-	-	-
	Melamine	30	*	15	*	26	*	-36	*
	Thermo	-7	-	20	-	-3	-	-57	*
	Thermo melamine	25	*	10	-	-5	-	-64	*
Poplar	Untreated reference	-	-	-	-	-	-	-	-
	Melamine	15	*	5	-	19	*	-30	*
	Thermo	-32	*	1	*	-5	-	-47	*
	Thermo melamine	-5	-	-13	*	-15	*	-62	*

The treatment of thermally modified wood with melamine resin can be summarized as follows: The negative bulking seemed to indicate an incomplete cell wall penetration of the impregnation solution. The negative bulking might also be a result of alkaline induced leaching of degraded cell wall components. The hardness was increased after melamine treatment of thermally modified wood except for poplar. MOE, MOR and WB were slightly increased or decreased depending on wood species.

7.4 Conclusions

Aim of this study was to improve the mechanical properties of thermally modified wood by treatment with melamine resin.

The reduced hardness of thermally modified wood was improved by melamine treatment and was significantly increased to values above untreated wood except for poplar.

Embrittlement is an issue of modified wood. Double treatment did not change the work in bending compared to thermally modified wood. However, non-structural usage such as decking and cladding would be most suitable for double modified wood with its increased durability, bending strength and surface hardness.

In indoor applications, the double modified wood also has the advantage of the appearance of dark thermally modified wood and the improved hardness properties of melamine treated wood.

Thermal modification in combination with melamine treatment can expand the field of application and create new markets for native hardwoods.

8 Paper VII: Natural weathering - Weathering protection of European hardwoods through double modification

(Published at the International Research Group on Wood Protection (IRG/WP 17-30715) - 2017)

Abstract

Beech and poplar were thermally modified, treated with melamine resin and both treatments were combined. The weathering performance (cracks and general appearance) of modified beech and poplar was assessed in natural weathering and correlated to the material properties work in bending (WB) and Brinell hardness. In addition, the equilibrium moisture content after exposure of 12 months and subsequent climatization was evaluated. Melamine treated beech and thermally modified poplar performed best while still showing serious cracks. The melamine treatment increased the equilibrium moisture content, indicating a rather hygroscopic behavior of the resin. All treated groups showed increased moisture contents after weathering and subsequent climatization. The thermal and melamine treatment decreased the WB substantially. The melamine treatment of the thermally modified wood (double modification) did not further decrease the WB. WB as an indicator of brittleness could not be used to explain the cracking behavior. Thermal modification decreased the Brinell hardness, whereas melamine treatment increased it. The increased Brinell hardness of melamine treated groups and the double modified groups can be accounted for the stabilized surfaces without erosion.

8.1 Introduction

Wood exposed outdoors faces changes and deterioration, quite in contrast to the user's expectations. Surface tensions lead to cracks and further degrade the surface (Altgen *et al.* 2016). Wood preservatives can provide protection from decomposition by fungi and insects. Some preservative systems face legal restrictions and might have toxic issues because non-target organisms are affected, too. Disposal at the end of service life might be challenging for preservative treated wood (Rapp 1999). Other techniques include modification of wood. They proved to be able to protect wood from the elements and to provide new material properties (Hill 2006). Thermal wood modification reduces the equilibrium moisture content (EMC) and thereby protects wood against fungal degradation and increases dimensional stability. It also provides a desired dark color (Esteves and Pereira 2009). Crack susceptibility, on the other hand is mostly unchanged (Feist and Sell 1987) and the hardness is reduced (Sundqvist *et al.* 2006). This restriction the use as outdoor flooring material, being a high value product with certain customer demands. The low weathering resistance and high crack susceptibility are drawbacks of thermally modified wood and can presumably be compensated by melamine treatment. Treatment with thermosetting resins such as melamine formaldehyde resin provide dimensional stability (Lukowsky 1999), excellent biological protection (Mahnert 2013), weathering protection (Hansmann *et al.* 2006) and increased hardness (Inoue *et al.* 1993a; Hansmann *et al.* 2006). The equilibrium moisture content

was unchanged (Rapp and Peek 1995). The combination of modification systems is capable to provide new material properties and join several advantageous properties. Improvements of the weathering properties through combined wood modification would not only expand the field of application but also create new markets for native wood as a renewable and sustainable resource.

Therefore, the aim of this study was to improve the weathering properties of thermally modified hardwoods through melamine treatment. The treatment performance was assessed via WPG, the altered mechanical properties after modification were evaluated through Brinell hardness and work in bending and the weathering performance was assessed in a natural weathering test. It was of interest whether the weathering performance can be explained by other material properties influenced by the wood modifications such as the hardness and the work in bending.

8.2 Material and Methods

8.2.1 Source material

Beech and poplar were cut to the specifics required for natural weathering (DIN EN 927-3 2006) and three-point bending (DIN 52 186 1978). The used resin (Madurit MW840 75WA) was provided by INEOS Melamines, Frankfurt, Germany.

8.2.2 Thermal modification

The thermal modification used in this study was provided by timura Holzmanufaktur GmbH. A vacuum process with maximum temperatures of 230 °C was carried out.

8.2.3 Treatment with melamine resin

Impregnation with several concentrations of an aqueous solution of methylated melamine formaldehyde resin was carried out in a vacuum pressure full cell process at 100 mbar 1 h and 12 bar 5 h. Curing of the specimens in laboratory ovens was carried out at a maximum temperature of 120 °C under dry conditions over several weeks for extra careful drying. For the calculation of the solution uptake (SU) and the weight percent gain (WPG) see Eq. 10 and Eq. 11, 7.2.3, p. 56.

8.2.4 Mechanical testing

Mechanical tests were conducted to describe the impact of the modifications on the material properties.

8.2.4.1 Three-point bending

The bending tests according to DIN 52 186 (1978) were performed using separately cut and treated specimens (10 x 10 x 180 mm³). A Zwick/Roell universal testing machine with a 10 kN load cell was used.

8.2.4.2 Brinell hardness

The hardness was tested based on EN 1534 (2000) 4 times on the backside of each of the field weathering specimens.

8.2.5 Natural weathering test

The natural weathering test was conducted according to DIN EN 927-3 (2006) with six specimens per treatment group. The specimens were treated as described above. The exposed surface was sanded flat (150 grid) prior to edge sealing and exposure. The specimens were exposed at 45-degree inclination facing south direction at the University of Göttingen. After each six months of exposure, the specimens were climatized at 20 °C and 65 % RH until equilibrium for crack evaluation according to DIN ISO 4628-4 (1997). Every specimen was evaluated for the number of cracks (0 (no cracks detectable) to 5 (cracks in large numbers)) and the width of cracks (0 (no visible cracks at 10x magnification) to 5 (very wide cracks, wider than 1 mm)). In addition to the crack evaluation, the overall appearance was subjectively evaluated using grades: 1 (excellent), 2 (good), 3 (satisfactory), 4 (sufficient) and 5 (failed). The authors considered this evaluation step advisable as the bare numbers of crack evaluations often insufficiently represent the appearance of the surfaces (Brischke *et al.* 2016).

The moisture content of the specimens was recorded before the start and after climatization after each six months to evaluate the EMC at 20 °C/65 %RH repeatedly over a longer period of weathering. To minimize the influence of the additional weight due to the chemical modification (Akitsu *et al.* 1993), the reduced equilibrium moisture content (EMC_R) was calculated based on the dry weight of the specimens before modification (Eq. 14)

$$EMC_R = \frac{Me-M2}{M2-WPG} * 100 \quad (14)$$

Me = Equilibrium mass at 20 °C/65 %RH [g]

M2 = Dry mass after curing [g]

WPG = Weight percent gain [%]

8.3 Results and Discussion

8.3.1 Impregnation and curing

The results of the impregnation and curing can be seen in Table 27.

Table 27: Natural weathering specimens and 3-point bending specimens of untreated and thermally modified beech and poplar after impregnation with melamine resin. Solid content (SC) and weight percent gain (WPG) in percent. Aim of melamine resin concentration 1 = 15 %WPG. 2 = 25 %WPG. Mean group values and standard deviation in parenthesis

Wood species	Treatment	SC [%]	WPG 3-Point Bending [%]	WPG natural weathering [%]
Beech	Melamine 1	23	20.0 (0.9)	19.4 (1.5)
	Melamine 2	32	29.6 (1.2)	26.3 (3.2)
	Thermo + melamine 1	23	18.1 (0.9)	14.8 (1.4)
	Thermo + melamine 2	32	25.7 (1.6)	23.6 (2.7)
Poplar	Melamine 1	12	10.9 (5.4)	11.7 (2.0)
	Melamine 2	18	15.1 (8.3)	22.2 (3.6)
	Thermo + melamine 1	12	17.6 (2.5)	18.0 (3.3)
	Thermo + melamine 2	18	25.0 (4.9)	27.2 (5.0)

The impregnation and curing resulted in WPGs of 15 % and 25 %. The impregnation resulted in even resin treatment of beech and thermally modified beech. Poplar was not treated evenly, some parts of some specimens showed refractory behaviour and therefore no or very little resin uptake. This resulted in higher standard deviations of the poplar treatment groups.

8.3.2 Mechanical testing

The assessed mechanical properties were work in bending in a 3-point bending test and the Brinell hardness (Table 28).

Table 28: Results of the mechanical testing, work in bending in a static three-point bending test and the Brinell hardness tested on the backside of the natural weathering specimens. Melamine resin concentration 1 = 15 %WPG. 2 = 25 %WPG. Mean group values and standard deviation in parenthesis

Wood species	Treatment	Work in bending [N/mm²]	Brinell hardness [N/mm²]
Beech	Untreated reference	21.7 (3.4)	40 (4)
	Melamine 1	9.8 (3.0)	71 (12)
	Melamine 2	9.4 (2.1)	88 (18)
	Thermo	10.8 (3.5)	31 (4)
	Thermo + melamine 1	10.8 (2.6)	49 (7)
	Thermo + melamine 2	8.6 (2.8)	65 (9)
Poplar	Untreated reference	15.1 (4.2)	18 (4)
	Melamine 1	13.0 (5.1)	22 (5)
	Melamine 2	11.4 (7.5)	29 (6)
	Thermo	6.6 (1.7)	12 (3)
	Thermo + melamine 1	6.1 (2.3)	19 (4)
	Thermo + melamine 2	6.3 (1.9)	24 (6)

8.3.2.1 Three-point bending

The work in bending (WB) is a value drawn from a static bending test but closely related to the (dynamic) impact bending strength (Kollmann 1951). Both thermal modification and treatment with melamine resin influenced the WB negatively. Beech showed similar reduction in WB by any treatment. The lowest values were recorded for double-modified specimens with high resin load. Poplar showed a stronger influence of the thermal treatment than of the melamine treatment resulting in lower WB values.

Reduction in WB was reported for thermal modification and for melamine treatment (Stamm 1964), (Boonstra *et al.* 2007) and is confirmed by the current results.

8.3.2.2 Brinell hardness

The hardness was measured at four different locations on the unweathered side of the natural weathering specimens before the weathering test. In general, the hardness decreased through the thermal treatment and was increased by the melamine treatment. The double-modified specimens showed hardness values above those of the untreated specimens. The hardness increased with the resin load, higher hardness values were measured for higher resin loads regardless of species and treatment. Beech with higher density showed higher hardness values treated and untreated. Hardness reduction through thermal modification of wood was reported by Wetzig *et al.* (2012). The increase in hardness through melamine treatment dependent on the resin load is according to the literature (Inoue *et al.* 1993a). Double modified hardwood was shown to have an increased hardness compared to untreated wood (Behr *et al.* 2018b) (see 7.3.2 p. 60).

8.3.3 Weathering performance

The results of the natural weathering modified beech and poplar can be seen in Table 29. The focus was put on the crack behaviour, as this is critical for a long service life in outdoor applications with or without coating. The degradation of the surfaces was visually assessed.

Table 29: Evaluation of the natural weathering test according to DIN ISO 4628-4 (1997) and subjective surface appearance according to grades 1 to 5 after 12 months. Melamine resin concentration 1 = 15 %WPG. 2 = 25 %WPG. Mean group values and standard deviation in parenthesis

Wood species	Treatment	Field test Number of cracks	Field test Width of cracks	Subjective surface assessment
Beech	Untreated reference	3.3	2.7	Failed
	Melamine 1	3.3	2.0	Sufficient
	Melamine 2	2.0	2.0	Sufficient
	Thermo	4.0	2.7	Failed
	Thermo + melamine 1	3.7	1.3	Satisfactory
	Thermo + melamine 2	3.7	1.3	Satisfactory
Poplar	Untreated reference	5.0	1.8	Failed
	Melamine 1	2.8	1.7	Good
	Melamine 2	2.7	2.0	Good
	Thermo	1.7	1.3	Sufficient
	Thermo + melamine 1	2.2	1.3	Satisfactory
	Thermo + melamine 2	1.8	1.5	Failed

8.3.3.1 Crack evaluation

The treatments were differently effective at protecting the surface. Both untreated references showed the most cracks and the widest cracks. The thermally modified beech performed as meagre as the references with slightly more cracks of the same width. Thermally modified poplar performed better

than the references, with distinctively less cracks. No improvement of crack behaviour was reported for thermally modified wood by other authors (Feist and Sell 1987). In contrast, Rapp (2001) reported of less cracks after heat treatment and weathering. Melamine treated poplar was the best performing material combination in this study, whereas melamine treated beech only performed slightly better than untreated references. There are inconsistent reports about the cracking behaviour of melamine treated wood. Hansmann *et al.* (2006) and Rapp and Peek (1995) state reduced cracking after melamine treatment, Lukowsky (1999) reported no reduction in cracks after melamine treatment. Rapp (1999) reported about increased cracking after melamine treatment. Cracking could in part be prevented by the double modification, especially for beech. There were still cracks but the width was considerably reduced. Mahnert (2013) also reported about reduced cracking of double modified tropical hardwoods compared with the thermally modified groups.

8.3.3.2 Equilibrium moisture content

The moisture contents of the beech and poplar specimens after several months of exposure and subsequent climatization can be seen in Figure 13.

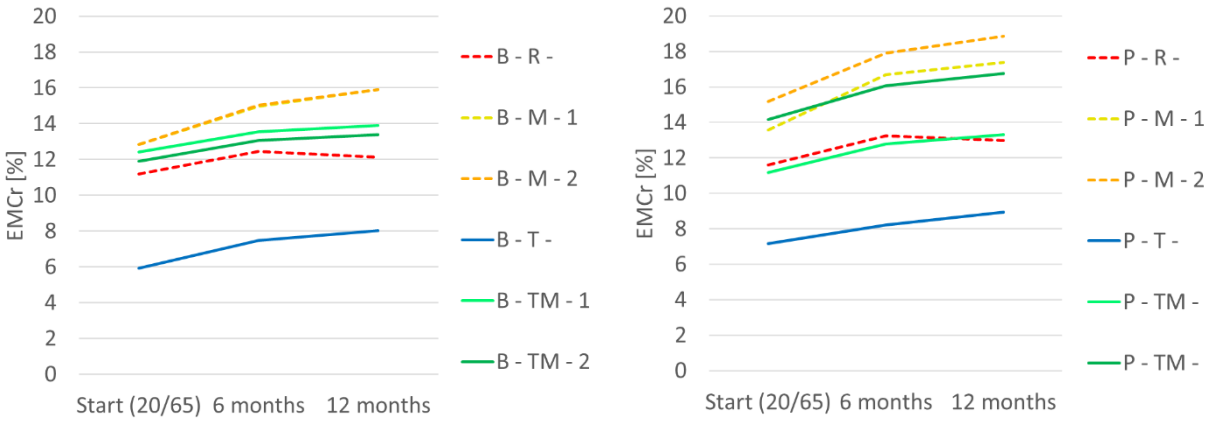

Figure 13: Moisture content (EMC_R) at 20 °C/65 %RH of the natural weathering specimens before and after repeated exposure (6 and 12 month) and climatization at 20 °C/65 %RH. Left side: beech (B), right side: poplar (P). Treatments: Thermal modification (T), melamine resin treatment (M) and double modification (TM) with varying resin content 1 = 15 %WPG. 2 = 25 %WPG.

The EMC of thermally modified wood was lower than the references. Over time, the EMCs of thermally modified beech and poplar increased by 2 %, whereas the references' EMCs increased only 1 %. Mitchell *et al.* (1953) reported an increase of EMC of thermally modified sawdust after repeated climatic cycles. Altgen (2016) described this behaviour as the reversible part of hydrophobation through thermal modification.

Melamine treatment is described as being neither hygroscopic nor hydrophobic (Lukowsky 1999). In this study, the EMC_R of melamine treated beech was 1.6 % higher than that of untreated wood regardless of resin load. After 12 months, this difference increased to 3.7 % and showed a rather hydrophilic

tendency. Melamine treated poplar showed the same trend but with a higher EMC_R of the higher resin load.

The EMC_R of double modified wood was generally higher than that of thermally modified wood. This was more pronounced for poplar, with higher EMC_Rs of the higher resin load, it was reversed for the beech thermo melamine groups with lower EMC_Rs of the high WPG group.

8.3.3.3 Surface degradation

The degradation of the surfaces had to be considered as well. Under the impact of UV radiation and water, lignin was decomposed and then the exposed fibers are eroded. This was the case for the untreated references and the thermally modified specimens. Jämsä *et al.* (2000) also recorded the same weathering and cracks on thermally modified wood. On the other hand, many authors report lignin stabilization through degradation, with the result of less leachable components (Esteves and Pereira 2009). The melamine treated specimens on the other hand, did not show any sign of erosion, the surfaces were stabilized by the treatment (Figure 14). They are therefore a potentially more suitable substrate for paints and varnishes.

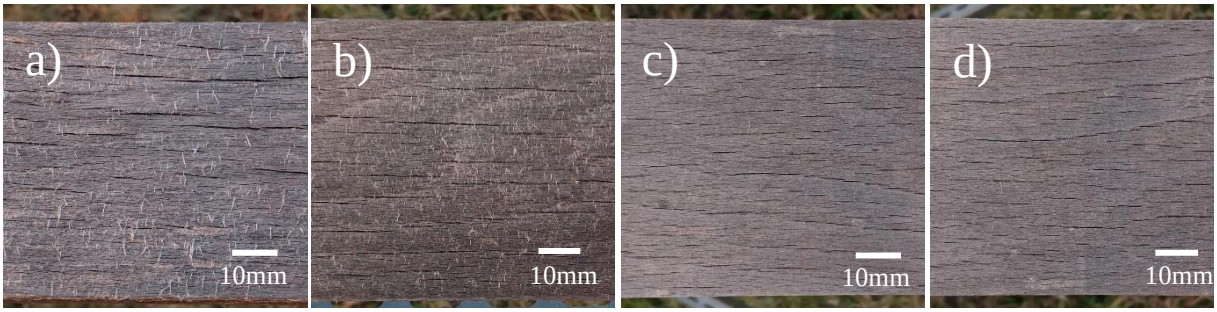

Figure 14: Modified beech after 18 months natural weathering: a) untreated beech; b) thermally modified beech; c) thermally modified wood treated with melamine resin; d) melamine treated beech

8.3.4 Weathering performance and material properties

The modification of wood altered the weathering performance and the mechanical properties (Table 28). Crack development is often associated with the stiffness of a material or the inability of a material for relaxation and stress distribution (Altgen *et al.* 2016). The mechanical properties could provide data to explain the crack behaviour of the modified materials.

The hardness is not a value typically associated with surface weathering. However, the increase in hardness through melamine resin might be an indicator for the stabilization of the surfaces shown in Figure 13. Higher hardness might have caused less erosion of melamine treated wood and double modified wood.

The work in bending (WB) of all modified groups was decreased, whereas the cracking behaviour was positively influenced by most modifications. Thermally modified beech was more brittle (-50 %) than the untreated references and was rated insufficient regarding cracks.

Thermo poplar performed slightly better than the reference regarding cracks and was even more brittle (-56 %). Melamine treatment of beech led to embrittlement of the references, but thermally modified wood was not further embrittled. Mahnert (2013) reported the same behavior for double modified hardwoods. The crack performance was positively influenced, especially for the double modified material. The same behavior was recorded for poplar. The melamine treated groups performed best of all materials and had the least reduction in WB. The crack behavior of double modified poplar depended on the resin load. The low WPG group showed satisfactory crack behavior and the high WPG group were rated as low as the untreated reference while both groups showed the same reduction in WB. The WB values did not provide a cohesive representation of the cracking behavior.

The equilibrium moisture content (EMC_R) of the treated groups changed depending on the treatment. There was no cohesive correlation apparent to support the weathering behaviour.

8.4 Conclusions

Modification of beech and poplar improved the weathering performance to different extends. Beech showed the least cracking after double modification and poplar after melamine treatment.

The cracking behaviour is rather difficult to predict based on other material properties. The work in bending (WB) is an indicator of the flexibility or brittleness of a material but did not correlate with the cracking behaviour. The increased hardness through melamine treatment was a good indicator of the reduced erosion of the weathered surfaces. The equilibrium moisture content (EMC) of wood was reduced through thermal modification and increased through melamine treatment. After long-time exposure, the EMC of modified wood increased stronger than that of untreated wood.

9 Paper VIII: Accelerated weathering – Performance of beech and poplar after double modification

(unpublished)

Abstract

Beech and poplar were thermally modified, treated with melamine resin and both treatments were combined. The performance of modified beech and poplar was assessed in accelerated weathering. Melamine treated beech and thermally modified poplar had the best crack performance while still showing cracks. The combined modification did not improve the performance of the single modification methods. The cracking behavior was evaluated using the amount and the width of the cracks. The two properties opposed each other; there were either many narrow cracks or few large cracks. Accelerated weathering tests were designed to evaluate material properties and performances faster than natural weathering. In this study, the results of the accelerated weathering had a low correlation with the natural weathering results for beech and could not be used to reliably predict the material performance. The results for poplar were more concise, the best performing material in both tests was the melamine treated group.

9.1 Introduction

Wood exposed outdoors faces changes and deterioration, quite in contrast to the user's expectations. The exposed materials can deteriorate through biological decay, destroying the structure and leading to a shortened service life. Surface tensions lead to checks, cracks and further degrade the surface (Feist and Hon 1984; Altgen 2016). The service life of such materials might also be shortened. Most chrome free preservatives can provide protection from decomposition by fungi and insects, but not from surface degradation through weathering and crack development. Some preservative systems face legal restrictions and might have toxic issues because non-target organisms are affected. Disposal at the end of service life might be challenging for preservative treated wood (Rapp 1999). Other techniques to protect wood in service include modification of wood. They proved to be able to protect wood from the elements and to provide new material properties (Hill 2006). Thermal wood modification reduces the equilibrium moisture content (EMC) and thereby protects wood against fungal degradation and increases dimensional stability. It also provides an aesthetically pleasing dark color (Esteves and Pereira 2009). Crack susceptibility, on the other hand is mostly unchanged (Feist and Sell 1987) and the hardness is reduced (Sundqvist *et al.* 2006). This restricts the use as outdoor flooring material, being a high value product with certain customer demands. The low weathering resistance and high crack susceptibility are drawbacks of thermally modified wood and can presumably be compensated by melamine treatment. Treatment with thermosetting resins such as melamine formaldehyde resin generally provided dimensional stability (Lukowsky 1999), biological protection (Lukowsky 1999),

weathering protection (Hansmann *et al.* 2006), increased hardness (Inoue *et al.* 1993a; Deka *et al.* 2007) and decreased crack susceptibility (Mahnert 2013). The combination of modification systems is capable to provide new material properties and join several advantageous properties (Behr *et al.* 2018b). Natural weathering tests with conditions close to the real environment are one way of testing the material performance but they also take the longest to conduct. Artificial weathering could deliver results earlier, the question remains, whether the results represent the material properties in natural weathering.

The aim of this study was to assess the weathering properties of thermally modified hardwoods after melamine treatment during an accelerated weathering test. It was of particular interest whether the weathering performance in accelerated weathering can be correlated to natural weathering.

9.2 Material and Methods

9.2.1 Source material

Whole slabs of beech and poplar were cut in two, every other half was subjected to the thermal modification process, the other half was kept untreated. After thermal treatment, the material was cut to the specifics required (150 x 78 x 20 mm³) for accelerated weathering tests (DIN EN 927-6 2006).

9.2.2 Thermal modification

Half the material for this study was subjected to thermal treatment. The thermal modification used in this study was provided by timura Holzmanufaktur GmbH (Rottleberode, Südharz, Germany). A thermal treatment, vacuum-press process (Vacu³) with a maximum temperature of 230 °C was carried out (Wetzig *et al.* 2012).

9.2.3 Treatment with melamine resin

One half of the untreated and thermally modified material was subjected to a downstream melamine treatment. The impregnations with aqueous solutions with several solid contents (SC) of methylated melamine formaldehyde resin were carried out in a vacuum pressure full cell process at 100 mbar for 1 h and 12 bar for 5 h. The SC of the solutions were adjusted to the density and solution uptake (SU) of beech and poplar to achieve similar WPGs for both species. For the calculation of SU and WPG see Eq. 10 and Eq. 11, 7.2.3, p. 56. The specimens were cured in laboratory ovens at a maximum temperature of 120 °C under dry conditions over three weeks.

After treatment all specimens of the six treatment groups (untreated, thermally modified, melamine treated (high SC and low SC) and double modification (high SC and low SC) were stored at 20 °C/65 %RH until equilibrium moisture content (EMC) was achieved. The surface which was later

exposed was sanded flat (150 grid) prior to edge sealing with a commercial sealant (Pyrotect Schutzlack 2K, Rütgers Organics GmbH, Mannheim, Germany) and climatized again until EMC was reached.

9.2.4 Accelerated weathering test

The accelerated weathering test was conducted according to (DIN EN 927-6 2006) in a QUV accelerated weathering tester (Q-Lab; Saarbrücken, Germany) with four specimens per treatment group and one as unexposed reference sample. The untreated group served as control. The specimens were exposed for 7 (beech) and 10 (poplar) weathering cycles according to DIN EN 927-6 2006. Each cycle involved 24 h conditioning (45 ± 3 °C, 95 % ± 1 %RH) and exposure to UVA light (maximum absorption at 340 nm; 0.89 W m^{-2} nm^{-1}) from a fluorescent light source over 48 cycles, each involving 2.5 h of UV irradiation at 60 °C and 30 min cold water spray (6–7 l min^{-1}).

The exposed surfaces were evaluated according to DIN ISO 4628-4 (1997). Every specimen was evaluated for the number of cracks (0 (no cracks detectable) to 5 (cracks in large numbers)) and the width of cracks (0 (no visible cracks at 10 x magnification) to 5 (cracks wider than 1 mm)).

9.3 Results and Discussion

9.3.1 Impregnation and curing

The results of the impregnation and curing can be seen in Table 30.

Table 30: Accelerated weathering specimens of untreated and thermally modified beech and poplar after impregnation with melamine resin. Solid content (SC) of impregnation solution; solution uptake (SU); weight percent gain (WPG) in percent. Mean group values and standard deviation in parenthesis.

Wood species	Treatment	SC [%]	SU [%]	WPG [%]
Beech	Melamine	25	98 (5)	19.3 (1.1)
		40	103 (5)	35.8 (1.9)
	Thermo + melamine	25	89 (4)	17.8 (1.2)
		40	95 (6)	32.8 (3.8)
Poplar	Melamine	10	166 (23)	11.8 (1.7)
		18	166 (27)	23.6 (4.5)
	Thermo + melamine	10	185 (10)	14.6 (0.6)
		18	186 (19)	28.5 (3.2)

Pre-trials were conducted to ensure that the treatment with two SCs results in WPGs of 15 % and 25 %. This goal was achieved for most of the treatment groups except for the high SC groups of beech. Poplar was not treated evenly, some parts of some specimens showed refractory behaviour and therefore no or very little resin uptake. This resulted in high standard deviations of some of the poplar treatment groups.

9.3.2 Weathering performance

The results of the accelerated weathering of modified beech and poplar can be seen in Table 31. The focus was on the crack behaviour, as this is critical for a long service life in outdoor applications with or without coating.

Table 31: Evaluation of the accelerated weathering of beech (7 cycles) and poplar (10 cycles) according to DIN ISO 4628-4 (1997). number of cracks (0 (no cracks detectable) to 5 (cracks in large numbers)) and the width of cracks (0 (no visible cracks at 10 x magnification) to 5 (cracks wider than 1 mm)). Solid content (SC) of impregnation solution.

Wood species	Treatment	SC [%]	Classification of number of cracks	Classification of width of cracks
Beech	Untreated reference	-	5	3
	Melamine 1	25	4	3
	Melamine 2	40	4	4
	Thermo	-	4	4
	Thermo + melamine 1	25	2	4
	Thermo + melamine 2	40	1	4
Poplar	Untreated reference	-	5	2
	Melamine 1	10	5	2
	Melamine 2	18	1	3
	Thermo	-	1	3
	Thermo + melamine 1	10	1	3
	Thermo + melamine 2	18	1	4

For both species the untreated references showed the highest number of cracks but not the widest cracks. Overall, the treatments were differently effective at protecting the surface from cracks. All treatments reduced the number of cracks, except for the low SC melamine treated poplar which showed the same number of cracks as the references. On the other hand, all modifications increased the width of the cracks, except for the low SC melamine treated groups.

The number of cracks of thermally modified wood decreased in both species in comparison to untreated wood, but the width of the cracks increased. No improvement of crack behaviour was reported for thermally modified wood by other authors (Feist and Sell 1987). However, Rapp (2001) reported less cracks after heat treatment and weathering.

Melamine treated wood showed rather similar results to the thermal treatment. The number of cracks was reduced, but the width of those cracks increased. This was more pronounced at the higher SC/WPG. There are inconsistent reports about the cracking behaviour of melamine treated wood. Hansmann *et al.* (2006) and Rapp and Peek (1995) stated reduced cracking after melamine treatment, Lukowsky (1999) reported no reduction of cracks after melamine treatment. Rapp (1999) reported increased cracking after melamine treatment. These reports were not specific on whether the number of cracks or the size of the cracks changed compared to untreated material.

Double modified material performed best regarding the number of cracks recorded in beech. Double modified poplar did not perform better than melamine treated or thermally modified poplar. Mahnert (2013) reported reduced cracking of double modified hardwoods compared with the thermally modified groups in an artificial weathering test. He used a less intense thermal treatment and a different impregnation solution formulation which might account for the differing results.

When comparing the data of the artificial weathering test with the natural weathering test (Behr *et al.* 2017a), only a minor coherence of the results was perceivable. Solely the number of cracks of modified poplar seemed generally cohesive between the two tests. It has been mentioned by other authors, that the results of artificial weathering have only a limited significance about natural weathering behavior ((Feist and Sell 1987; Sudiyanni *et al.* 1996; Brischke *et al.* 2016). Feist and Sell (1987) found that the surfaces of naturally and artificially weathered beech were comparably smooth but with different severity of cracking. There were fewer cracks in artificially weathered thermally treated specimens than untreated specimens, whereas naturally weathered thermally modified beech showed the same number of cracks as the untreated beech. Sudiyanni *et al.* (1996) found a coherence of the outdoor and artificially weathered surfaces of DMDHEU modified and untreated wooden surfaces. The results of the surface performance of the other treatments (e.g. acetic anhydride, paraformaldehyde, PF resin) in their study scattered largely and showed a low coherence of artificially and naturally weathered specimens. Overall, they reported a more severe deterioration of the artificially weathered surfaces than the outdoor weathered surfaces at a supposedly equivalent exposure (1080 h artificial weathering; 1 year outdoor weathering). The conditions the specimens were exposed to in the respective tests were evidently very different. The amount and intensity of UV radiation, the amount of water sprayed, the sharp and rapid changes of climatic conditions in the artificial weathering test are different to natural weathering.

The number of times climatic conditions change was earlier identified as possibly the number one factor for the development of cracks in wooden surfaces. Surface tension caused by changing moisture content as a function of environmental changes.

In natural weathering, the temperature, humidity and exposure to radiation also vary largely by site and throughout the years. However, the long-term effect of natural weathering and artificial weathering might be the same, causing delignified, grey and eroded surfaces (Feist and Hon 1984). For crack development, however, the specific conditions seemed to be highly relevant. The most influential factor for cracks is the change of the moisture content. Moisture gradients are often the steepest at the exposed surfaces. The subsequent swelling and shrinking induce unbalanced stresses in wooden surfaces. Precipitation and dew are the main reasons for increased moisture on the surfaces. If an exposed wooden component was wet during the night (dew) and the sun heated up the surface in the morning, the top layers of the surface heat up after the water has evaporated, causing shrinkage of the top layers. The underlaying layers of cell walls are still wet and bulked. This causes differential swelling and stresses and can lead to checks and cracks in the surface. Moisture changes naturally occur during rain events or day night transitions and temperature changes. Without weather changes like rain, this would mean one change from dry to wet during 24h, 7 times a week. In comparison the accelerated weathering test procedure has 48 changes of UV light (hot, dry) water spray (cold, wet) and one 24 h condensation phase

in one week. Thus, the accelerated weathering yields seven times the rate of natural weathering and is more aggressive towards crack development.

9.4 Conclusions

Modification improved the weathering performance of beech and poplar to different extends. Beech showed the least cracking after double modification and poplar after melamine treatment. The outdoor weathering behavior was rather difficult to predict based on accelerated weathering performance as the results differed from the natural weathering tests of the same materials. A general observation was confirmed for natural and accelerated weathering. Wood modification can reduce the number of cracks and checks in exposed surfaces. There were less cracks in modified materials but also some larger cracks as well. Melamine treatment could potentially be used to further reduce the appearance of surface cracks of thermally modified hardwood.

10 General discussion

Several studies about the specific aspects of the topic melamine resin treatment of hardwood and thermally modified hardwood have been conducted and are discussed as a whole in the following chapters.

10.1 Influence of curing conditions and process control, properties of melamine treated wood

Gravimetric methods were used to monitor the solution uptake (SU) and weight percent gain (WPG) after impregnation and curing, respectively. SU is linearly influenced by wood species, density, and moisture content. Wood density can be considered, but not really be changed, if a certain wood species is to be treated. The solid content (SC) will be adapted to achieve the desired WPG. The WPG is, in general, not influenced by the curing process and cannot be used to control the 'quality'. Other methods to control the curing process results are the technical and biological properties of the product, but this can take a long time as is not suitable for process control.

10.1.1 Chemical analysis

Changes in the amount, composition or constitution of the impregnation agent in the specimens caused by the curing process were recorded using differential scanning calorimetry, nitrogen, and formaldehyde analysis. The differences in chemical and mechanical properties were used to analyze the influence of the curing processes.

10.1.1.1 Differential scanning calorimetry

The basic curing characteristics of methylated melamine formaldehyde resin (MMF) can be determined under dynamic conditions by differential scanning calorimetry (DSC). The reaction enthalpy of uncured and cured samples can be used to determine the degree of curing (degree of conversion). Studies have been conducted to analyze the curing characteristics of urea formaldehyde (UF) and melamine formaldehyde (MF) resins (Szesztay *et al.* 1996; Xing *et al.* 2005; Bergmann *et al.* 2006), with and without catalysts, in the presence of powdered wood, and different wood components. Generally speaking, the reaction of thermosetting resins was accelerated by catalysts, making them react at lower temperatures in the DSC. The same was found to be true for resins mixed with wood powder. The catalyzing effect is explained by the acidity of wood (Devallencourt *et al.* 2000). For the combination of beech and MF in this study, the goal was to analyze the curing reaction of melamine resin in solid wood. As this has not been done before, the experiment had to be dialed in first. The SC of the impregnation solution was increased to 50 % to increase the chemical reaction in the DSC to be recordable. The specimens consisted of wood, water, resin, and pH buffer. The pH buffer had an inhibiting effect of about 10 °C on the curing temperatures in the DSC tests. An onset temperature of

100 °C was recorded without the use of triethanolamine (TEA), and 110 °C with 1 % TEA (see 4.5, p. 36). Following Mahnert (2013), and with regard to production scale impregnation, all impregnations were conducted using 1 % TEA as pH buffer. A SC of 20 % resulted in about 10 % melamine resin in the specimen – too low to record the curing reaction. Further, the amount of wood content in the mix with resin could inhibit the reaction and reduce the reaction enthalpy due to diffusion effects (Xing *et al.* 2005).

The test series with incrementally longer curing durations at different temperatures showed the residual reaction enthalpy compared to uncured specimens showing the enthalpy of the complete curing reaction. The degree of curing was positively correlated with curing time and temperature. This could confirm the results of Lukowsky (1999), who demonstrated that the curing process is more complete at higher temperatures and showed a lower limit of approx. 100 °C for complete curing (see p. 28). Curing at lower temperatures (80 °C) would have to be indefinitely longer and eventually would never be complete. Hagstrand (1999) explained this by the formation of an incompletely cured network, which is sterically hindered by its immobility after reaching the gelation point. In the presence of wood, this could mean that the resin condenses to a higher molecular weight before they would crosslink (Xing *et al.* 2005). During the curing in the DSC, no water can escape, as the crucibles are sealed. Condensation reactions produce water, which would evaporate in an open reaction (drying oven, etc.). The presence of the water of the impregnation solution and the reaction water will potentially further influence the chemical reactions. The pressure build-up in the crucible differs from most ambient pressure curing conditions. Using DSC with high-pressure crucibles was still a close schematic simulation of melamine resin curing in solid wood. The results display a rather realistic picture of complete MF curing in wood at 120 °C within several hours. For the comparison with product dimensions it must be considered that the specimens in the crucibles were 4 x 4.5 mm (cylindric) and thus rather instantly heated and subsequently cured. A board of 30 mm thickness has to be heated through first to ensure even curing even in the middle of that board. The curing process has to be oriented at curing the center of the board; measurements should be taken when the core of boards of varying thickness reaches the maximum curing temperature.

Bergmann *et al.* (2006) analyzed the influence of wood and wood components on the curing of MF resins. They found the influence of the components increasing in the order cellulose, wood flour, lignin, and hemicellulose. In their study, 20 % wood flour content in the resin mix lowered the curing temperature by 47 °C, similar to what was found in this study with a WPG of approximately 50 %. The most influential component was xylan (hemicellulose), decreasing the curing temperature by 89 °C. An explanation is given by the indication of the pH values of the wood components, with hemicellulose being the most acidic of them. The results of Bergmann *et al.* (2006) could be an indication of how the degraded hemicellulose and the potentially altered pH value of thermally modified wood could influence resin curing.

Referring to the objectives 1 and 2 of this study, the DSC analysis provided basic data for the curing process of melamine formaldehyde resin impregnated into beech wood and cured in situ. The DSC analysis showed the influence of curing temperature and duration on the degree of conversion (degree of curing). The principles of the test could potentially be used for different species of wood or other types of resin, too.

10.1.1.2 Nitrogen analysis

The nitrogen content of impregnation agents was used to monitor retention values after curing (weight percent gain, WPG) or determine the fixation after a subsequent extraction or leaching procedure or long-term weathering in an outdoor application. As the nitrogen content of wood is negligible (0.1 % – 0.2 %), all the nitrogen detected after treatment will have originated from the resin. Every melamine molecule contains six nitrogen atoms, approximately 50 % of the base resin, depending on the formulation (Rapp 1999). When the WPG and nitrogen content values were correlated, an overall accordance was achieved. The higher the WPG, the higher the nitrogen content. When comparing the dry and wet processes, a discrepancy could be seen. The WPG of the 120 °C curing at dry and steam conditions were 17.2 % and 14.8 %. In contrast, the nitrogen contents were rather close: 7.45 % and 7.98 %. The same pattern emerged for the curing at 105 °C: dry and steam curing resulted in 16.5 % and 15.1 % WPG, and 7.73 and 7.63 % nitrogen content, respectively. Steam curing resulted in the same nitrogen content but lower WPGs. Another major component of the resin is formaldehyde. The analysis of the formaldehyde content will complement these findings (10.1.1.3, p. 85).

The influence of the curing conditions on nitrogen fixation (NF) are expected to show higher fixation values the higher the curing temperature and the longer the curing is (Wepner 2006). When the extraction method ‘leaching’ was used, a time sensitive distinction could be made between dry-cured specimens (see Table 9, p. 29). The longer the curing, the higher the fixation. Higher temperatures also led to higher nitrogen fixation values. This was also observed by Sint (2010) for the curing of methylated melamine formaldehyde (MMF) in bombax wood: 90 °C curing led to high leaching values and 120 °C curing led to low leaching values after leaching according to DIN EN 84 (1997). In the separately conducted nitrogen fixation test (hot water extraction after milling) the influence of the curing temperature seemed to be benign, leading the author to conclude that the curing temperature does not have a significant influence on the fixation of the resin. This was separately tested in paper II. Hot water extraction found uncured melamine resin to have the same fixation values as MMF cured at 120 °C for 48 h. A leaching procedure following DIN EN 84 (1997), on the other hand, resulted in clear differences of cured and uncured specimens and a positive influence of time and temperature on NF.

When the humidity of the curing process was varied, the results varied, too. Here, higher humidity partially led to lower fixation rates (see Table 9, p. 29), or they were rather indistinguishable (see Table 10, p. 32). Schaffert (2006) stated a fixation value of above 90 % for the DMDHEU curing under hot steam atmosphere as sufficiently high. However, he also reported about inexplicable variations of the

fixation values between the different modification agents. In this study, only one resin formulation was used. Bollmus (2011) stated an influence of the amount of resin used on the nitrogen fixation of DMDHEU: higher concentrations resulted in higher fixation values. In the present study, only one concentration was used. Mahnert (2013) treated production-relevant sized boards of several thermally modified hardwood species with MF and used the nitrogen content and fixation to control the treatment quality across the cross section (outer layer – core layer) and along of the boards (end – middle – end) and found slightly higher nitrogen contents at the ends and in the middle of the boards. The fixation, however, was high throughout all placements. In addition, he treated thermally modified Scots pine specimens with the same resin and found lower fixation values (85 %). Reasons for the different fixation values between the species were not discussed.

Nitrogen fixation analysis as a measure of curing control has proven to be a challenge, several changes in methodology have happened in the hope of more reliable results: Soxhlet extractions were initially used and later replaced by hot water extraction (HWE) (Krause 2006; Schaffert 2006). HWE was found to give unreliable results (fixation values of cured and uncured MF in paper II, 3.3, p. 18) and was replaced by a leaching procedure following DIN EN 84 (1997). This enabled clear distinction between uncured and fully cured specimens. Krause (2006) used nitrogen content and fixation to analyze the influence of different catalysts on the curing reaction of DMDHEU but referred to the formaldehyde emission as a measure to evaluate the fixation after different curing processes. It was, however, difficult to differentiate between different curing processes, e.g., 105 °C and 120 °C after 4 h of curing (the DSC results suggested there should be clear differences). Nitrogen analysis was a valuable tool to help analyze the influence of the curing conditions on the material properties, but it would be difficult to only rely on nitrogen analysis.

10.1.1.3 Formaldehyde analysis

The influence of temperature and duration of dry curing processes were congruent with the nitrogen fixation values. Longer durations and higher temperatures led to lower formaldehyde emissions (FA-E). The temperature had a more severe influence on the FA-E than the duration. Increasing the curing duration from 4 h to 24 h compared to raising the temperature of dry curing for 24 h from 105 °C to 120 °C reduced the FA-E from 239 mg/kg to 227 mg/kg (105°C) and from 224 mg/kg to 129 mg/kg (120 °C), respectively. As a relevant property for wood products in interior application (DIN EN 13986 2015) and a measure of the degree of curing, the formaldehyde emissions were analyzed in multiple studies (Petersen *et al.* 1972; Lukowsky *et al.* 1998; Krause 2006; Wepner 2006) which were unanimously represented in the above-mentioned studies. This study comes to the same result. A complete curing has either released the formaldehyde during the curing process, or fixed it permanently in the network (Lukowsky *et al.* 1998). Schaffert (2006) recommended high maximum curing temperatures for low formaldehyde emissions. Wepner (2006) used 140 °C to 150 °C in a press for

curing beech veneers treated with DMDHEU. Prolonging the curing processes achieved lower formaldehyde emissions.

The humidity had a distinct influence on the formaldehyde emissions. The formaldehyde emissions (tested after curing) were lower at high humidity curings. Still temperature dependent, the FA-E values of high humidity curing were low (63 mg/kg at 105 °C and 29 mg/kg at 120 °C) after 24 h curing processes at 80 % steam level (see Table 9, 29p.). Wepner (2006) recorded lower formaldehyde emissions of DMDHEU treated veneers with a higher moisture content. Krause (2006) and Schaffert (2006) reported the same behavior for curing of DMDHEU treated solid wood. Petersen *et al.* (1972) reported twice the emission of formaldehyde during the curing process of particle boards with 15 % EMC compared to 10 % EMC. The amount of formaldehyde in the resin during curing influenced the crosslinking properties of the resin (Xing *et al.* 2005). They describe the influence of formaldehyde on the complete crosslinking of UF resins into a glass-state in DSC investigations, where a higher formaldehyde ratio led to more crosslinking. Correlating this mechanism, the lower formaldehyde content and the lower nitrogen fixation values in this study suggest that the high humidity during steam processes could cause incomplete curing and lower fixation.

The formaldehyde analysis showed the influence of the curing conditions on the chemical properties. It would be possible to use the formaldehyde emissions as curing control.

10.1.2 Influence of the curing conditions on mechanical properties and dimensional stability

10.1.2.1 Mechanical properties

The influence of the curing conditions on the mechanical properties after different curing processes were analyzed and compared to the nitrogen fixation and formaldehyde properties.

The work in bending (WB, static bending test) was the most sensitive property towards differences of the curing processes. High temperatures, long curing durations, and dry conditions led to the most reduction in WB. Here, a rather complete resin network is expected (Lukowsky 1999). Generally, the more complete the curing is, the stiffer the resin network and the larger the reduction in IB or WB (Lukowsky 2002). Less reduction in WB was recorded for incomplete curing (90 °C dry conditions), which also showed reduced nitrogen fixation values. Another factor influencing resin network formation and the subsequent mechanical properties was the formaldehyde content. It was shown that the high humidity conditions reduced the formaldehyde content by almost 50 %, and the same consistent differences were not recorded for the WB. The influence was more pronounced for processes at 120 °C than at 105 °C or 90 °C. No more plastic deformation in bending tests were recorded (Bollmus 2011; Mahnert 2013). Bollmus (2011) named the polymerization of the resin (DMDHEU) and potential cross-linking of the resin to cell wall components as potential reasons. According to Lukowsky (1999) and

Devallencourt *et al.* (2000), cross linking was not the main reason for the mode of action of MMF resins. Formaldehyde (gas) treatment caused embrittlement of the wood samples treated therewith (Rowell 1983). Here, a pure cross-linking effect was shown, with low impact bending values and increased hardness and MOR values. The formaldehyde treatment included fixation of the formaldehyde in wood using hydrochloric acid (Burmester and Wille 1976). It has to be noted that this step was not undertaken in the present study, and the formaldehyde might not be properly fixated to act as a modification agent.

The bending strength of beech was slightly increased after melamine treatment (MOR untreated: 134 N/mm², minimum MOR: 105 °C, 24 h, 0 % RH: 128 N/mm², maximum MOR 120 °C, 24 h, 100 % RH: 154 N/mm², see addendum paper III, 4.5, p. 36). The MOR of high humidity curing was slightly higher than that of dry curing, but standard deviations were as large as the differences between the treatment groups. MOR seemed to be higher when the work in bending was also higher. Again, the differences were not significant. Other aspects influencing the MOR are further discussed in chapter 10.2.1, p. 90. The bending strength greatly depends on the tensile and compression strength, as both stresses are present. The tensile strength is known to decrease after wood modifications (Bollmus 2011). An increase of the compressive strength was not measured directly but the increased Brinell hardness is a strong indicator for that.

The influence on hardness by the different curing conditions was not investigated. It was expected that the influence of curing temperature, duration, and humidity would rather be benign, and other factors such as resin concentration were more influential (see paper VII, 8.3.2.2, p. 72). The hardness of wood products is an issue when used as flooring. Hence, increasing the hardness was sought to be achieved with many different modifications (Epmeier *et al.* 2004). Hardness was increased regardless of the method but to varying degrees. The methods included chemical modification with acetic anhydride (Epmeier *et al.* 2004) to strictly cell wall impregnation modification with melamine resin tested through nano indentation (Gindl *et al.* 2004) or lumen filling with, e.g., wax treatment (Scholz 2011).

The mechanical properties were influenced by the curing condition to a varying degree. The bending strength was not influenced meaningfully and would not be suitable as quality control. Work in bending, however, was quite sensitive to the curing parameters and could be used in the future to characterize the influence of curing process parameters on the material properties.

When regarding full scale production, the mechanical properties as well as the FA-E are critical properties to be considered. The processes will most likely be conducted employing hot steam conditions and at a maximum temperature of 120 °C rather than 100 °C (Rapp 1999; Schaffert 2006; Mahnert 2013). Thus, the mechanical properties such as WB would be affected less negatively while achieving low formaldehyde emissions of the product.

10.1.2.2 Dimensional stability

The dimensional stability (anti-swell-efficiency ASE) was recorded for dry processes of double-modified material (see paper I, p. 13 and paper V, p. 37). The ASE of melamine-treated wood was caused by the bulking and was therefore indirectly monitored via bulking (Rapp 1999). In this study, lower bulking values were recorded for steam curing than for dry curing (see Table 12, p. 36). Generally, treatment with MF achieved ASE values as high as 40 % to 50 % when high solid content impregnation solutions were used (Rosca *et al.* 2003; Krause 2006; Mahnert 2013). Stamm and Seeborg (1936) and Sint *et al.* (2012) recorded higher dimensional stabilization of MF treated wood when cured at higher temperatures and higher nitrogen fixation. A more complete resin curing is quoted as a potential reason (Sint *et al.* 2012). Formaldehyde is important for resin formation during curing. It was shown that the formaldehyde content was very different for dry and steam processes (45 – 49 g/kg and 24 – 26 g/kg respectively, see paper III, 4.3.3.2, p. 31). Via the differences in bulking, a general difference in ASE of dry and steam processes can be considered. When formaldehyde was split off early in the curing process, it could have potentially led to fewer 3D connections in the network (Hagstrand and Oksman 2001). A less connected network is more flexible (see higher WB values) and could also mean less dimensional stabilization of the treated wood. This was also reported by Klüppel and Mai (2013), where lower bulking values were recorded after wet curing than after dry curing. In contrast, Schaffert (2006) did not record an influence of the humidity of the curing process on the dimensional stability of DMDHEU treated wood.

10.1.3 Microscopy and curing conditions

The properties of MMF treated wood were influenced by the curing conditions, as established in the previous chapters. Detecting and verify changes in material properties through imaging techniques has been attempted using both light microscopy techniques and electronic imagery.

10.1.3.1 Light microscopy

Light microscopy techniques have been used by several authors (Biziks *et al.* 2015; Mahrdt *et al.* 2015) to detect the changes in wooden materials after gluing or wood modification and was expected to work for this purpose, similarly with the modifications in this study. Transverse sections were analyzed; radial and tangential sections were not suitable for visual analysis. Safranin stained the untreated samples well but not the treated specimens. Safranin is commonly used to stain wooden cell walls in microscopy. Melamine seemed to block the access to the cell wall constituents, as reported with PF resin by Biziks *et al.* (2015). They visualized the penetration depth of different molecular weight phenol formaldehyde (PF) resins through the inability of safranin to stain the cross sections of modified beech wood. As the MF in this study has a molar mass sufficiently small enough to fully penetrate the cell walls, no untreated parts of the specimens were detected.

Brilliant sulphoflavine (BSF) stained the treated specimens but not the untreated ones. However, no variances of differently cured specimens in staining were detectable. BSF staining is an established,

nonspecific protein method (Leemann and Ruch 1972) and was successfully used by Mahrdt *et al.* (2015) to detect the UF bond line and UF penetration by combined dyeing and fluorescence microscopy imaging. In this study, the nitrogen of the resin was used as the detectable protein equivalent. As for safranin staining, a rather even penetration of the specimens across the cell walls could be concluded, leaving no difference between the curing variations to be detected. Further analysis of the resin distribution was conducted using electron microscopy.

10.1.3.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy

The WPG results (see Table 9 p. 29) suggested a higher residual resin content in the dry-cured specimens than the steam-cured specimens. The results of the bending tests also could be explained by the same mechanisms, or a different resin network formed under the different curing conditions (Klüppel and Mai 2013). The analysis of scanning electron microscopy imaging and the elemental examination with energy dispersive X-ray spectroscopy could potentially quantify the influence of curing conditions on melamine-treated wood (Rapp 1999) and provide information on the structural integrity of the wooden matrix (Bollmus 2011). Comparing the results of EDX imaging of transverse surfaces showed no clear differences of the dry- and steam-cured specimens. There was, however, a distinct difference to the untreated specimens, as no nitrogen was detectable (no images recorded, not shown). Granules of pure melamine resin formed in the lumens of dry- and steam-cured specimens, with a more frequent occurrence in the steam-cured specimens. Evaporation of water, condensation reactions, and resin network formation happen simultaneously during a curing process. There is a constant concentration adjustment between impregnation solution in the lumens and the cell wall. While the water evaporates from the lumens, the resin remains on site. The resin concentration in the lumen increases, forcing more resin into the cell wall in an osmotic effort to maintain balance. This continues until the water has evaporated or until the gelation point of the resin is reached (Hagstrand 1999), and it is immobilized (Lukowsky 1999). Excess resin remained in the lumen and formed granules (Rapp 1999). Furuno *et al.* (2004) and Mahnert (2013) reported that the granules formed above a certain solution concentration of PF and MMF resin, respectively.

The line scans complemented that situation, showing relatively high resin concentrations at the intersection of lumen and the cell wall (S3), with a gradual decline in nitrogen concentration in the secondary cell wall (S3) and a rather even distribution across S1 and the middle lamella (ML) (see Figure 9, p. 43). Investigations employing UMSP revealed different resin distributions. Higher MMF concentrations in beech towards the ML were reported by Kielmann *et al.* (2014), as analyzed by UMSP. Mahnert *et al.* (2013) also reported higher resin concentrations in the ML than in the S2 of MMF-treated koto and limba via UMSP measurements. In contrast, Rapp (1999) used SEM-EDX and TEM-EELS and recorded a slightly higher nitrogen concentration in the ML than in the S2 and a steeply rising gradient in the S3 towards the lumens, similar to the results in this study. RAPP (1999) explained the findings with the higher accessibility of lignin-rich areas such as the S3 and ML over the cellulose-rich

S2, and a resin diffusion gradient from the lumen towards the ML. Furuno and Goto (1973) found lower resin concentrations in the S2 than in the ML. Gindl *et al.* (2003) recorded higher MMF concentrations in the S2 than the ML using UMSP. The behavior is explained by the higher affinity of the hydrophilic MMF resin towards the S2 as a less lignified cell wall region. A slightly lower nitrogen content was attributed to the steam-cured specimens. The distribution of nitrogen across the cell wall itself did not seem to be affected by the curing conditions and showed a similar pattern.

10.2 Material properties of double modified wood

10.2.1 Mechanical properties

The investigated material properties were Brinell hardness, modulus of elasticity, modulus of rupture (MOR, bending strength), and work in bending (WB, work to maximum load). Four species were investigated (beech, ash, lime, and poplar), featuring a broad spectrum of densities. The tested species reacted similarly, therefore only the properties of beech will be discussed. The mechanical properties are influenced by the natural variability of wood such as grain orientation, knots, density, which is why only a selection of defect-free specimens were treated and tested.

Hardness (Brinell) was tested and found to decrease after thermal treatment and increased after melamine treatment, including in double-modified wood. These results confirmed the literature (Lukowsky 1999; Hill 2006; Esteves and Pereira 2009; Mahnert 2013; Lahtela and Kärki 2014). Hardness is foremost a function of the density of a wood-based material (Gindl *et al.* 2003), and the treatments influenced the material in the expected way: lower after heat treatment and increased after melamine treatment. The increase in density was caused by the incorporation of the resin into the cell walls and partly in the lumen. In this study, several SCs were used to match the WPGs of the different wood species. This might have resulted in an uneven increase in hardness when comparing the species, as the amount of resin also contributes to the increase in hardness (Kielmann *et al.* 2013). The SC for the treatment of untreated and thermally modified wood were also adapted to match the density and solution uptake. Thermally modified wood treated with melamine resin reacted differently regarding density and hardness than untreated wood. The density of wood only treated with melamine resin, and double-modified wood, increased by 9 % and 16 % with 20 % and 25 % SC, respectively. The increase in hardness was 57 % and 55 % (see Table 23, p. 61). Melamine treatment of thermally modified wood was as effective in increasing hardness as treating unmodified wood. Different solid contents (SC) of the impregnation solutions for thermally and untreated wood made it difficult to compare the increase in hardness. Thermally modified cell walls are more hydrophobic; the swelling due to solution uptake is lower (Esteves and Pereira 2009). However, both treated beech variations showed similar hardness increases. The differences in density are discussed further in the next paragraph (10.2.2 below, p. 92). The hardness of natural wood depends on the EMC (Kollmann 1951). This phenomenon should also be considered for modified wood. The EMC at 20 °C/65 %RH of the thermally modified beech was 5.1 %

compared to 11.9 % of the untreated specimens (Table 22, p. 59). In thermally treated wood, the EMC decreased with increasing treatment intensity, as does the decrease in hardness (Esteves and Pereira 2009). The mass-loss-induced hardness decrease has a stronger influence than the reduced EMC could have. The EMC of (double-) modified wood is discussed further in chapter 10.2.3, p. 93.

The bending strength (MOR) of untreated and thermally modified wood was slightly increased by melamine treatment in this study (from 109 N/mm² to 114 N/mm² and from 86 N/mm² to 99 N/mm², respectively). Resin treatment has been reported to increase (Sun *et al.* 2013) or decrease (Lahtela and Kärki 2014) the MOR, depending on type of resin and WPG. The common trait of resin-treated wood has been the lack of plastic deformation, followed by an abrupt rupture of the test specimens (Figure 12, 7.3.3.1, p. 62). This behavior has been described for melamine and DMDHEU treated wood and double-modified wood (Bollmus 2011; Mahnert 2013). An increase of MOR has been described for double -modified wood by Lahtela and Kärki (2014) when mild thermal treatment was involved rather than high thermal treatment temperatures. Krause (2006) described the incorporation of the resin in the cell walls as a potential reason for the rigidity of the specimens. Cross-linking of resin and cell wall components or the stiff three-dimensional network of the resin in the cell wall are described as reasons for the loss of plasticity.

The most notably influenced mechanical property investigated was the work in bending (WB). WB was determined in the three-point bending test, too. As it shares high correspondence with the dynamically determined impact bending strength (IB), they will be discussed in conjunction. The influence of melamine treatment on the WB of wood was discussed in the paragraph above (10.1.2.1, p. 86) and by other authors (Lukowsky 1999; Epmeier *et al.* 2004). The influence of melamine treatment of thermally modified wood was rather minimal; no significant further decrease of WB was detected. Few authors have described the influence of resin treatment on WB or IB of thermally modified wood. Mahnert (2013) reported the IB to be rather unchanged, noting that melamine treatment of other authors led to a decreased WB (Epmeier *et al.* 2004). Mahnert (2013) named the recombination of thermal treatment degradation products and resin monomers as a potential reason for strengthening the wood structure and prevent a further decrease of IB. Lahtela and Kärki (2014) treated pine with melamine resin and a subsequent thermal modification and also reported the IB of double-modified material to be only slightly reduced compared to melamine or thermally treated specimens. The melamine and thermal treatment of Lahtela and Kärki (2014) are interchanged compared to this study and to Mahnert's (2013). During their curing and subsequent thermal treatment, the temperatures for complete resin curing (120 °C) will occur before the temperatures for the development of thermal degradation products (140 °C – 170 °C and higher). This renders the potential recombination of resin and thermal degradation products improbable. However, the resulting mechanical properties of the different process combinations were very similar. The IB or WB of either thermal or melamine treatment are already significantly reduced; it could be argued that further reduction would involve serious deterioration of the wooden matrix. The discussed

increase in density of the double-modified material through melamine treatment could also increase the WB or prevent further decrease. The bulking of double-modified specimens compared to melamine-treated ones is rather low, even negative at times, fostering the density increase (see 10.2.2, p. 92).

10.2.2 Dimensional stability

The increase of the dimensional stability of thermally modified poplar through melamine treatment was the focus of paper V (see chapter 6.3.3, p. 49). The dimensional stability was only marginally increased, depending on the thermal modification temperature. Material from two boards treated at maximum temperatures of 210 °C and 230 °C, respectively, were subsequently treated with melamine resin. The ASE of the lower temperature thermal treatment increased slightly from 45 % to 52 %, the ASE of the 230 °C treated specimens did not change (from 52 % to 50 %). The double-modified samples (230 °C) had a slightly negative ASE compared to the thermally treated specimen. Similar negative ASE values (high thermal modification temperature of 230 °C) were also recorded for beech, ash, and lime. All four species (including the poplar treated at 230 °C) were treated in the same thermal modification and also in the same melamine treatment (see addendum, paper V, 6.5, p. 52). The SC of the impregnation solution was adapted to the varying densities and solution uptakes to achieve similar WPGs. The ASE of melamine-treated wood was WPG-dependent (Rosca *et al.* 2003). A positive ASE after melamine treatment with 10 % and 25 % SC of thermally modified tropical hardwoods (210 °C) was reported by Mahnert (2013). The bulking was zero for the 10 % and positive for the 25 % solution. When the same author treated thermally modified (180 °C and 220 °C) pine with 15 % and 30 % melamine resin, he reported positive bulking for the 180 °C-treated and negative bulking values for the 220 °C-treated pine. 15 % melamine had lower bulking than 30 % melamine. In this study, the SC and WPG were rather low (wood density and solution uptake dependent). If the goal was to maximize the ASE through melamine treatment, a higher WPG would have been more suitable. However, the ASE of MF is limited, as an increase in ASE levels of approx. 40 % were observed at 30 % WPG (Mahnert 2013). Potential explanations for negative bulking of double-modified wood partially lie in the properties of thermally modified wood such as the increased hydrophobicity, limited water uptake, and limited subsequent swelling. As the swelling due to polar solvent (water) uptake of the thermally modified cell wall is limited, less resin can penetrate the cell walls (Mahnert 2013). Less resin in the cell wall would lead to less potential in permanent bulking (Mahnert 2013). The main mode of action of impregnation modifications such as melamine treatment regarding ASE is bulking rather than fixating the dry state (Hill 2006) and thus, restrictions of the bulking will greatly interfere with the bulking efficiency. Degradation products of the thermal treatment partly evaporate during treatment (Fengel 1966) and partly remain in the wood matrix (Altgen *et al.* 2016; Wentzel 2018) and can cause a) increased hydrophobicity and b) a bulking effect. Some of those degradation products are (water-) soluble and can be leached out, decreasing the volume and thus the dimensional stability of the specimen (Biziks *et al.* 2014). This effect was mentioned as the reversible part of thermal modification by Altgen (2016). When

impregnated with a melamine resin solution (pH 9 – 10), these degradation products might have leached into the alkaline impregnation solution, as suggested by Mahnert (2013). The combination of a potential alkaline leaching of thermally degraded cell wall components and the decreased swelling and bulking could lead to the reduced and even negative bulking seen with low SC resin treatment of wood thermally treated with high temperatures.

10.2.3 Weathering properties

Outdoor usage without ground contact (Use Class 3.1 and 3.2 (DIN 68800-1 2011)) are potential applications for modified wood products. Untreated, non-durable wood species would not be suitable, as a durability class 2 or higher is required for these applications (DIN EN 350-2 1994). Grey surfaces are another issue, as well as checks and cracks and surface erosion. These are the main concerns when unfinished (without lacquer or paint) wood surfaces are used outdoors.

Color changes, especially greying, is a common trait of all wood species and rather unavoidable when no surface protection layer is applied. It might therefore be acceptable or subject to perception management (Kaudewitz 2016).

Surface cracks are an aesthetical issue as well as a potential safety hazard and also a subject of material integrity. Splinters can cause harm; cracks could entrap water and cause permanently increased moisture content of wood components and potentially lead to accelerated degradation of the material.

Greying and subsequent erosion is caused by repeated UV degradation of cell wall components on the surface (50 µm – 100 µm) and by the subsequent leaching through water or damage by insects such as wasps. This mechanism can continue for decades. Less erosion was found on melamine-treated and double-modified specimens than on untreated and thermally modified specimens. The thermal modification did not differ from the untreated specimens in terms of crack development. Lignin was not altered much during thermal treatment (Hill 2006). Lignin was most vulnerable to UV degradation (Lin and Gierer 1972). The properties of modified wood towards UV were unchanged, the lignin degraded and was washed out. The cellulose was left on the surface, turning it white or grey. The resin treatment did not inhibit the greying but stabilized the surfaces. A potentially mechanical stabilization of the surface was suggested (Mahnert 2013). UMSP investigations of Mahnert *et al.* (2013) showed high nitrogen content in the middle lamella where most lignin is located. Lignin was not chemically stabilized through the melamine treatment and could still be degraded and washed out, turning the surface grey over time. However, the three-dimensional matrix of resin mechanically stabilized the surface and led to a slower weathering erosion.

Testing the change in crack susceptibility of modified wood was the focus of the weathering tests. The weathering stability of thermally modified wood has been investigated before (Feist and Sell 1987; Hill 2006; Esteves and Pereira 2009) and the verdict was heterogeneous. It depended on the treatment

intensity, treatment process, and wood species (Feist and Sell 1987). Weathering of double-modified wood was subject to only very few studies and can therefore mostly be discussed with results gathered by Mahnert (2013). Otherwise, the single modifications will be discussed, but as the previous chapters have shown, the influence of MMF on thermally modified wood was different than on untreated wood. In this study, thermally modified beech and poplar (230 °C) were treated with two different melamine resin concentrations to achieve 15 % and 25 % WPG in both species. Weathering of thermal modification of beech resulted in more cracks of the same size compared to the untreated controls ('references'). The treatment of poplar resulted in fewer cracks of smaller size. The influence of the thermal treatment was species-dependent, as reported by Feist and Sell (1987). The double modification of beech resulted in slightly more cracks of smaller size; poplar showed no change in crack susceptibility after double-modification compared to thermal treatment. Mahnert (2013) compared the weathering behavior of koto and limba after thermal and double modification in two accelerated weathering setups. One test was the QUV accelerated weathering (DIN EN 927-6 2006) and the other a custom-built device following the nautical standard (EN 60 945 2002). After accelerated weathering, both species showed a "70 % to 80 % increase of the crack index" (evaluation of sum of crack width and number of cracks, following DIN ISO 2648-4 (1997)). Depending on the species, there was a considerable improvement compared to thermally modified wood. Much like the results in this study, weathering and crack susceptibly with or without treatment was species-dependent. It has to be noted that results of accelerated and natural weathering are difficult to compare (see paper VIII, 9.3, p. 78). This is also mentioned by Mahnert (2013). He suggested that material development have to be accompanied by long-term natural weathering tests. The conditions differ greatly between tests, UV spectrum of the light source, exposure time, weathering cycle schemes, and amount of water spray.

Reasons for crack development in resin treated wood have previously been discussed (Rapp 1999; Krause 2006; Bollmus 2011). Most authors concluded that differential swelling due to drying and wetting of the surface led to tensions higher than the wood matrix can absorb. Wood species with a high potential to exert these tensions (high-density wood such as beech) are more prone to develop cracks. Properties of modified wood such as low flexibility and low impact bending strength could potentially showcase the inability to absorb stresses. They could not be linked to crack susceptibility in this study (chapter 8.3, p. 70). The increased dimensional stability was also not an indicator for crack susceptibility of double-modified material (Mahnert 2013). Rapp (1999) reported the slowly increasing EMC of MMF-treated wood to cause increasing crack development. Higher moisture uptake could cause more movement and induce more cracks. The EMC_R levels during natural weathering in this study did increase over time. The initial EMC_R (20 °C/65 %RH) of untreated, melamine-treated (low WPG), thermally modified, and double-modified (low WPG) beech were 11 %, 13 %, 6 %, and 12.5 %. After one year of outside weathering, they were recorded at 12%, 16 %, 8 %, and 14 %, respectively (Figure 13, p. 73). The EMC_R of the various treatments and their respective crack susceptibility did not support this assumption that the increased EMC_R led to more crack development. All treatment groups showed

increased EMC_R values but showed different levels of crack development (see paper VII, 8.3, p. 70), mostly reduced crack susceptibility. Other reasons for crack development might be rooted in the source material (wood) and the treatments it received before the weathering test began. Microcracks are reported to form during technical drying of lumber as well as during thermal treatment (Altgen *et al.* 2014) and during curing of melamine-treated specimens (Mahnert 2013). These drying-induced tensions caused microcracks, not visible or detectable on a macroscopic scale of other drying defects (e.g., cell collapse and cracks). Once microcracks were formed, the low flexibility of the stiff resin network could facilitate crack development more easily (Bollmus 2011). Bollmus (2011) found ray cells of beech especially susceptible to damage by curing processes. She reported that very low resin concentrations or even water impregnation and subsequent hot steam curing damaged the ray cells (collapse, detachments) and significantly decreased the tensile strength. The SEM imaging (paper IV, chapter 5.3, p. 39) showed more microcracks in melamine-treated beech after dry curing than after steam curing. Steam curing could be more suitable to cure resin in wood with regards to crack susceptibility during weathering. Mahnert (2013) used steam curing during double modification and recorded an improvement in crack susceptibility compared to the thermally treated specimens. However, wood species, thermal treatment, and impregnation solution were different from the present study. The evaluation of weathered surfaces and crack susceptibility is an ongoing debate, since objective parameters such as crack width and number of cracks (DIN ISO 4628-4 1997) can differ from the user's perception of the surfaces and the intended use (Kaudewitz 2016). Gellerich *et al.* (2017) found that crack width rather than the number of cracks was the decisive measure of surface quality assessment. Analog to these findings, a subjective assessment (from 'excellent' to 'failed') was assigned to the natural weathering specimens (chapter 8.3.3, p. 72). It showed the width of the cracks to correlate best with the subjective visual assessment.

Melamine treatment was used to alter the weathering performance of thermally modified beech and poplar. In the natural weathering test, the crack susceptibility was reduced, and the surface erosion was decreased.

11 Conclusions & Outlook

The study can be concluded by returning to the objectives and answering the posed questions. An outlook for the potential of products made of double-modified wood is given.

11.1 Material properties and curing control

The questions of the objectives of this study can be answered as follows:

1. What are the effects of the curing conditions on the microstructure, chemical composition and resin distribution in the wooden matrix, and the cell wall components and the resulting material properties?

The effects of the curing conditions on the microstructure in the form of microcracks were detected by scanning electron microscopy. There were fewer cracks in steam-cured specimens than in dry-cured specimens. The chemical composition was altered in the following ways: The nitrogen content was increased compared to uncured specimens and was roughly the same for steam and dry curing. The nitrogen fixation was lower after steam curing than dry curing. The formaldehyde content was lower after steam curing than after dry curing. The formaldehyde emissions were substantially lower after steam curing. According to energy dispersive X-ray spectroscopy, the resin distribution was about the same across the cell wall for dry and steam curing, with potentially lower nitrogen content in the cell wall and more resin in the lumen after steam curing. The resulting material properties were increased hardness and slightly increased bending strength for both processes, and slightly lower work in bending after steam curing.

2. Can the interactions of the curing conditions and the material properties be exploited as curing control mechanisms?

Nitrogen fixation: Leaching instead of hot water extraction gave more accurate results. Steam curing resulted in lower fixation values than dry curing. It might be difficult to be used as curing control, as low fixation values after dry curing would indicate not fully cured specimens, but high humidity curing showed lower fixation values even after sufficiently long curing at high temperatures. The formaldehyde emissions were sensitive to curing duration and temperature. The formaldehyde emissions were very sensitive to humidity. The formaldehyde content reacted primarily to humidity; steam curing resulted in low formaldehyde content. Nitrogen and formaldehyde analysis are elaborate methods and might be used to develop a curing process rather than monitor the mass production of modified wood. The mechanical properties might not be suitable to be used as curing control: The work in bending showed high variability and would be difficult to use as curing control. Hardness was not influenced by the curing conditions and thus not suitable as curing control.

3. Was melamine treatment suitable to positively alter the mechanical, water-related, and weathering properties of thermally modified wood?

The hardness improved greatly depending on resin concentration. The bending strength was slightly increased by resin treatment. The work in bending was rather unaltered depending on wood species. The equilibrium moisture content of double-modified wood was found to be higher than that of thermally modified wood. The resin itself is potentially hygroscopic or created micropores to contain water. The weathering properties were improved. Crack susceptibility was lower depending on species and resin load of thermally modified hardwoods. The surface was stabilized and more protected against erosion after melamine treatment.

Some notes for future developments: Hot steam curing processes could potentially benefit the crack stability of resin-treated wood. The low formaldehyde content led to less reduction of work in bending. A potentially less stiff resin network might have been formed. The specimens for the weathering tests in this study were cured in laboratory ovens under dry conditions. If cured under hot steam conditions, the crack susceptibility could maybe improve further.

11.2 Upscaling and market prospects of double-modified wood

The results gathered in this thesis should be used to prepare the upscaling of the production of modified or double-modified wood products. It is crucial to know the field of application of the product. Which are the most important properties for that product? The hardness, durability, flexibility, or color? Most of the properties are interdependent; not a single one can be changed without influencing the other. But setting the priorities right can still influence the overall outcome. The investigated properties can be used to monitor the product characteristics. When a production is set up, regulations have to be respected regarding the labor protection law (German Occupational Safety and Health Act) and explosion protection (Guidelines for Explosion Protection and Prevention) as formaldehyde and methanol are emitted during the curing process. Rapp (1999) analyzed the disposal of melamine-treated wood and concluded that it is nontoxic and could even be used as fertilizer or for composting, as it has long-term nutritional value to plants (nitrogen) since it would degrade slowly.

The potential market for a double-modified product would have to recognize the properties of the material over the costs. High-quality outdoor applications with high requirements regarding dimensional stability, durability, surface integrity, hardness, and the aesthetics of exclusive hardwood would be suited. Potential markets are pool surroundings, seating areas, and decking in hot climates or even maritime applications (Mahnert 2013). Further development expanding the usage could be low or no emissions (formaldehyde) or fire retardancy. The double-modified materials were clearly developed for exterior applications. The material will be perceived as a new wood species. If accepted by the market as a new species, the material will potentially be used for various applications, not only the specific application it might have been developed for. A modified wood might have been developed as a decking

material. An architect working with this material will design the deck surrounding the pool. Then the deck is supposed to seamlessly integrate into the restaurant area and further to the bar of a hotel. Here, different regulations concerning fire safety or emissions might apply. This opens up future possibilities and challenges for the scientific community to promote wood as a universal building material.

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