Karl-Christian Mahnert, Stergios Adamopoulos, Gerald Koch and Holger Militz*

Topochemistry of heat-treated and N-methylol melamine-modified wood of koto (*Pterygota macrocarpa* K. Schum.) and limba (*Terminalia superba* Engl. et. Diels)

Abstract: To broaden the knowledge about the chemical changes at the cell wall level of differently modified tropical hardwoods, heat-treated and N-methylol melamine (NMM)-treated samples of koto (*Pterygota macrocarpa*) and limba (*Terminalia superba*) were prepared. UV microspectrophotometry (UMSP) was applied at 278 and 240 nm as specific wavelengths to analyze chemical alterations of the samples caused by heat and NMM treatment, respectively. The absorbance of koto exceeded that of limba before and after treatment, potentially due to the higher extractive content of the former. Regardless of the wood species, the absorbance of the samples increased with increasing intensity of the NMM treatment. Additionally, the absorbance of lignin within the spectrum of 230–350 nm was altered due to the NMM treatment. The functionality of applying specific wavelengths for the analysis of different modification methods of wood was proven. However, the comparison with literature did not show differences in the absorbance, which could be assigned to the characteristics of tropical hardwoods.

Keywords: heat treatment, lignin condensation, N-methylol melamine, UV absorption, UV microspectrophotometry, wood modification

***Corresponding author: Holger Militz,** Wood Biology and Wood Products, Burckhardt-Institute, Georg August University of Göttingen, Büsgenweg 4, 37077 Göttingen, Germany, Phone: +49-551-393558, Fax: +49-551-399646, e-mail: hmilitz@gwdg.de

Karl-Christian Mahnert: Wood Biology and Wood Products, Burckhardt-Institute, Georg August University of Göttingen, Büsgenweg 4, 37077 Göttingen, Germany

Stergios Adamopoulos: Wood Biology and Wood Products, Burckhardt-Institute, Georg August University of Göttingen, Büsgenweg 4, 37077 Göttingen, Germany; and Technological Educational Institute of Larissa, Department of Forestry and Management of Natural Environment, 431 00 Karditsa, Greece

Gerald Koch: Institute for Wood Technology and Wood Biology, Federal Research Institute of Rural Areas, Forestry and Fisheries (vTI), Leuschnerstr. 91, 21031 Hamburg, Germany

Introduction

The term wood modification summarizes the physical and chemical processes applied to extend the service life of wood by decelerating biological degradation and improving the wood properties without biocide treatment. Various modification techniques with different intensities are available (Homan and Jorissen 2004), which can be classified as active (chemical, thermal, and surface modification) and passive (impregnation modification) modification (Hill 2006).

Thermal modification between 160°C and 260°C leads to an increased biological resistance (Tjeerdsmas et al. 2000) and dimensional stability (Burmester 1975) of wood, which are attributed to the thermal degradation of wood polymers, mainly hemicelluloses (Militz 2002). Commercial treatment variants are, e.g., Plato®-Process, ThermoWood®, Stellac, Retification, or oil heat treatment (Welzbacher 2007). The chemical composition of wood, the treatment atmosphere (steam, air, nitrogen), and other parameters (temperature, duration, medium of heat transfer) influence the results (Zaman and Alén 2000; Militz 2002; Wang and Cooper 2005).

The depolymerization and hydrolysis of hemicelluloses begins below 180°C (Garrote et al. 2001; Rowell et al. 2009). The liberation of acetic and formic acids via hydrolysis belongs to the essential mechanisms, and the decreasing pH values of wood accelerate hemicelluloses depolymerization (Sundqvist et al. 2006). Cellulose, though accessible to hydrolysis mainly in the paracrystalline regions, has a higher thermal stability. Thus, the degree of crystallinity of thermally treated wood is elevated (Andersson et al. 2005). Lignin has the highest thermal

stability (Kollmann and Fengel 1965; Wienhaus 1999). The main thermal degradation occurs at temperatures above 200°C (Sivonen et al. 2002) by the cleavage of the polysaccharide lignin complexes, depolymerization of lignin macromolecules (Burtcher et al. 1987), and their demethoxylation. The demethoxylated aromatic rings with their additional active sites in positions 3 and 5 undergo condensation reactions (Wikberg and Manu 2004; Hill 2006). The solubility of the cross-linked lignin is decreasing (Fengel and Wegener 2003). Accessory compounds of wood also degrade, to some extent, during thermal treatment (Bourgois and Guyonnet 1988; Manninnen et al. 2002; Esteves et al. 2008). In thermally treated wood, elevated amounts of monosaccharides, syringaldehyde, syringic acid, and sinapylaldehyde are formed, just to mention a few of them (Rosa and Pereira 1994; Esteves et al. 2008).

Wood modified with melamine formaldehyde, for example, was investigated a long time ago (Stamm 1964). For impregnation, the melamine resin is diluted with water to a given concentration, and the impregnated wood is subsequently cured between 80°C and 120°C. The resin penetrates the cell walls by diffusion. During curing, the monomers cross-link and a 3D network is formed within the cell wall, but covalent chemical bonds to the cell wall polymers do not play an essential role (Lukowsky 1999). The dimensional stability, surface hardness, strength, resistance to decay, weathering, and color changes of such treated woods are improved (Stamm 1964; Pittman et al. 1994; Miroy et al. 1995; Rapp and Peek 1999; Gsöls et al. 2003; Gindl et al. 2004; Krause et al. 2004; Hansmann et al. 2006; Deka et al. 2007). The natural appearance of the modified wood remains unchanged (Hansmann et al. 2006), but its embrittlement is considerable (Rosca et al. 2003).

Rapp et al. (1999) quantified the cell wall penetration by melamine by electron energy loss spectroscopy. UV microscopy was employed to estimate the concentration of melamine-urea-formaldehyde (MUF) resin (Gindl et al. 2002) and the occurrence of MUF in the treated cell walls (Gindl et al. 2003).

There is an extensive know-how concerning the modification of commercial woods from the temperate zone. However, information about the treatment of tropical timbers is very limited, though their tailor-made improvement would open an enormous resource of woods suited to specific end uses. To make a progress in this field, two important timbers of tropical origin, limba (*Terminalia superba* Engl. et Diels) and koto (*Pterygota macrocarpa* K. Schum.), were modified in the present paper by heat and melamine treatment. The effects were studied by UV microspectrophotometry at the cell wall level.

Materials and methods

Heat treatment

Quartersawn sapwood boards of koto (*Pterygota macrocarpa* K. Schum.) and limba (*Terminalia superba* Engl. et Diels), 10×30×3000 mm³ and 100×50×2500 mm³ (R×T×L), respectively, were heat treated in the Plato-Process® (Plato BV, Netherlands). In the first step (Phase 1), wood is submitted to hydrothermolysis in a steam environment at superatmospheric pressure at approximately 160–180°C. The high moisture content (MC) of the wood contributes to an increased reactivity of the cell wall components. In this step, acid catalyzed cleavage of carbohydrates, formation of formaldehyde, furfural, and other aldehydes occurs. Additionally, lignin is cleaved, and its autocondensation begins. Then, wood is dried to 10% MC in a regular drying process (Phase 2), and subsequently, it is cured at 170–190°C (Phase 3) (Ruyter 1989; Boonstra et al. 1998; Tjeerdsma et al. 1998a). In this last step, autocondensation of lignin is completed (Tjeerdsma et al. 1998b).

Melamine modification

Conditioned (20°C and 65% RH) and end-grain-sealed with the commercial coating Pyrotect Schutzlack 2 K (Rütgers Organics GmbH, Mannheim, Rhineland-Palatinate, Germany), koto and limba sapwood samples (25×50×50 mm³, R×T×L) were impregnated with a solution of N-methylol melamine compound (NMM). Before impregnation, the oven-dry density of the samples was determined.

The NMM compound Madurit MW840/75WA (Ineos Melamines, Frankfurt a.M., Hessen, Germany) was supplied as an aqueous stock solution with a solid content of approximately 75%. By mixing the resin with tap water, solutions of 10% and 30% NMM solid content were prepared and stabilized by the addition of 1% triethanolamine. The pH was adjusted to a pH of 10 by adding NaOH.

For impregnation, a full-cell process in a steel reactor was applied (vacuum of 600 mbar for 30 min followed by a pressure phase of 120 min at 12 bar) as recommended for native and tropical timbers (Krause 2006, 2008; Schaffert 2006; Sint 2010; Bollmus 2011).

The samples had been wrapped in plastic bags to retard the loss of moisture (Krause 2006), then curing of the NMM resin was conducted in a drying oven at 120°C for 48 h. The oven dry mass of the samples was determined after drying at 103°C for 24 h to subsequently calculate the solution uptake (SU) $[SU=100(m_2-m_1)/m_0]$ and weight percent gain $[WPG=100(m_3-m_1)/m_0]$, where m_2 is the weight of the sample after impregnation, m_1 is the weight of the conditioned sample before impregnation, m_0 is the oven-dry weight of the sample before impregnation, and m_3 is the oven-dry weight of the sample after curing. Calculations were based on 15 samples for each NMM concentration.

The NMM molecule contains six nitrogen (N) atoms, and the nitrogen content of untreated wood is negligible. Thus, C/N analysis permits the control of nitrogen fixation $[NF=100(n_e/n_{ne})]$ in the wood, where n_e and n_{ne} represent the amount of nitrogen in the extracted and non-extracted wood, respectively. The higher the fixation, the more thorough is the curing of the resin in the wood tissue (Wepner 2006). To this purpose, the NMM-modified wood was ground in a ball mill, and 1 g was extracted in 60 ml demineralized water at 85°C for

Figure 1 UV microscopic scanning 2D profiles of koto (left) and limba (right) at 278 nm showing higher absorption in the heat-treated wood tissue (b, d) compared to the untreated (a, c). Arrows are pointing at areas of maximum absorption because of the presence of condensed lignin. Size of UV pictures: (a) 241×186 pixels; (b) 230×143 pixels; (c) 189×176 pixels; (d) 147×145 pixels.

16 h. Extracted and non-extracted powder was oven dried and subsequently analyzed in a LECO CHN 2000-Analyzer (LECO Instrumente GmbH, Mönchengladbach, North-Rhine Westphalia, Germany).

Cellular UV microspectrophotometry

From heat-treated and NMM-modified material, samples of 1×1×5 mm³ (R×T×L) were cut and immediately embedded with Spurr's epoxy resin (Spurr 1969) under mild vacuum. Several cycles of evacuation and ventilation were applied (Kleist and Schmitt 1999).

Ultrathin transverse sections (thickness 1 µm) of the embedded samples were cut with a diamond blade and subsequently transferred to non-reflective quartz slides. After immersion in glycerine, the sections were covered with a quartz coverslip. Instrument: Zeiss UMSP 80 micro spectrophotometer (Carl Zeiss Jena GmbH, Jena, Thuringia, Germany); wavelength selected for lignin: 278 nm (the absorbance maximum of hardwood lignins according to Fergus and Goring 1970). A maximum at 240 nm is characteristic for melamine and melamine compounds (Gindl et al. 2003); thus, NMM-treated wood was scanned at this wavelength. Software: APAMOS® (Carl Zeiss Jena GmbH, Jena, Thuringia, Germany); the rectangular field of the examined tissue was digitized at a geometrical resolution of 0.25 µm². The photometrical resolution amounted to 4096 grayscale levels, which were converted to 14 colors for the visualization of the absorbance intensities. Overall, more than 100 scanning profiles and 150 UV-absorbance spectra were taken from the individual cell wall layers and cell types for the topochemical analyses.

Photometric point measurements: spot size of 1 µm² in the range 230 nm and 350 nm. Instrument: MSP 800 microspectrometer (J&M Spectralytics GmbH, Essingen, Baden-Wuerttemberg, Germany) data evaluation was done by the software TIDAS-DAQ (J&M Spectralytics

GmbH, Essingen, Baden-Wuerttemberg, Germany) and PANORAMA ProColorSearch (Labcognition, Analytical Software GmbH&Co KG., Cologne, North-Rhine Westphalia, Germany). The spectra were taken from the individual cell wall layers and were evaluated statistically.

Scanning electron microscopy

The NMM-modified wood samples (3×3×5 mm³, R×T×L) were prepared with a razor blade for cross-sectional microscopic observation. The samples were attached to aluminum stubs and dried overnight in a vacuum oven at 25°C. The samples were then sputter coated with 12 nm gold and examined by a FEI Quanta 250 field emission scanning electron microscope (FEI Company, Eindhoven, Netherlands); acceleration voltage: 15 kV.

Results and discussion

Topochemistry of heat-treated wood

Representative 2D UV scans of untreated koto and limba at 278 nm (Figure 1) show the characteristic lignin distribution in the cell walls (Koch and Kleist 2001; Koch et al. 2006; Scholz et al. 2007; Carrillo et al. 2008; Adamopoulos and Koch 2011). The UV absorbance of heat-treated fiber tissue is generally elevated compared to that of the untreated sections. The cross sections of the scanned

Figure 2 Representative UV spectra of S2 layers from fibers (F) and axial parenchyma (AP) in heat-treated koto (a) and limba (b).

fibers were especially dominated by highly absorbing regions (0.74–0.94 and above) at the compound middle lamella (CML) and cell corners (CC) (black arrows in Figure 1b, d). This can be interpreted as a manifestation of the increased degree of condensation of lignin and higher contents of aromatic degradation products caused by the mild thermal conversion processes (Wienhaus 1999) occurring during heat treatment. The chemical conversion of polysaccharides and their degradation products (e.g., furfural, formaldehyde, formic, and acetic acid) (Mitchell et al. 1953; Bourgois et al. 1989; Boonstra and Tjeerdsma 2006; Gonzales-Pena and Hale 2011), the splitting of the aliphatic side chains from lignin, which increases the amount of conjugated double bonds (Goldschmid 1971; Ucar et al. 2005), and the condensation between furfural and lignin contribute to the increasing UV absorbance. The higher degree of conjugation stabilizes the π - π^*

Wood species/NMM concentration	Oven-dry ^a density (g cm ⁻³)	SU ^a (%)	WPG ^a (%)	Nitrogen content ^b		
				n_e (mgg ⁻¹)	n_{ne} (mgg ⁻¹)	NF (%)
Koto (10%)	0.60	108	8	27.9	22.9	82.3
Koto (30%)		90	20	70.6	66.7	94.6
Limba (10%)	0.51	136	12	26.9	23.4	87.0
Limba (30%)		131	29	87.7	83.7	95.4

Table 1 Information on the untreated wood and the NMM modification.

^{a,b}Mean values of 15 and 2 repetitions, respectively. n_e and n_{ne} , N in non-extracted and extracted woods, respectively. NF, nitrogen fixation.

transitions and causes a shift of the spectral band toward a lower frequency. The resulting absorption at higher wavelengths (Goldschmid 1971) is referred to as bathochromic shift (Nic et al. 2012).

Figure 3 Representative UV spectra of the S2 layers from fibers in the NMM-modified koto (a) and limba (b). The absorption is low in the untreated tissues and rises with increasing NMM concentration (10% and 30% NMM).

The S2 layers of the fibers and the axial parenchyma of the untreated control samples (Figure 2) show the typical hardwood lignin UV spectra with a maximum at 278 nm and a local minimum at about 250 nm (Irbe et al. 2006). The fibers generally show a higher absorbance than the axial parenchyma due to the higher lignin contents in the former (Fergus and Goring 1970a,b). The spectral differences before and after heat treatment are, in the case of koto, larger than those of limba (Figure 2). Probably, the higher content of the extractives in koto could explain this observation. Kleist and Bauch (2001) as well as Mayer et al. (2006) found an increasing UV absorbance in the cell walls of Sapelli heartwood with higher extractive contents. The UV spectra of heat-treated woods display a slight plateau in the wavelength range of 310 nm, which makes the pronounced maximum of the untreated samples to appear less prominent. The carbonyl groups on the lignin side chains and the condensation of the aromatic rings with furfural and other hemicellulose degradation products may have contributed to this observation (Sander and Koch 2001).

Figure 4 SEM images of koto (a) and limba (b) modified with 30% NMM showing numerous NMM deposits in the cell lumens.

Modification with NMM

For both species, the solution uptake (SU) was independent of the NMM concentration in the impregnation solution (Table 1). However, the SU and weight percent gain (WPG) of limba are higher than those of koto. Obviously, the lower oven-dry density of limba (Table 1) and the corresponding higher proportion of the void volume lead to this data.

As expected, the increasing concentrations of NMM yielded a higher WPG and nitrogen content. The nitrogen content was similar in both species after the treatment with 10% NMM. As shown in Table 1, the fixation of the NMM increased by 7–12% at 30% NMM concentration. Assuming a cross-linking between the NMM and wood compounds, this observation could be a hint of the different bonding behaviors of the wood species with the NMM

Figure 5 UV measurement (red rectangle) of the NMM deposits in the vessel lumen of limba (a) and the UV spectra from three different NMM deposits (b).

resin. Nevertheless, a relevant extent of chemical bonding between the melamine resin and wood was not observed in previous publications (Lukowsky 1999; Rapp 1999). Probably, a higher extent of crystallization of NMM occurs in the case of its application in 30% solution (Markov 2006).

Topochemistry of NMM-modified wood

In both species, the UV absorbance of the S2 layers of the fibers at the melamine-specific wavelength of 240 nm increased distinctively, as expected, with an increasing intensity of NMM treatment (Figure 3). As the monomer of the NMM contains an aromatic ring, its delocalized π electrons contribute to UV absorbance (Jaffé and Orchin 1962). Compared to the spectra of

the native wood (Fergus and Goring 1970a,b; Frankenstein et al. 2006), the spectra of the NMM-treated wood display elevated absorbances between the minimum at 250 nm and the maximum at 278 nm (Figure 3). The cell wall matrix is masked by the NMM, and the voids are filled with the resin. This contributes to the observed spectral behavior.

Deposits of the NMM are visible microscopically (Figure 4). The detected deposits, i.e., the “excess NMM”, were not diffused into the cell wall because of the saturation effects (Lukowsky 1999). Thus, self-condensation and the formation of the deposits occur outside the cell wall. Explicit UV point measurements (resolution of $1 \mu\text{m}^2$) of the NMM deposits (Figure 5) showed a distinct absorbance maximum of the NMM at 240 nm confirming the applicability of this wavelength to characterize NMM modification.

Figure 6 UV microscopic scanning 2D profiles of the NMM-treated koto (left) and limba (right) obtained at a wavelength of 240 nm. A progressively increasing UV absorption is observed from untreated (a, d) to 10% (b, e) and 30% NMM (c, f) treated wood. Size of UV pictures: (a) 194×154 pixels; (b) 184×210 pixels; (c) 199×159 pixels; (d) 169×111 pixels; (e) 185×128 pixels; (f) 209×199 pixels.

The aromatic compounds of the lignified cell walls and constituents of the extractives were detected in the untreated tissue at a wavelength of 240 nm (Figure 6a, d). A progressively increasing UV absorption was seen in the 10% (Figure 6b, e) and 30% NMM-treated material (Figure 6c, f). The UV absorbance reached a maximum of 0.64 in the CML of the fiber tissue, confirming the reported higher concentrations of melamine resin in the middle lamella compared to the S2 layers (Rapp 1999). The higher mean UV absorbance of the cell types with increasing NMM concentration is most distinctive in the ray parenchyma of koto and limba (Table 2). A potential explanation is the easy accessibility of the ray parenchyma, even to liquids distinctively more viscous than the impregnation solution applied in this study (Olsson et al. 2001). Additionally, the permeability in the radial and tangential direction was not influenced by the sealing of the samples prior to impregnation.

Comparing UV measurements from different wavelengths

At both wavelengths (240 nm or 278 nm), the UV absorbance of the fibers was clearly below that of the vessels in the heat-treated and NMM-modified koto and limba (Figure 7). This is because the lignin in the vessel cell walls predominantly contains strongly absorbing guaiacyl type units, whereas the fiber cell wall shows a lower absorbance due to the lignin being dominated by syringyl units (Fergus and Goring 1970a,b; Terashima et al. 1986). A distinct increase in the UV absorbance from the untreated to the heat-treated tissue was observed at 278 nm only, while scanning at 240 nm did not show considerable alterations. As expected, the opposite was observed for the NMM-treated wood. An unchanged absorbance behavior in the NMM-treated wood at the wavelength of 278 nm has been also reported previously (Sint et al. 2012). However, the

Tissue	UV absorbance					
	Untreated		10% NMM		30% NMM	
	Koto	Limba	Koto	Limba	Koto	Limba
Fiber	0.26	0.27	0.32	0.42	0.40	0.34
Vessel	0.32	0.29	0.35	0.33	0.47	0.43
Ray parenchyma	0.26	0.29	0.40	0.35	0.51	0.44
Axial parenchyma	0.25	0.30	0.29	0.38	0.38	0.36

Table 2 Mean UV absorbance of different cell types of NMM-modified koto and limba.

Figure 7 UV absorption of the S2 layers of the fibers (F) and vessels (V) from koto (a) and limba (b). Samples were prepared from the controls (C), heat-treated (H), and 10% and 30% NMM-modified (NMM) materials. Samples were scanned at 240 nm and 278 nm. Each column represents the mean value of five UMSP scans taken from the relevant S2 layers of the tissues at the same wavelength.

progressively increasing UV absorption at 240 nm from the untreated to the 10% and 30% NMM-treated tissue (Figure 6) was not confirmed in the case of the S2 layers of the fibers and vessels (Figure 7). This result could be explained by the general variability of the SU in wood.

Conclusions

Both wood modification approaches affect the UV absorbance of wood cell walls. For heat treatment, the alteration of the described UV absorbance is due to the condensation reactions taking place in the lignin molecules. Because of the highest concentration of lignin in the cell corners, these areas show the strongest increase in UV absorbance. Additionally, the formation of the low molecular

degradation products formed during heat treatment contributes to the increasing overall absorbance. The modification of wood with melamine leads to an increased UV absorbance at the wavelength of 240 nm. With regard to the distribution of the NMM in the cell wall, a specific increase in the UV absorbance of the wood tissue toward the middle lamella was observed. The comparison with other literature did not reveal topochemical differences between modified hardwoods from temperate and tropical origins.

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