UV-microspectrophotometry: A method to prove wood-modification with MMF?

Karl-Christian Mahnert[1,2], Stergios Adamopoulos[3], Gerald Koch[4], Holger Militz[2]

[1]Norwegian Institute of Wood Technology, Forskningsveien 3B, 0373 Oslo, Norway [e-mail: karl.mahnert@treteknisk.no]

[2]Wood Biology and Wood Products, Burckhardt-Institute, Georg August University of Göttingen, Büsgenweg 4, 37077 Göttingen, Germany [email: hmilitz@gwdg.de]

[3]Technological Educational Institute of Thessaly, Department of Wood & Furniture Design and Technology, 431 00 Karditsa, Greece [e-mail: adamopoulos@teilar.gr]

[4]Thünen Institute of Wood Research, Leuschnerstr. 91, 21031 Hamburg, Germany [e-mail: gerald.koch@vti.bund.de]

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ABSTRACT

The modification of wood with methylolated melamine formaldehyde resin (MMF) belongs to the group of impregnation modifications. In the course of this study, Koto sapwood samples were impregnated with MMF-solutions in a full-cell vacuum-pressure process. The samples were cured at a maximum temperature of 120 ºC for 24 hours. To characterize the modification, the solution uptake (SU) and weight percent gain (WPG) of the samples were calculated. The fixation of the melamine as parameter for the degree of curing was examined by C/N analysis. Areal UV-microspectrophotometry (UMSP)-scans of ultra-thin transverse sections of an untreated control and MMF-modified samples at 240 nm were recorded. Additionally, photometric point measurements with a spot size of 1 µm^2 in the range 230 nm and 350 nm were conducted. UMSP was proven as suitable technique for the quantitative analysis of MMF-modified wood.

INTRODUCTION

The impregnation modification of wood with methylolated melamine formaldehyde resin (MMF) has been scientifically investigated by various researchers during the last decades (Stamm 1964, Pittmann *et al.* 1994, Lukowsky 1999). MMF belongs to the group of amino resins and has been commercially used since the 1940s. The MMF is diluted with water to a given concentration, and then the wood is impregnated with the diluted MMF to be subsequently cured at temperatures between 80-120 °C. MMF does not alter the original colour of the wood (Hagstrand 1999). It improves the surface hardness and dimensional stability of wood (Inoue *et al.* 1993, Miroy *et al.* 1995, Rapp 1999, Gindl *et al.* 2003), and from a concentration of about 7.5 % MMF in the impregnation solution also the durability of wood in laboratory (Sailer 2000; Rapp *et al.* 1996; Rapp 1999) and outdoor exposure trials (Rapp 1999). Considerable embrittlement (Rosca *et al.* 2003) and low long-term weathering stability (Rapp *et al.* 1999), however, are disadvantages of this modification approach. In order to quantify the cell wall penetration by amino resins, electron energy loss spectroscopy (Rapp *et al.* 1999) was used to assess MMF. UV-microscopy was employed to determine the

concentration of melamine-urea-formaldehyde resin (MUF) (Gindl *et al.* 2002). The techniques mentioned above allow for spotty analyses of cell wall tissue only, whereas one UV-microspectrophotometry (UMSP) covers the entire cross-section of a cell. If suitable for the detection of MMF-resin in the cell wall, the use of UMSP would allow the investigation of larger sample areas in a shorter period of time.

EXPERIMENTAL

MMF-modification

Koto (*Pterygota macrocarpa*) samples (25 × 50 × 50 mm^3, R × T × L) were conditioned at 20ºC and 65% RH and end-grain-sealed with the commercial coating Pyrotect Schutzlack 2 K (Rütgers Organics GmbH, Germany). Subsequently, the oven-dry density of the samples was determined. The samples were afterwards impregnated with a solution of the MMF Madurit MW840/75WA (Ineos Melamines GmbH, Germany). This resin was supplied as an aqueous stock solution with a solid content of approx. 75%, and diluted with tap water to obtain impregnation solutions with a solid content of 10% and 30%. These solutions were pH-stabilised by adding 1% of triethanolamine before pH 10 was adjusted by addition of NaOH. A full cell impregnation process (vacuum of 600 mbar for 30 min followed by a pressure phase of 120 min at 12 bar) was applied. Curing of the MMF was conducted in a drying oven at 120 °C for 48 h. The oven dry mass of the modified samples was determined after drying at 103 °C for 24 h. Subsequently solution uptake (SU) with M and M_i as mass of sample before and after impregnation (Eqn. 1) and weight percent gain (WPG) with M_1 and M_2 as oven-dry mass of the sample before and after modification (Eqn. 2), were calculated. The calculations were based on 15 replicates per modification intensity.

$$SU\ (\%) = M_i - M\ /\ M \times 100 \quad (1)$$

$$WPG\ (\%) = M_2 - M_1\ /M_1 \times 100 \quad (2)$$

Nitrogen fixation

A melamine molecule contains six nitrogen (N) atoms and the nitrogen content of untreated wood is negligible. Thus, C/N analysis allows the examination of nitrogen fixation (NF) (M_1 and M_2 as nitrogen content of sample before and after extraction) (Eqn. 3) in the wood. To examine NF, MMF-modified wood was ground in a ball mill and one gram was extracted in 60 ml demineralized water at 85 °C for 16 h. Extracted and non-extracted powder was oven-dried and subsequently analysed in a LECO CHN 2000-Analyzer (LECO Instrumente GmbH, Germany).

$$NF\ \% = M_2\ /\ M_1 \times 100 \quad (3)$$

Cellular UV microspectrophotometry

Samples of 1 × 1 × 5 mm^3 (R × T × L) from untreated controls and samples modified with 10% and 30% MMF were cut at and embedded with Spurr's epoxy resin under mild vacuum. During hardening of the resin, several cycles of evacuation and ventilation were applied (Kleist and Schmitt 1999). 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, these sections

were covered with a quartz cover slip. A Zeiss UMSP 80 micro spectrophotometer (Carl Zeiss AG, Germany) set to a wavelength of 240 nm was used for areal scans the samples. The rectangular field of the examined tissue was digitised at a geometrical resolution of 0.25 µm² with the help of the software APAMOS® (Carl Zeiss AG, Germany). The photometrical resolution amounted to 4096 grey scale levels which were converted to 14 colours for visualisation of 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 with a spot size of 1 μm^2 in the range 230 nm and 350 nm were conducted using an MSP800 micro-spectrometer (J&M Spectralytics GmbH, Germany). Spectra were taken from the individual cell wall layers and were evaluated statistically. The data was evaluated with the software TIDAS-DAQ (J&M Spectralytics GmbH, Germany) and PANORAMA ProColorSearch (Analytical Software GmbH & Co KG).

RESULTS AND DISCUSSION

MMF-modification and nitrogen fixation

With increasing MMF-concentration in the impregnation solution, WPG and nitrogen content increased as expected (Table 1). Since fixation is positively correlated with the thoroughness of curing (Wepner 2006), curing of the samples in the course of this study is considered sufficient. The fixation of MMF increased by about 12% at 30% MMF concentration compared to modification with 10% MMF-content. It is assumed that a higher extent of crystallisation of MMF occurs in case of its application in the 30% solution (Markov 2006).

Table 1: Information on the MMF-modified Koto.

MMF concentration	Oven-dry density (g/cm^3)	SU (%)	WPG (%)	Nitrogen content		
				ne (mg/g)	e (mg/g)	NF (%)
10%	0.60	108	8	27.9	22.9	82.3
30%		90	20	70.6	66.7	94.6

ne: non extracted, e: extracted

Cellular UV microspectrophotometry

The areal scans of fibre tissue of Koto are depicted in Figure 1. Aromatic compounds of the lignified cell walls and constituents of extractives were detected in the untreated fibre tissue at a wavelength of 240 nm (Figure 1 a). A progressively increasing UV absorption was seen in the 10% (Figure 1 b) and 30% MMF treated tissue (Figure 1 c). UV absorbance reached a maximum of 0.64 in the CML of the fibre tissue, confirming the reported higher concentrations of melamine resin in the middle lamella compared to the S2-layers (Rapp 1999). This is due to the fact that the fastest diffusion path into the cell wall is through the compound middle lamella (Wallström and Lindberg 2000). The increase of absorption of the cell walls with increasing intensity of the MMF-modification is caused by the increasing number of MMF-monomers. Each monomer contains an aromatic ring, and its delocalized π-electron contributes to the UV absorbance (Jaffé and Orchin 1962).

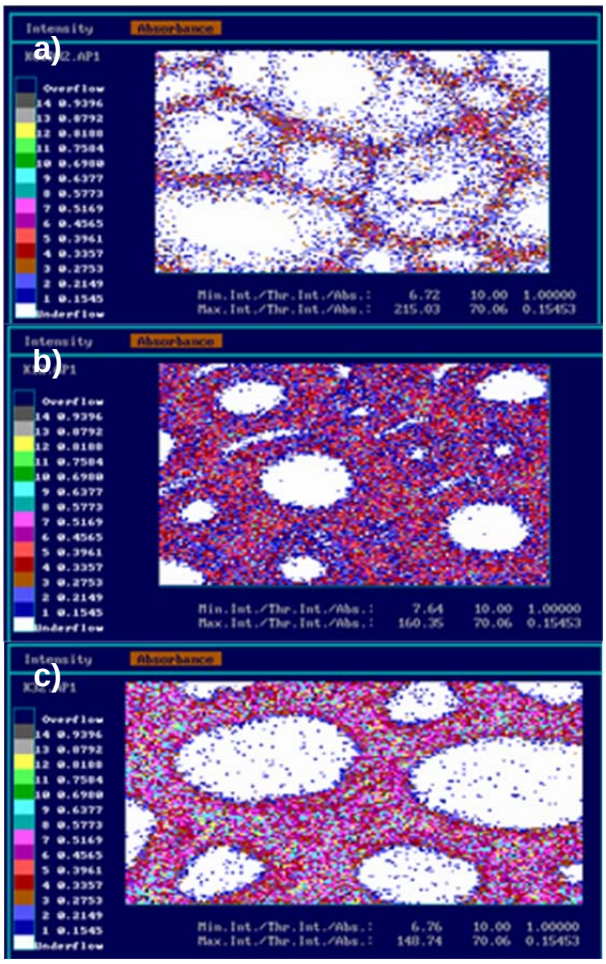

Figure 1: UV microspectrophotometric scanning profiles of the untreated control (a), koto treated with 10% (b) and 30% MMF resin (c).

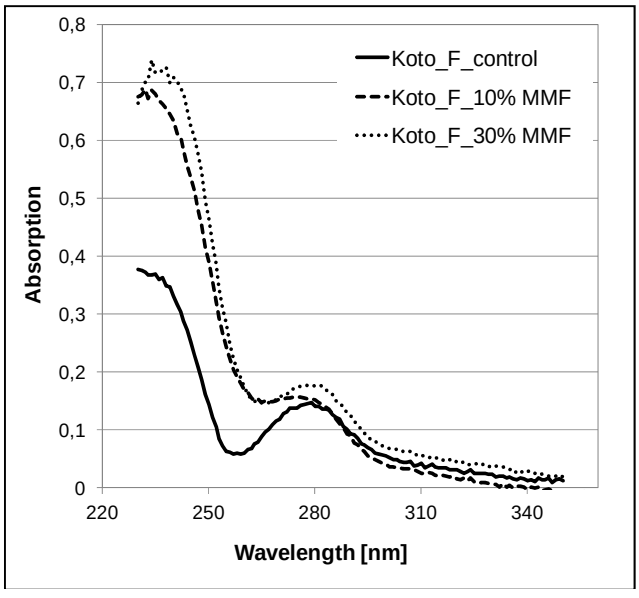

Figure 2: UV absorption from UMSP point measurements.

The photometric point measurements also show a tendency of increased absorption with increasing intensity of the MMF-modification (Figure 2). The spectra of the control corresponds to the spectra of native wood as reported by Fergus and Goring 1970a, b;

and Frankenstein *et al*. 2006), whereas the spectra of MMF-treated wood display elevated absorbances between the absorbance minimum at 250 nm and the maximum at 278 nm. The cell wall matrix is masked by the MMF and the voids are filled with the resin (Devallencourt *et al*. 2000). This contributes to the observed spectral behaviour. The wavelength of 240 nm had been used for the detection of undisclosed MMF by UV-microspectroscopy by Gindl *et al.* (2003). Photometric point measurements of a MMF deposit conducted in the course of this actual study (results not reported in this paper) showed the maximum absorption of the actual MMF to be at 240 nm, too. Sint *et al.* (2013) applied UMSP to examine MMF-modified *Bombax ceiba* and *Bombax insigne* wood at a wavelength of 278 nm. Thus, they could only detect areas of the cell wall which were chemically similar to lignin, since lignin of hardwoods has a maximum absorption at this wavelength (Fergus *et al.* 1970a).

CONCLUSIONS

In this study, the suitability of UMSP for the examination of MMF-modified wood was examined. Therefore, samples of Koto were modified with impregnation solutions of 10% and 30% MMF-concentration. The different modification intensities were characterized by calculation of WPG and determination of the nitrogen-fixation. Subsequently, areal and point-photometric UMSP-scans of ultra-thin sections of the samples were recorded. The results derived from the UMSP-scans coincide with the results obtained from the supplementing investigations. Thus, the authors consider UMSP suitable for the detection of MMF in the cell walls of modified wood. Additionally, a tendency of increasing absorption with increasing modification intensity was observed.

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