VARIOUS INSTRUMENTAL METHODS FOR QUANTIFYING PHENOL-FORMALDEHYDE RESIN INTO BEECH WOOD

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ABSTRACT

In this paper, phenol-formaldehyde (PF) resins with different average molecular weight (M_w) oligomers were used, to evaluate the effect of molecular size on the allocation of impregnated chemicals in wood microstructure at different hierarchical levels (from wood tissue to single cell wall layers). Light microscopy (LM) and various other alternative instrumental methods, as UV microspectrophotometry (UMSP) and micro X-ray computed tomography (µXCT), have been used and to determine, as well visualize, the micro-distribution and penetration depth of resin into wood matter. Therefore, European beech wood (*Fagus Sylvatica* L.) blocks of 25x25x10 mm³ were vacuum impregnated with different molecular sizes at three aqueous solutions concentration of 9, 18 and 27%. Due to different procedure and physical back ground of methods, obtained micro-images passed certain level of image processing and comparison between methods were performed (Fig 1).
The presence of chemical agent in the wood, in terms of LM, was detected by way of their identification on the specimen cross-section as result of different intensity of safranin staining, but in UMSP, based on UV light absorbance at 278 nm by phenolic-based compounds. While, the incorporation of resin into wood can be measured and visualized by using µXCT, only based on porosity changes between one and the same volumes of interest (VOI) selected from one and the same sample before and after the treatment. Despite of so such distinctness between techniques, our results appears stronger or weaker positive correlation between the methods. Based on roughly estimation of obtained results, might be that LM could be useful to give first expression (quantitative) on resin distribution into wood tissue and in some cases could substitute more complicated method as UMSP. Concerning to X-ray CT, our preliminary results shows, that it might be the promising technique to evaluate and visualize resin distribution into wood at different hierarchical levels and 3D.

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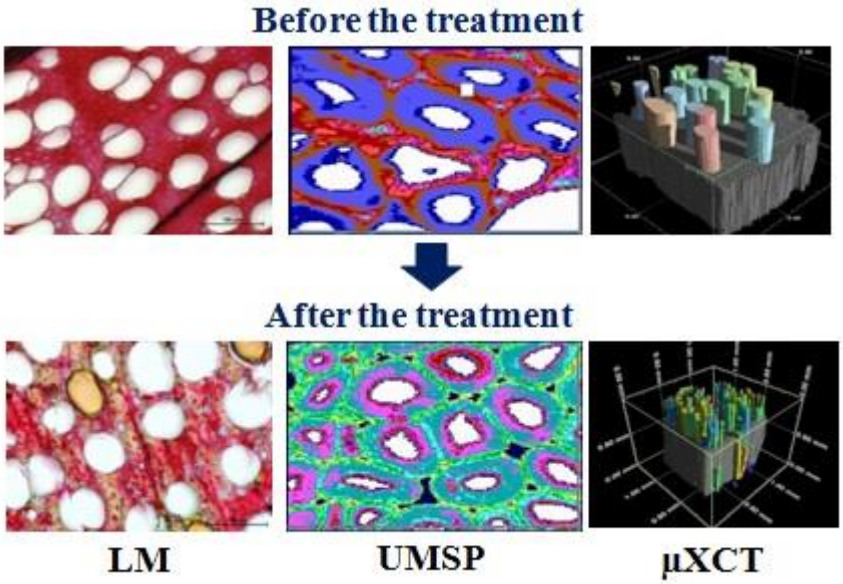

Figure 1. Obtained Micro-images using different methods corresponding the presence of resin into wood after the treatment due to color changes

Key words: Phenol-formaldehyde resin, light microscopy, micro X-Ray CT, UMSP

INTRODUCTION

Within the next 20-30 years, large amounts of beech wood will be available on the market. Therefore, some of the wood processing enterprises in Germany, as Pollmeier Massivholz gmbd & co, are already looking forward to broaden the application area for beech wood via new, innovative products. A promising use of beech wood would be the production of laminated veneer lumber (LVL) from modified veneers (Bicke and Militz 2014) and medium density fibre boards (MDF) with modified fibres, where the modification agents could be aromatic compounds from synthetic oil refinery or bio-based aromatic compounds from pulp and paper industry (different types of lignin). Detailed study of the impact of the treatment of beech is, therefore, a prerequisite for product optimization.

The most commonly applied methods to study the microstructure of untreated wood as well as wood treated with PF resin oligomers of different molecular sizes, are light microscopy (LM) and scanning electron microscopy (SEM). Furuno et al. (2004) and Biziks et al. (2015) observed that PF resin in wood tissue is mainly localized in the vessel and fibre lumen, when wood is treated with large molecules of PF resin oligomers. However, it should be noted that with LM and SEM, there is a risk of inducing artefacts during sample preparation, such as artificially damaging the resin film in vessel or fibre lumen, during sectioning, surface preparation and micro slide preparation. This is especially valid for resin treated wood, which breaks more easily due to its increased brittleness. To minimize the breaking of cell walls during slicing of 1 µm thick slices, emending of sample in Spurr´s epoxy resin is applied by UV-micro-spectrophotometry (UMSP). Aforementioned methods are also limited in obtaining data on the internal volume of samples (latent porous structure).

Micro-X-ray Computed Tomography (µ-XCT), however, offers the opportunity to investigate wood microstructure without generating artificial defects during sample preparation. The last

decade, high resolution X-ray computed tomography (XCT) has matured as a modality for three dimensional (3D) characterization of many materials, including wood; wood based products and modified wood.
The aim of this work was to compare the information obtained between different methods about changes in anatomical structure at different hierarchical levels: macro-level (macro porosity); at micro level – changes in cell wall thickness, distribution of resin into wood cell wall at different cell wall layers; as well distribution of treatment agent at 3D - after treatment, with different molecular sizes of PF resin oligomers.

MATERIAL AND METHODS

Wood

Two types of specimens were cut from European beech (*Fagus sylvatica*) wood. Prior to the evaluation of biological durability of PF resin treated wood, specimens measuring 25x15x50 mm^3 were cut to investigate the distribution of the resin in the block. To assess the resin penetration in the cell wall (bulking coefficient) second type of specimens with dimensions of 25x25x10 mm^3 (*r x t x l*) were prepared. After the drying at 103±2°C for 24 hours the specimens were impregnated using vacuum at the same day. Ten blocks per treatment were used.

Phenol-formaldehyde resins

Before being used for impregnation, the stock solutions of different types of PF resin were diluted to 9%, 18% and 27% (w/w). As listed in table 1 four types of resin with different characteristic parameters were used to prepare the aqueous solutions.

Table 1: Characteristic parameters of PF resin compositions used in the study

Resin composition	Solid content [%]	Catalyst	Amount of Catalyst [%]	Amount of formaldehyde [%]	Free phenol [%]
A	49.5	NaOH	1.6	<1	<4
B	49.0	NaOH	1.6	<1	<4
C	58.4	NaOH	1.6	<1	<4
D	47.8	NaOH	1.6	1.88	0.24

Treatment of wood

Oven-dried specimens were impregnated with solutions of PF resin in an autoclave by using a two-step vacuum impregnation method. After the impregnation, to assess the amount of PF resin in the wood, specimens were oven dried and the weight percent gain (WPG) was calculated.

Light microscopy

To achieve high quality transversal cuts of PF treated wood, with thickness of 25-30µm, Leica microtome blades (Leica DB80 HS) were used and adapted to the microtome (Sartorius Werke, Göttingen, Germany). The slices were stained with 0.09 % safranin solution for 5-7 minutes and then the cuts were dehydrated with two ethanol solutions (50% and 99%). Prior the embedding the slices on glass with Euparal 3C-239 (Waldeck GmbH & Co KG), they were additionally dried at 42°C for 15-20 min. An Elipse E600 microscope (Nikon, Japan)

equipped with the digital camera Nicon DS-Fi1c linked to a computer was used. Image processing was done using the software of NIS-elements (version 4.10). The measurement of the penetration depth of PF resin into wood was carried out by way of their identification on the specimen cross-section as result of different intensity of safranin. The assumption was, that, the higher the intensity of safranin is, and the less resin is in the specimen cell walls and vice versa.

RESULTS AND DISCUSSION

Light microscopy (LM)

To get deeper insight in how molecular sizes of PF influence the resin penetration and distribution in beech wood due to oligomers, investigations by light microscopy were done. The existence and distribution of PF resin in wood tissue and different cell walls was observed by LM. Our experimental set up and microphoto-images clearly show that we were able to observe the retained resin in wood tissue, the quantification of resin was done based on different availability of cationic dye as safranin to bonding on the surface of wood tissue. Transversal sections of the untreated and treated European beech wood with PF resin stained by safranin are shown in (Figs. 3a and 3b). 27% and 3% weight increase in untreated and PF resin treated slices after staining was observed, respectively. It appears that more safranin was adsorbed between the cell wall constituents of untreated wood compared to the treated one, evidently, it might be related to gradual occupancy of wood tissue by the resin, which resulted in less accessible area available for molecules of dye. As well it might be due to changes on surface energy (polarity) of treated wood, where the availability to develop enough strong and number of bonds between dye and wood cell wall polymers are diminished.

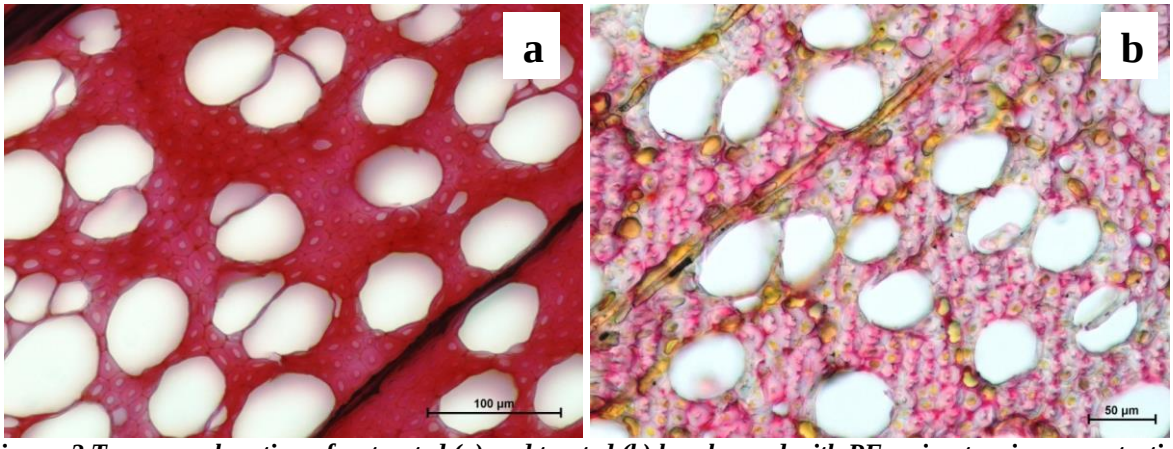

Figure. 3 Transversal section of untreated (a) and treated (b) beech wood with PF resin at resin concentration of 27%. Scale bar = 100µm

In the case of specimens treated with a different concentration of resin, LM observations showed that the amount of adsorbed safranin into the wood slightly decreases with raising the solution concentration. The purple color of untreated section (Fig. 3a) slightly changed to light violet/light yellow (Fig. 3b) by treatment with a higher concentration. Those color changes can be explained by increased quantity of resin penetrated into the wood. The same tendency was observed between wood specimens treated with different M_w of resin oligomers. Remarkable difference in WPG was not observed between transversal sections of wood blocks treated with LMW and HMW resins. However, the extent of color changes between PF resin treated specimens was obvious. The more violet-white/yellow light color increased proportionally in wood blocks treated with LMW than those of HMW oligomers.

We can confirm that those dissimilarities also might be explained by different dislocation (retention) of resin across the specimen, which mainly belongs to the color changes of wood cell walls, hence related to quantity of resin incorporated in the cell walls.

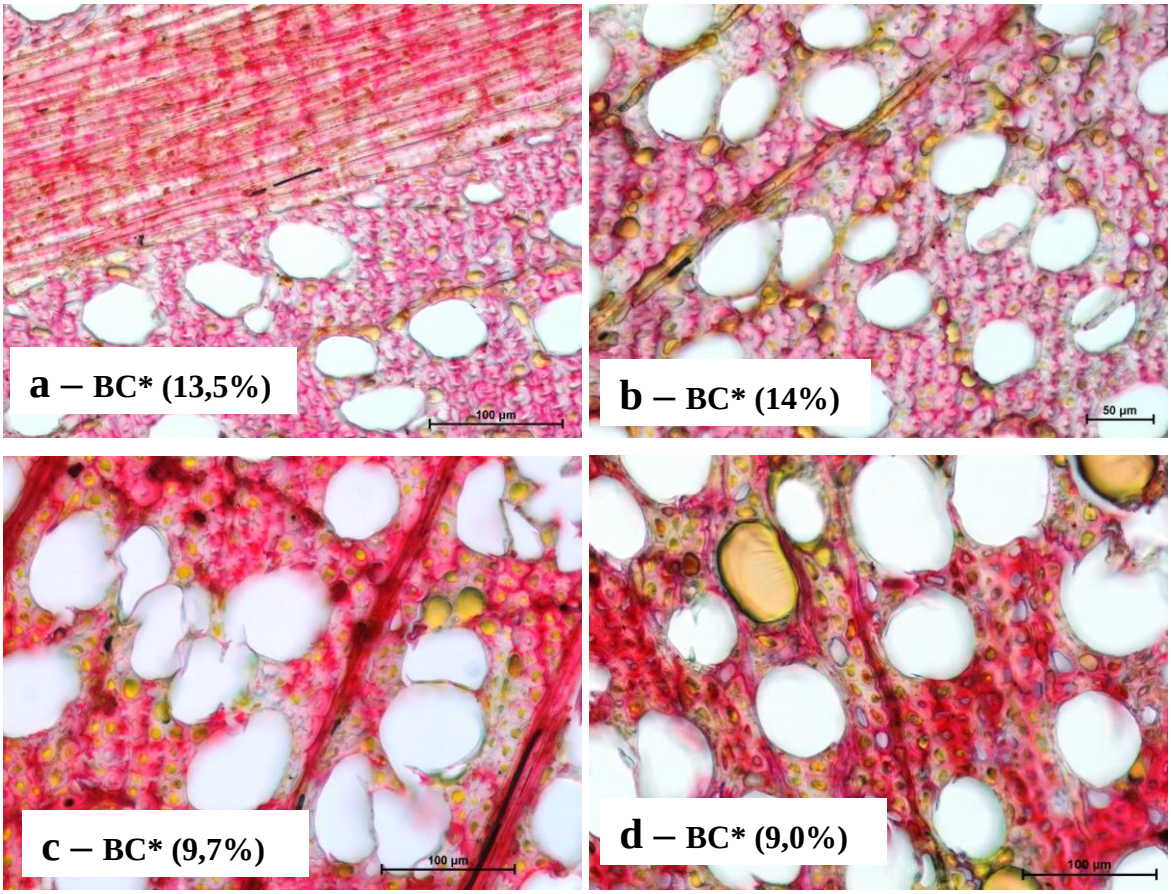

Figure. 4 The relationship between bulking and amount of safranin color on the transversal sections of wood blocks treated with different molecular weight and polydispersity of PF resin: a) A; b) B; c) C and d) D g/mol. Scale bar 100 µm. BC* - bulking coefficient of beech wood impregnated with 27% solution.

(Fig. 4) shows good correlation between bulking of cell walls and amount of safranin on the transverse section of beech wood caused by treated with different molecular weight of resins.

All results related to resin distribution into beech wood evaluated by UMSP and X-ray micro-computed tomography X-ray µCT will be presented during the conference.

CONCLUSIONS

Herein, the influence of M_w of PF resin oligomers on the penetration depth of resin into beech wood cell walls was studied. Beech wood treated with highest concentration of PF resin with different molecular sizes of PF resin oligomer solutions exhibited highest weight percent gain (WPG) about 21-24%, while bulking coefficient (BC) was between 9 till 15%. Hence, there was no any impact of oligomer sizes to WPG (penetration into woody tissue) observed, whereas penetration depth into cell walls significantly depends from molecular size of oligomers. Both PF-A and PF-B resins showed about 30 till 40% better penetration ability into cell walls compared to resins PF-C and PF-D. In comparison with previous researches, we have developed of LM method which is suitable for the determination of PF resin at micro-scale level. This study demonstrated that safranin is useful indicator to visualize and quantify the cell walls penetrated with resin from non-penetrated ones. Good correlation

between reduced amount of safranin colour and presence of resin into the cell walls was found. The cell walls were in higher extend penetrated by resin with low average molecular weight oligomer compare to HMW resins.

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