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IMPORTANCE OF BEECH WOOD PRE-TREATMENT FOR IMPREGNATION WITH MIMOSA TANNIN EXTRACT

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Abstract:

In this paper, the effect of beech wood pre-treatment on the industrial tannin extract fixation efficiency after vacuum impregnation, was investigated. The temperature of wood drying was set at 60°C for 24hours till reaching the moisture equilibrium (i.e. for those conditions) in order to eliminate thermal degradation of wood and of implemented tannin; and moreover to keep bridges via water molecules present deeply in wooden matrix for connection with newly created bonding sites. Samples were immersed under water for 12hours. Water, as a polar solvent, decreased the content of in wood present small molecules, e.g. broken-down parts of hemicelluloses, non-bonded water-soluble extractives at 60°C to even higher extend than at ambient temperature (0.49mg vs. 0.23mg glucose equivalent per 1g of dried wood). This free space was shown to be advantageous for direct reaction of tannin with wooden polymers, since tannins can bond with carbohydrates; and slightly improved leaching resistance was also observed. However, in case of waterborne protection development without hardeners addition, better fixation conditions have to be established.

Key words: *condensed tannins; beech wood; total saccharide content; leaching; impregnation.*

INTRODUCTION

Wood goes along with human existence for thousands of years. As a natural material, its major drawback is that is easily attackable by various decay organisms when exposed to high humidity. Tannins, polyphenolic high-molecular weight compounds (Hagerman et al. 1998), that significantly contribute to natural resistance through their microbial toxicity (Scalbert 1991), occur rather in smaller amounts in wood. Therefore, some species having lower tannin content, such as European beech *(Fagus sylvatica* L.*),* belong to those deciduous trees with lower durability.

The utilization of available material delivered from bark was a hot topic even in the ˈ80s (Laks et al. 1988) and continuously maintains the role of promising for usage in several fields (Pizzi 2019). When considering the development of fully bio-based natural wood protection with low VOCs emission, commercially available tannin extract offers a suitable tool. On one hand, several research groups confirm the positive influence of tannins on wood protection (Anttila et al. 2013; Da Silveira et al. 2017), however they are issues with proper fixation within wood (Sablík et al. 2016). On the other hand, Sommerauer et al. (2019) found that addition of specific eco-friendly hardeners contributes to even lower leaching rates.

As tannins easily bond with proteins and saccharides (Jakobek 2015), released space in wood cell previously taken by weakly bonded saccharide moieties might improve the reaction kinetics of wood modification, so that, ideally, no synthetic biocides will be needed in future.

OBJECTIVE

The main objective of the present research was to evaluate the effect of beech wood pre-treatment on the final impregnation efficiency and leaching resistance of tannin extract being implemented into wooden structure via its aqueous solution through vacuum impregnation. Two temperatures of samples leaching were selected: ambient and 60°C, respectively. In order to verify the gained bonding capacity of tannin, total saccharide content of leachate was also investigated.

MATERIAL, METHOD, EQUIPMENT

Beech wood pre-treatment, drying and hardening temperature selection & Tannin extract

European beech *(Fagus sylvatica* L.*)* obtained from Training Forest Enterprise (Olomoučany, Czech Republic) was cut into 1x1x1cm cubes and dried at 60°C for 24hours to obtain moisture equilibrium. The drying temperature 103°C is mostly used to obtain zero moisture content for the comparison of weight percent gain. However, these conditions lead to permanent degradation of chemical components as well as surface cracks. Therefore, in this study the temperature was adjusted to 60°C on purpose. This was done in order to reduce those structural changes due to strong drying conditions and to allow water molecules present in wooden structure to connect with the implemented polyphenols via H-bonds that might be beneficiary for further fixation mechanism.

These specimens were then either i) non-leached and used directly for the impregnation (N); or ii) leached at ambient temperature for 12hours (AL), or iii) leached at 60°C for 12hours (L), and then subsequently dried at 60°C for one day prior to impregnation. The specimens were weighted before (N, AL, L) and after the leaching procedure (AL, L).

Weibull AQ industrial wattle tannin extract from *Acacia mearnsii* was kindly supplied by TANAC S.A. (Brazil).

Total Saccharide Content

Ten beech samples of dimensions 1x1x1cm were put into a sealable flask with 80mL of water for each group (i.e. AL and L, which were later used for the tannin treatment) and kept in demineralised water for 12hours. After each hour aliquot of 1mL was taken out and immediately freezed until the analysis.

The quantification of total saccharides present in wood samples being leached into water was accomplished according to slightly adjusted colorimetric assay described by Albalasmeh *et al.* (2013), later adapted also for thermally modified wood by Čermák *et al.* (2019).

To the mentioned aliquot of leachate filled up with demineralised water to the final volume of 2mL, 1mL of fresh 5% w/w phenol solution (PENTA, Czech Republic) was added and stirred on vortex. Just after the short stirring, 5mL of concentrated sulphuric acid (PENTA, Czech Republic) was poured into the mixture, moderately stirred and kept reacting for 10minutes. The mixture was then vortexed and kept in water bath at 30°C for further 20minutes. Then followed colour stabilisation at ambient temperature for another 30minutes. Prior to analysis, the mixture was thoroughly stirred on vortex again and the absorbance of the solution in visible light at 490nm was measured spectrophotometrically (Metash, China).

The determination of the total amount of leached saccharides was based on calibration curve of glucose (Sigma-Aldrich, Czech Republic) as a standard solution in the concentration range of 20 – 400 µg/mL (R^2=0.9952). Demineralised water served as a reference and one blank measurement in each set ensured output reliability. The final saccharide concentration was expressed in mg glucose equivalent (GluE) on 1g dried wood.

Wood impregnation

For each group (TN, TAL, TL), ten beech samples were put into glass beaker filled with 5% w/w aqueous tannin solution and kept under vacuum (conventional laboratory vacuum pump connected to desiccator) for 30minutes and then under atmospheric pressure for additional 15minutes to allow deeper penetration of impregnating agent via water molecules of the solvent. During the whole procedure samples were underwater, ensured through the application of second beaker with loadings. Samples were afterwards oven-dried at 60°C for 24hours until the related moisture equilibrium. The same procedure without tannin (i.e. demineralised water) was performed with control samples (WN, WAL, WL) while monitoring the weight.

Leaching test and statistical evaluation

Fast leaching test after impregnation and drying was performed in two cycles, i.e. 12hours of immersion in water followed by drying at 60°C for 24hours with monitoring weight changes at the end of each cycle. The mass loss was calculated based on differences from that at dried state derived from impregnation process. The statistical significance was evaluated with ANOVA and Tukey's post hoc test at a 95% confidence level using SPSS Statistics 19 software (IBM).

RESULTS AND DISCUSSION

Total Saccharide Content

The following diagram (Fig. 1) represents the sum of carbohydrates derived from untreated beech wood in hourly intervals of solubilisation in water and subsequent reaction with Phenol and Sulphuric acid.

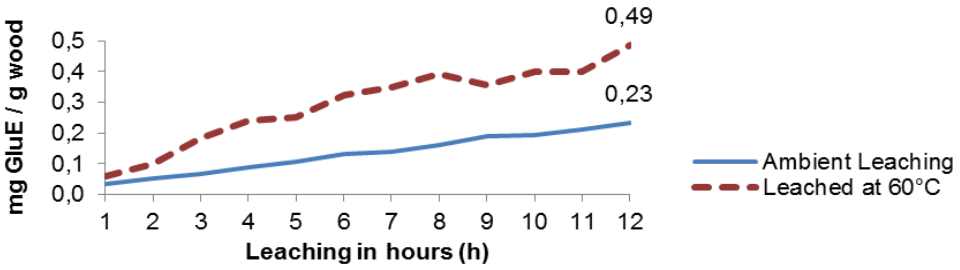

Fig. 1.

Total amount of carbohydrates leached out from beech wood samples after up to 12hours of exposure in demineralised water at ambient temperature (blue, solid line) vs. at 60°C (red, dashed line).

The increasing tendency with the exposure time of wood in water is evident from both curves. After 12hours at ambient temperature, the amount of glucose equivalent reached 0.23mg per 1g dried wood, in case of contact with 60°C water even 0.49mg. However, it has to be taken into consideration that the assay does provide the information about saccharides (expressed in glucose units as the most typical carbohydrates moiety found in extractives and as basement of the polymeric wood components), but does not count the other present parts of water soluble extractives, so the space being accessible for impregnating solution is even bigger and not neglectable.

Impregnation efficiency and leachability

Fig. 2 shows resulting uptake and mass loss after impregnation with tannin solution and subsequently two leaching steps (Fig. 2.a) in comparison to mass loss of control samples (Fig. 2.b).

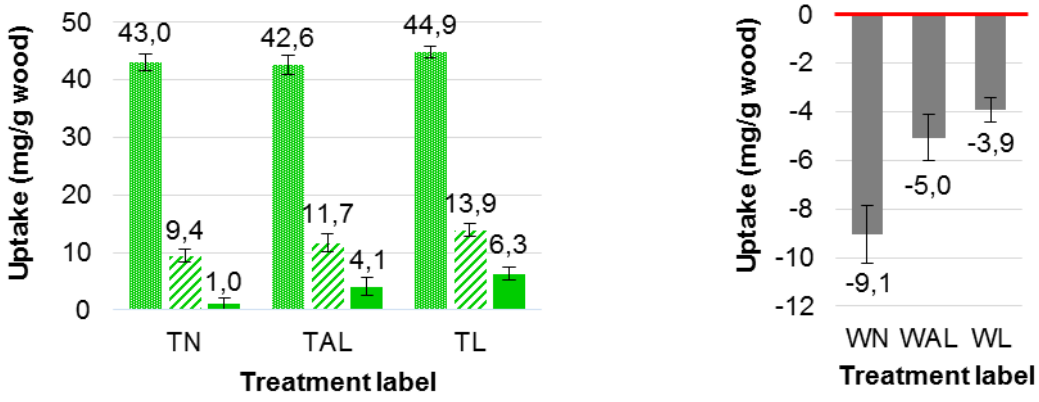

Fig. 2.

Solid uptake after impregnation and remaining amount of impregnation agent after following leaching cycles: a – samples impregnated with tannin solution (from left: first column – uptake after impregnation, second column – remaining after the first leaching cycle, third column – remaining after the second leaching cycle); b – reference samples after second leaching cycle.

While the solid uptake does not differ so much between the groups (Fig. 2.a), the improvement in terms of better leaching resistance in wooden matrix is visible, i.e. remaining in TN 1.0±1,0; TAL 4.1±1.6; TL 6.3±1.1mg on 1g of dried wood after two leaching cycles. The same observations were carried out with control samples, which confirmed the decreasing tendency of mass loss after pre-treatment in the following order WN > WAL > WL (Fig. 2.b). Thus, the lowest mass loss of control samples (Fig. 2.b, WL) is in accordance with the highest leaching resistance of tannin samples (Fig. 2.a, TL – third column). The dependence of those procedures, i.e. non-leaching (N) and leaching at 60°C (L) as a result of beech samples exposure to water at higher temperature prior to impregnation on remaining impregnant was confirmed as statistically significant (p-value <0.001; α=0.05).

CONCLUSIONS

The elimination of “free” accessible carbohydrates and easily soluble extractives from wood has an essential impact on leaching behaviour of solid tannin and possibly leads to different fixation and/or distribution options within wood cell.

However, considerable part having oligomeric structure still hinders tannins from their proper penetration into wood cell walls and therefore this extract needs to be firstly fractionalised and at the same time functionalised to allow *in-situ* fixation with wooden polymers. Moreover, results from this study will be implemented into the currently running tannin extract modification (on laboratory scale) and further directions will be supported with additional analytical and screening techniques.

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