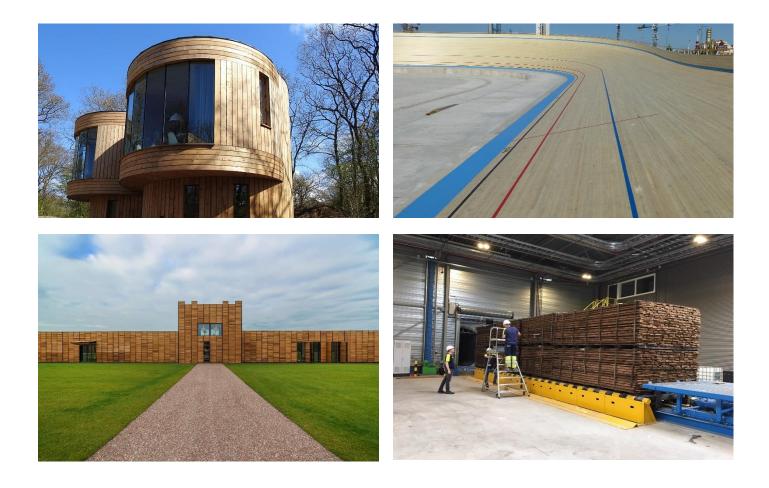
# 9<sup>th</sup> European Conference on Wood Modification ECWM9

September 17 and 18, 2018, Arnhem, The Netherlands

# PROCEEDINGS







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# 9th European Conference on Wood Modification

Burgers' Zoo Arnhem, The Netherlands 17-18 September 2018

In association with: COST FP1407 ModWoodLife

Edited by:

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#### Preface

SHR was one of the first research institutes in Europe, who already in the 1990's did substantial research work to develop wood modification processes. It appeared, that this research area was very complex, and that for a successful application of potential processes different expertise's was needed. A good network between research partners and industry was needed and the "European Network on Wood Modification" was created. 15 years ago, in 2003, the first European Conference on Wood Modification "ECWM" was held to present the outcomes of this EU financed network. Since than, ECWM's were held each 2-3 years at different places around Europe, and now we can celebrate the 9<sup>th</sup> ECWM in the Netherlands, organized by SHR where it all began.

As already before, ECWM 9 is linked up to the European COST organisation. Thanks to the COST Action FP 1407 ModWoodLife to join and strengthen our network!

The participation of researchers of all around the world make it obvious that the name "European conference" is much too small...so: a warm welcome to researchers from industry and academia from Europe and abroad! This success has led, once again, to a large number of abstracts submitted to the organizers. In general, these abstracts were of a high quality and the members of the Scientific Committee had a hard time to select 44 full presentations and 50 poster presentations out of the many applications. We hope we have found the right balance between scientific and applied presentations to reach the key goal of ECWM: to attract researchers from academia and industry to join their expertises in this very exciting research area "wood modification".

The local conference organizers from SHR have done a great job this past year to make us feel welcome in The Netherlands and to let the conference be a success. Thank you very much to Bôke and team!

Holge filth

Prof. Dr. Holger Militz Chairman of Scientific Committee Georg-August-University Göttingen, Germany

#### Scientific Committee

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Mrs. Jos Gootjes, SHR	SHR; The Netherlands

### Wood modification in practice

The European Conference on Wood Modification takes place on the 17<sup>th</sup> and 18<sup>th</sup> of September 2018 in Arnhem, The Netherlands and is organised by SHR. At this conference researchers and people from industry from all over the world will come together to share their knowledge and experiences with the latest developments on wood modification methods, applications and products. The conference was given the subtitle "Wood modification comes home", which refers to the role The Netherlands and SHR have played – and still play – in the development and industrial application of modified wood.

Techniques and methods designed for improving wood properties are almost as old as mankind itself. However the scientific and industrial rise of wood modification became significant under the influence of a number of social and economic developments in the eighties and nineties of the previous century. A strong need was felt to find alternatives for the use of tropical hardwoods and preservative treated wood, which were both under pressure for a variety of reasons. The discussions regarding a clean environment, sustainable forest management, wood use and the increasing wood demands from emerging markets in Asia also had a big impact. Wood modification was recognized to have the ability to offer a more, better and sustainable way of making use of wood as a durable material in a broad range of applications. Besides that, it was found to be a supreme method for upgrading the properties of lesser used timber species and to provide technical solutions to overcome some of the natural deficiencies of wood as water uptake, decay and dimensional changes.

Over the last decades an enormous amount of scientific work has been performed and published. We have seen many innovative modification ideas, methods and techniques passing by during the previous eight ECWM's. To make a real impact, ideas need to be developed further and put into practice. We are proud that in The Netherlands we have created a setting with a high level of knowledge, innovative thinking combined with entrepreneurship, which lead to a variety of flourishing companies involved in industrial production of modified wood. Not only producing companies, but also the wood processing industry has adopted modified wood as a highly appreciated durable material. We can declare that modified wood has become a lasting factor in the wood processing industry.

For these reasons SHR and we as the organising team, are excited to welcome you all here in The Netherlands for the 9<sup>th</sup> European Conference on Wood Modification. We hope you will enjoy your stay here in Arnhem and become inspired by all attendees, presenters and new insights this conference has to offer.

Welcome!

The organising team

## COST 1407 - Foreword

It is our pleasure that COST Action FP1407 "Understanding wood modification through an integrated scientific and environmental impact approach" (ModWoodLife) in part of 9th European Conference of Wood Modification. The conference brings together researchers from across Europe and beyond that jointly are addressing the mounting pressure on renewable resources (as a material source, for recreational, ecological, and other uses). By maximising the efficiency of materials derived from them, the wood modification community plays an important role. The efficiency can only be achieved if new methods to improve the functionality, durability, properties, and environmental impacts will be developed. Wood modification addresses these requirements directly, allowing wood to be used in more applications, including increased use of under-utilised species. Wood modification also addresses undesirable characteristics of wood such as fungal resistance, UV-stability, and moisture sensitivity. The COST Action FP1407 has been successful in addressing these needs in the past 3 years. We are in the last year of the Action and therefore it is even more important for us to be at ECWM9. Only sustainable collaboration and joint efforts will deliver the impacts. That objective of the Action FP1407, to characterise the relationship between wood modification processing, product properties, and the associated environmental impacts in order to maximise sustainability and minimize environmental impacts, has great value for the forest sector, for researchers, and society at large.

Wishing you a successful and memorable conference full of fruitful discussions.

Andreja Kutnar Chair, COST FP1407

Denis Jones Vice-Chair, COST FP1407

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### The Maillard reaction for wood modification: The influence of reagent concentrations, reaction temperature and soaking time on the leachability and cell wall penetration of reagents

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Keywords: beech, pine, leachability, Maillard reaction, wood modification

#### ABSTRACT

Finding efficient ways to decrease wood decay caused by fungi and increasing its dimensional stability is an important issue in timber construction and other applications. A possible way to avoid wood decay by fungi and increase its dimensional stability, is by reducing the water content of wood. Water is a primary condition for fungal growth and induces shrinking or swelling in wood. By bulking the wood cell walls with chemical reagents, the space where water normally occurs gets occupied. For effective protection using impregnation modification, it is a requirement that the bulking agent is located mainly in the cell wall of the wood and is non-leachable in service. To create a commercially-viable process, the modification requires a water-based delivery system, the use of low-toxicity impregnation agents, thermal-curing and no concerns regarding toxicity at end of life of the modified wood product. In previous work it was found that the use of the Maillard reaction appeared to be a promising way of bulking the cell wall (i.e., when reacting lysine, glucose, and citric acid), but with varying success and a high degree of leaching. To reduce leaching and increase of wood bulking, reaction conditions like soaking time, reagent concentrations and reaction temperature were investigated in this work to determine their effect on wood treated with lysine, glucose and citric acid. In general, it was observed that lower soaking times, higher reaction temperatures, and higher reagent concentrations were favourable for the Maillard reaction to proceed.

#### **INTRODUCTION**

When exposed to changing atmospheric conditions, wood is susceptible to degradation by fungi and shows dimensional instability. This restricts its use in some situations like outdoor exposure, its use in bathrooms or basements, etc. To prevent degradation, non-durable wood products need to be treated when used in applications where they are susceptible to deterioration.

A possible way to increase the resistance to decay while increasing its dimensional stability, is by controlling the cell wall moisture content of the wood. In order to control the cell wall moisture content, it is necessary that the wood is treated with chemical solutions which diffuse into the wood cell wall and can be fixed in place. The presence of these chemicals will cause bulking of the cell wall, decreasing the cell wall volume accessible to water (Rowell and Banks 1985). The reduction of cell wall moisture content limits the ability of fungal degradative agents

to penetrate the cell wall and ensures that most fungal species cannot degrade the wood (Papadopoulos and Hill 2002, Rowell 2006). A requirement of any such wood modification system is that it should be nontoxic under service conditions and, furthermore, there should be no release of any toxic substances during its service life, or after disposal or recycling of the modified wood (Hill 2006). This requires that the polymeric network formed in the cell wall should react with the wood polymers or become entangled with them. Furthermore, the modification polymer should not display hygroscopic behaviour.

A method of impregnation modification that could meet all above mentioned requirements is based on the Maillard reaction. This type of reaction is well-known in food chemistry, where it is responsible for the browning in many foods during baking (Ames 1998; Manzocco et al. 2001). The essence of the reaction is that a reducing sugar, condenses with a compound possessing a free amino group, to give a condensation product (Echavarría et al. 2012). Subsequently, a range of reactions takes place, including cyclizations, dehydrations, retroaldolizations, rearrangements, isomerizations and further condensations, which ultimately lead to the formation of polymers and co-polymers, known as melanoidins (Echavarría et al. 2012). The composition of its chemical structure is relatively unknown due to the complexity of the products that are generated in the reaction (Kim and Lee 2009). The advantage of this reaction is that it is an aqueous process and initiated by heat only, making it relatively straightforward to apply to wood in a commercial process. In addition, the reaction does not require the use of strong acids or bases, which could degrade the wood structure.

In earlier experiments (Peeters et al. 2018), the influence of the Maillard reaction on beech and pine wood was investigated. The wood samples were impregnated with one amine (glucosamine, lysine, or glycine), sugars (glucose or xylose) and an extra reagent to improve the reaction (MgCl<sub>2</sub>, maleic acid, or citric acid). The samples were soaked for 24 hours in the solutions and reacted at 120°C for 72 hours. The results of the preliminary research showed that when lysine, glucose, or citric acid were reacted a high weight percentage gain (WPG) was obtained (18% for beech and 40% pine). In contrast to most other experiments, a significant amount of the reaction products was still present after leaching. After leaching, the WPG for beech was 11% and 25% for pine. The swelling coefficients showed that swelling occurred only in some of replicates. This preliminary screening reaction has shown that the Maillard reaction does show promise and is worthy of investigation as a potential new wood modification system, however the amount of leaching should decrease tremendously and the increase in volume of the modified wood should be repeatable.

The aim of this research is to investigate the necessary reaction conditions to obtain a lower percentage of leaching and that trap a higher amount of water-insoluble reaction products in the cell wall. For this, different reaction temperatures, soaking times, and reagent concentrations were tested. In general, it would be good if the reactions perform well at low temperatures, since at temperatures under 100°C no special industrial equipment is necessary. The use of short soaking times is also favoured, since then more wood can be treated in a certain period. In previous experiments, chemical reagents were used in concentrations of 0.1 mg mL<sup>-1</sup>. These concentrations are not economically feasible, so reactions that perform well at lower concentrations are preferable. Lower concentrations could potentially improve the leachability (possibility of less unreacted reagents) and the penetration into the cell wall (lower density of the solution).

#### EXPERIMENTAL

Small (20 x 20 x 5 mm) and defect-free sapwood specimens (beech – *Fagus sylvatica* L. and pine – *Pinus sylvestris* L.) were used for the modification studies. Samples were cut such that growth rings were parallel to the tangential face, to prevent diamonding during the leaching

tests. This size of sample was selected in order to ensure even penetration of reactants into the wood sample and allow for good access of the reagents to the cell wall.

To weigh the wood samples, a balance was used (minimum reading is 0.1 mg). The size of the wood samples was determined with a precision of +/- 0.01 mm with a digital calliper. Air was removed from wood samples during the aqueous impregnation step in a desiccator with a vacuum pump at ambient temperature and 100 mbar. Before determining the volume and weight of the unmodified, modified, and leached wood samples, they were dried for 16 hours at 103°C in an oven. After this the wood samples were removed from the oven and cooled down to ambient temperature in a desiccator over silica gel.

For the reactions lysine (CAS Number: 56-87-1), glucose (CAS Number: 50-99-7), and citric acid (CAS Number 77-92-9) were used. All chemicals were purchased from Sigma Aldrich (Slovenia).

First, the volume and weight of unmodified wood samples were measured. Then, samples were treated in 100 mL aqueous solution combining: 0.1/0.1/0.1, 0.1/0.02/0.02, 0.02/0.1/0.02, 0.02/0.02/0.1 and 0.02/0.02/0.02 g mL<sup>-1</sup> of lysine/ glucose/ citric acid. These concentrations were chosen to obtain high quantities of reagents that are completely soluble in water, while still having a solution density and viscosity that allows for easy penetration into the wood. Control samples were treated with water only. All experiments were done in 5 replicates. The wood was placed into the amine-sugar solution, then transferred for 1 h into the vacuum chamber to make sure that all the air was removed from the wood lumen. The wood was subsequently soaked for either 8, 24, 48, or 96 hours (four groups) in the solution to allow for diffusion of reagent into the cell wall. The wood samples were then removed from the solution and put into an oven for 72 hours at either 70, 90, 110, or 120°C. To summarise, a total of 11 tests was performed for pine and beech (4 to test the reaction temperature, 4 to test the influence of soaking time and 5 to test the influence of the concentrations). Details can be found in Table 1. After their respective treatment was done, the wood samples were removed from the oven and the volume and weight of the modified wood was determined.

Table 1: Reaction conditions				
Changed Parameter	Reaction T (°C)	Soaking time (h)	Concentrations lysine/ glucose/ citric acid (mg mL <sup>-1</sup> )	Symbols in charts
Reaction T	70	24	C1: 0.1/0.1/0.1	
	90	24	C1: 0.1/0.1/0.1	$\Delta$
	110	24	C1:0.1/0.1/0.1	$\diamond$
	120	24	C1: 0.1/0.1/0.1	0
Soaking time	120	8	C1: 0.1/0.1/0.1	•
	120	24	C1: 0.1/0.1/0.1	0
	120	48	C1: 0.1/0.1/0.1	٥
	120	96	C1: 0.1/0.1/0.1	8
Concentrations	120	96	C1:0.1/0.1/0.1	8
	120	96	C2: 0.1/0.02/0.02	0
	120	96	C3: 0.02/0.1/0.02	0
	120	96	C4: 0.02/0.02/0.1	0
	120	96	C5: 0.02/0.02/0.02	0

In table 1 can be seen that, when one parameter (temperature, soaking time or concentration) is changed, the two other parameters are held constant. When the temperature and concentration were held constant, values of 120°C and 0.1/0.1/0.1 were chosen, since at that temperature and concentration it was already proven that the Maillard reaction can take place (Peeters et al., 2018). When the soaking time was held constant, the original time chosen was 24 hours as in former experiments, but for the experiments where concentrations were changed, 96 hours were used, since due to unexpected situations, the samples could not be harvested earlier, whereas longer soaking times were not considered critical for the Maillard reaction to occur.

Leaching tests on the wood samples in water were performed in deionised water, which was changed three times a day. 3 leaching cycles of two days each were used until stable weights and sizes were obtained. After each leaching cycle, the wood was dried in the oven and volume and weight gain determined.

The volumetric swelling coefficients (S) were calculated according to the formula (Stamm 1964):

$$S(\%) = ((V_w - V_d)/V_d) \times 100$$
(1)

where  $V_w =$  volume of water saturated wood  $V_d =$  volume of oven dry wood.

The weight percentage gain (WPG) and volume change (VC) were calculated according to the formulas:

$$WPG(\%) = ((W_m - W_u)/W_u) \times 100$$
(2)

Where  $W_m$ = weight of wood after modification or leaching  $W_u$ = weight of unmodified wood

$$VC(\%) = ((V_m - V_u)/V_u) \times 100$$
(3)

Where 
$$V_m$$
= volume of wood after modification or leaching  $V_u$ = volume of unmodified wood

#### **RESULTS AND DISCUSSION**

This discussion is limited to the post-leaching results as they signify the results of reagents that interacted with the wood or polymerised. WPG and VC were calculated after modification in comparison with the unmodified wood samples. S compares the volume of dry modified, leached wood with the volume of the same specimen in a water saturated state. High values of S indicate a small difference between conditions and a higher degree of swelling. The WPG is an indication for the quantity reagent entered the wood, but the reagents can be present both in the lumen and cell wall. The VC of the wood after modification indicates the amount of final product that has actually penetrated into the cell wall, whereas the swelling coefficient indicates how much space was occupied by the wood modification agents that may have been occupied with water in the absence of modification. An increase in WPG but with relatively low VC and a high swelling coefficient, means that reaction products are present in the cell lumen, but not in the cell wall. On the other hand, with efficient penetration into the wood mass (and not lumina), and good Maillard reaction yield, high VC and low S can be achieved even with a relatively low WPG.

Figure 1 shows that for beech samples after leaching, the VC was not significantly different among the groups of specimens with different modification treatments. A higher WPG is obtained when higher reaction temperatures are used. Soaking time had no influence on the modification yield of beech. Surprisingly, the reaction with lysine as main component was not at all successful. This was unexpected since lysine, being the primary amine, is thought to, together with the sugar, induce the Maillard reaction.

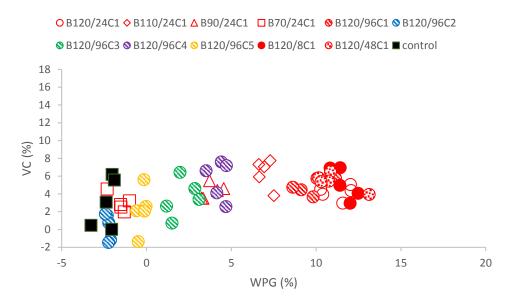


Figure 1: WPG vs. VC of beech (B), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

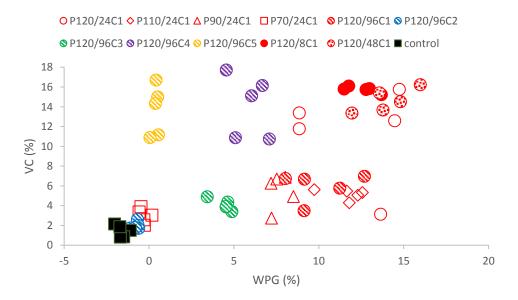


Figure 2: WPG vs. VC of pine (P), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

Figure 2 shows that for pine specimens, a higher WPG was obtained when higher reaction temperatures were used. Interestingly, volume increased and was retained after leaching at a 120°C treatment temperature. Lower soaking times are favoured for pine as a soaking time of 96 hours had a much smaller volume increase at about the same WPG as other treatments with lower soaking times. As with beech, no reaction occurred with an excess of lysine. A volume increase was seen for reagents in low concentrations. This can be explained by the fact that less viscous solutions can penetrate into the wood cell wall more effectively. When citric acid was used in excess, a volume increase was observed, which is expected since citric acid is known to dimensionally stabilize wood (Feng et al. 2014).

In order to be successful, wood modification methods like the one studied here must for polymers in the cell wall. Therefore, samples should show a volume increase compared to the control samples, with concomitant reduction of swelling coefficients. This general trend can be

seen with beech treated at 120 °C after being soaked for 96 hours in the solution of 0.02/0.02/0.1 mg mL<sup>-1</sup> lysine/glucose/citric acid achieving the greatest decrease of S, compared to the control samples (treatment B120/96C4 in Figures 1 and 3). However, in the case of pine, for certain treatments a volume increase is observed, but the swelling coefficients are equal to the control sample (Figures 1 and 4). Yet, the pine treatment P120/96C4 showed the most promising results, since the highest VC and at least a trend towards a reduction in S were recorded.

If the products of the Maillard reaction were to occupy many spaces that the water molecules occupy during swelling of unmodified wood (which would be the optimal outcome of this modification procedure), a much higher reduction in S would have been achieved. From the presented results it is not possible to claim such a success, as the S values of samples with even the highest VC did not differ from the rest of the results. This means that Maillard reaction products do occupy space in the cell wall, but water can still enter the cell walls, creating an additive effect (the cell walls are "bulked" by the Maillard reaction products and the water). Therefore, in future experiments, reagents with less hydrophilic groups should be used to create a less hydrophilic environment.

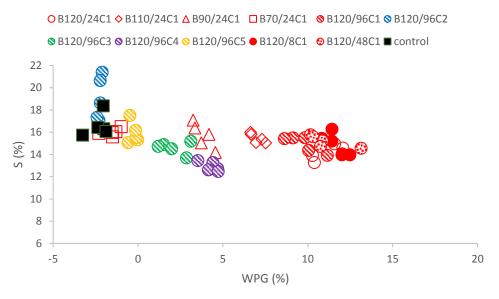


Figure 3: WPG vs. S of beech (B), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

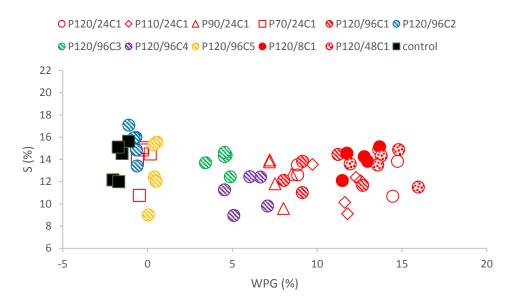


Figure 4: WPG vs. S of pine (P), which was modified via the Maillard reaction with different values for reaction temperatures, soaking times and reagent concentrations (see Table 1) and subsequently leached.

#### CONCLUSIONS

- From the results it can be seen that the Maillard reaction in wood produces better results at higher reaction temperatures. Therefore, new experiments will be performed at 140 and 160°C. The fact that the reaction doesn't perform well at 70°C and 90°C means that more sophisticated industrial equipment will be necessary if this type of modification will be scaled up.
- Soaking times in reagent solutions as short as 8 hours were enough for a successful Maillard reaction, in samples of the size used in this experiment.
- Concentrations of 0.1 mg mL<sup>-1</sup> produced the highest WPG. Unfortunately, concentrations of 0.1 mg mL<sup>-1</sup> are not economical feasible. For pine, however, using lower reagent concentrations of 0.02 mg mL<sup>-1</sup> or an excess of citric acid resulted in a lower WPG, and there was a high-volume increase, which is favourable.
- Since the experiments where wood was modified with an excess of lysine show no swelling or WPG, the main question is if the Maillard reaction actually took place. It may be possible that an esterification reaction with the free OH groups from the wood constituents and glucose with the carboxylic acid from citric acid is what took place in this case, and the glycine was leached out. To better understand the mechanism of such reactions, future experiments will examine effects decreased lysine concentrations with high concentrations of citric acid and glucose.
- Reagents with fewer hydrophilic reactive groups should be tested in future experiments.

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