# Enhancing wood durability and physical properties through innovative bio-based sustainable treatments (BioCoPol)

## FINAL REPORT

<table>
<thead>
<tr>
<th><strong>Title of the research project</strong></th>
<th>Enhancing wood durability and physical properties through innovative bio-based sustainable treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coordinator of the project</strong></td>
<td>Dr. Marion Noël</td>
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</tbody>
</table>

## BASIC PROJECT DATA

<table>
<thead>
<tr>
<th><strong>Project period</strong></th>
<th>01.05.2014-31.07.2017</th>
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</thead>
<tbody>
<tr>
<td><strong>Contact information of the coordinator</strong></td>
<td>Department Architecture, Wood and Civil Engineering - Bern University of Applied Sciences Route de Soleure 102 CH-2500 Bienne - Switzerland Tel. +41.32.344.03.35 Fax. +41.32.344.03.90 E-mail <a href="mailto:marion.noel@bfh.ch">marion.noel@bfh.ch</a></td>
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## URL of the project

http://[web address]

## FUNDING

<table>
<thead>
<tr>
<th><strong>Total budget in EUR</strong></th>
<th>€ 728'505.-</th>
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<tbody>
<tr>
<td><strong>Public funding from WoodWisdom-Net Research Programme:</strong></td>
<td>Total funding granted in EUR by source:</td>
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<tr>
<td><strong>Austria</strong></td>
<td>€ 182'850.-</td>
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<tr>
<td>Federal Ministry of Agriculture, Forestry, Environment &amp; Water Management (BMLFUW)</td>
<td></td>
</tr>
<tr>
<td><strong>France</strong></td>
<td>€ 135'030.-</td>
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<td>French Environment and Energy Management Agency (ADEME)</td>
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</tr>
<tr>
<td><strong>Switzerland</strong></td>
<td>€ 182'830.- = CHF 195'616.-</td>
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<tr>
<td>The Commission for Technology and Innovation (KTI; in the Federal Department of Economic Affairs FDEA)</td>
<td></td>
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</table>
### PROJECT TEAM (main participants)

<table>
<thead>
<tr>
<th>Name, degree, job title</th>
<th>Sex (M/F)</th>
<th>Organization</th>
<th>Country</th>
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<tbody>
<tr>
<td>P. Corbat, Director</td>
<td>M</td>
<td>Corbat Holding SA</td>
<td>Switzerland</td>
</tr>
<tr>
<td>E. Fredon, PhD, Assistant professor</td>
<td>M</td>
<td>Lorraine University (LERMaB)</td>
<td>France</td>
</tr>
<tr>
<td>P. Gérardin, PhD, Professor</td>
<td>M</td>
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<td>France</td>
</tr>
<tr>
<td>C. Grosse, MSc., PhD candidate</td>
<td>F</td>
<td>Lorraine University / BFH AHB</td>
<td>France / Switzerland</td>
</tr>
<tr>
<td>C. L’Hostis, MSc., PhD candidate</td>
<td>M</td>
<td>Lorraine University (LERMaB)</td>
<td>France</td>
</tr>
<tr>
<td>M. Noël, PhD, Scientific collaborator</td>
<td>F</td>
<td>BFH-AHB</td>
<td>Switzerland</td>
</tr>
<tr>
<td>R. Schober, Director</td>
<td>M</td>
<td>Pongauer Jägerzaun</td>
<td>Austria</td>
</tr>
<tr>
<td>M.-F. Thévenon, PhD, Sc. collaborator</td>
<td>F</td>
<td>CIRAD (BioWooEB)</td>
<td>France</td>
</tr>
<tr>
<td>G. Tondi, PhD, Scientific collaborator</td>
<td>M</td>
<td>SUAS - Kuchl</td>
<td>Austria</td>
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### DEGREES (if relevant)

Degrees earned or to be earned within this project.

<table>
<thead>
<tr>
<th>Year</th>
<th>Degree</th>
<th>Sex (M/F)</th>
<th>Name, year of birth and year of earning M.Sc., D.Sc., etc. Degree</th>
<th>University</th>
<th>Supervisor of thesis, supervisor’s organization</th>
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<tr>
<td>2018</td>
<td>PhD</td>
<td>F</td>
<td>C. Grosse, 1990 MSc. 2015</td>
<td>Lorraine University</td>
<td>P. Gérardin, M. Noël, Lorraine University</td>
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<td>2017</td>
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<td>SUAS</td>
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<td>2017</td>
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<td>Year</td>
<td>Degree</td>
<td>Gender</td>
<td>Name</td>
<td>Institution</td>
<td>Mentor</td>
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PROJECT SUMMARY
A summary of the project, preferably one page only

BioCoPol’s target was to promote the use of wood as technological material. Because of limiting drawbacks: sensitivity to water, moisture and biological degradation, leading to deterioration or deformation, other materials are frequently preferred to wood, however natural and sustainable. Especially, some indigenous species are abundant, while not performing well enough to guarantee efficient consumption, as European Beech, species chosen for this project.

BioCoPol focused on wood chemical modification, because this process allows to reach a wide range of properties. Chemical modification implies structural changes of wood, leading to high dimensional stability, significant reduction of the equilibrium moisture content, and high resistance against bio-degradation.

Besides, BioCoPol’s challenge was to develop only bio-based treatments for wood modification, and to focus on the global environmental impact by trying to keep the energy consumption during treatment as low as possible, and to avoid any emission and any leaching during treatment or use.

Several variants have been elaborated or optimized:
- Lactic acid based modification: in-situ polymerization, with or without pre-polymerization, treatment either used in melt or water solution.
- Bio-polyesters modification: in-situ polymerization, based on citric/tartaric/succinic acid/anhydride in water based solutions, combined or not with glycerol or polyglycerol. (For both of the above treatments, wood was treated anhydrous, moist or wet.)
- Tannins reticulation in wood with many bio-based co-reagents, treatments in water solutions.

All the variants have been combined together. Citric/succinic/tartaric acids were supposed to catalyse the lactic acid polymerization, glycerol to avoid wood embrittlement, tannins to improve durability.

All treatment procedures consist in impregnation followed by moderate to strong heat treatment, similar to the commercial existing processes.

The results obtained are numerous, miscellaneous but conclusive. Several variants were very promising, conferring excellent dimensional stability and durability with no detrimental impact on the mechanical properties. Those variants have been chosen for up-scaling and pieces up to 0.13 x 0.26 x 2 m³ were treated for long term exposure.

Two PhD theses, three MSc. theses and two BSc. project works have been carried out in the frame of the project. Many oral presentations in international conferences have been made, several scientific papers are under review and both PhD students have been awarded for their work. A project sharepoint allowed good communication and project flow.
1.1 Introduction

1.1.1 Background
Describe the background of the project and the basic problem that it sought to address.

BioCoPol's aim was to improve properties of wood outdoors by chemical modification. All partners had previously developed promising treatments leading to specific properties improvement. In all cases, optimization was however necessary. The project foundation lies in wise combination of treatments to reach excellent properties. Lactic acid treatment conferred outstanding dimensional stability and durability. However, treated wood had a tendency towards embrittlement and required rather severe process conditions to reach this level of properties. The combination with glycerols or polyglycerols was expected to avoid brittleness, while combination with tannins or chemical catalysts was expected to reach the same durability with softer treatment conditions. With tannins treatment for wood, conferring excellent durability, mechanical resistance and fire resistance, the challenge was to design a reticulation process only based on bio-based co-reactives, inducing good fixation in wood structure and long-term protection especially against weathering. Polyglycerols had been evaluated as very good modification agents conferring excellent dimensional stability and durability. However, rather high leaching was to be assumed during product service life. To avoid this drawback, reaction with several acids/anhydrides was proposed: citric/tartaric/succinic acid/anhydride were evaluated in combination with glycerol and polyglycerols.

1.1.2 Objectives
Describe the project objectives.

[Protection of wood outdoors is of tremendous importance for the promotion of this material. The final objective of BioCoPol was to provide a selection of very efficient chemical modification treatments in terms of properties, sustainability and market implementation ability. This is why all variants had to be bio-based, economically competitive and providing long service life.]

1.2 Results and discussion
Main achievements of the project, quality, innovativeness, industrial relevance and contribution to competitiveness, environmental and societal impact.

[The first half of the project was dedicated to scientific evaluation and the second half to technical up-scaling. The economical evaluation was carried out to gauge the market, and constant environmental concern was raised to guide technical choices.

All details of chemistry and treatment processes are thoroughly reported in national reports, abstracts and scientific papers. Only practical results are summarized in this report.]
1. Scientific results

a. Optimization of single-treatments

Prior to treatment combination, the optimization of each single-treatment was conducted to evaluate the maximal potential of each.

i. Lactic acid treatment

Lactic acid treatment consists in the impregnation of lactic acid oligomers into anhydrous wood structure by brief vacuum step followed by long thermal treatment to induce in-situ polymerization. The impregnation step leads easily to 60/70% of weight impregnation uptake (WPG$^1$ ≈ 30%) on small samples (≈ 40/45% on 100 x 100 x 600 mm$^3$). The association of temperature and duration of the thermal treatment plays a crucial part in the overall treatment efficiency. Temperature range of 120/180°C for duration range 48/120h were combined and led to the optimal condition of 160°C/48h, where all properties are optimal: 70% ASE$^2$, leaching rate (NF X 41-568, 2014$^3$) < 2%, 50% decrease in hygroscopicity, weight loss due to fungal attack (EN 113$^4$) < 3% with Coriolus versicolor and Coniophora puteana, increase of mechanical strength coupled with MOE$^5$ increase.

To improve lactic acid oligomers fixation, maleic anhydride was evaluated as a compatibilizing agent: performance was not improved.

To make the treatment easily transferable to industry, lactic acid (water solution 85%) was also used as raw material with no pre-polymerization step. Not only anhydrous wood, but also wood at 12% MC and at FSP was impregnated to evaluate the drying influence. On anhydrous wood, the lactic acid treatment gives very promising properties, similar to those obtained with lactic acid oligomers treatment, except for slightly increased leaching rate. The biological resistance evaluation is still running for wood at 12% and 30% MC.

ii. Tannin-based treatments

The tannin-based treatments were historically composed of tannins and hexamine copolymer. Within BioCoPol, alternative natural solutions like lactic acid and lactic acid oligomers, citric acid and PEG$^8$ but also several comonomers like glyoxal, formaldehyde, maleic anhydride, furfuryl alcohol and fufural were tested. Treatment conditions were optimized, according to temperature and duration of the curing step, which have a significant influence on properties. The leaching rate varies from 70% for tannin-glyoxal cured at 100°C/1h, to 0% for tannin-maleic anhydride cured at 160°C/40h. Formulations showing the higher water resistance were selected for biological evaluation: the tannin-maleic anhydride, the tannin-formaldehyde (+ 1% boric acid)

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$^1$ Weight Percent Gain  
$^2$ Anti Swelling Efficiency  
$^3$ NF X 41-568 (2014), AFNOR, Wood preservatives - Laboratory method for obtaining samples for analysis to measure losses by leaching into water or synthetic sea water.  
$^4$ EN113 (1997), Wood preservatives. Test method for determining the protective effectiveness against wood destroying basidiomycetes. Determination of the toxic values.  
$^5$ Modulus of Elasticity  
$^6$ Moisture Content  
$^7$ Fibre Saturation Point  
$^8$ Polyethyleneglycol
and the original tannin-hexamine (+ 1% boric acid) formulations were the best performing products in screening and EN113 biological tests with results very close to the standard demands (< 3% mass loss). According to mechanical resistance, most of the tannin-based treatments show a 20% increase of Brinell hardness, 10% increase of the compression strength and maximum 15% decrease of the MOE. All tannin treatments improve the fire resistance: ignition time 4 to 7 times longer than for untreated beech. Artificial and natural weathering evaluation showed that all treated samples see their appearance modified in a similar tendency to untreated controls with better results for the formulation with formaldehyde which degraded after a longer time. Because tannin-based treatments are not penetrating into the wood cell wall, water sensitivity and anti-swelling efficiency present only limited improvements (< 8% ASE). To better understand and to optimize the treatments, a step of tannins purification and characterization was carried out.

### iii. Treatments based on (poly)glycerols / bio-based acids and anhydrides

The focus was on in-situ polymerization of glycerol with citric/tartaric acid and succinic anhydride, all bio-based and readily available. All components are water based solutions, except succinic anhydride, first mixed with glycerol at 130°C for 15 min before being solubilized in water. Temperature and duration of thermal treatment play a significant role into treated wood properties. 120°C appears to be a temperature threshold to get drastic improvement in fixation of treatment in wood structure, evaluated by leaching resistance. For dimensional stability, higher temperature (140/160°C) is necessary to reach ASE values comparable to commercially modified wood, even though there is quite proportional decrease in hygroscopicity at high relative humidity to temperature increase. Because the wood cell wall is modified by the treatment, and because of thermal treatment, treated wood shows a slightly more mechanically fragile behaviour. For biological resistance, promising results have been obtained for some variants, whereas tartaric acid-based treatments show limited efficiency against fungi. Among all variants evaluated, the reaction of succinic anhydride with glycerol gave the best performance.

#### b. Combinations of treatments

##### i. Lactic acid / tannins

The best lactic acid-based treatment for wood is constituted of lactic acid oligomers impregnated and polymerized into anhydrous wood through high temperature and long duration curing. Because of their biocidal effect, hydrolysable tannins were considered as a possibility to soften treatment conditions while keeping excellent durability. Even if hygroscopicity of treated wood is not as much decreased when tannins are added to the mixture as with single-treatments, biological resistance of lactic acid, not pre-polymerized, with lower temperature conditions, is improved. The addition of hydrolysable tannin might save time in the process (no pre-polymerization necessary) and energy (decrease in temperature).

##### ii. Lactic acid / bio-based acids

Citric and tartaric acids have been considered as catalysts of the lactic acid in-situ polymerisation. No significant improvement in performance was noticed.
iii. Lactic acid / glycerol

The addition of glycerol into lactic acid-based treatments was attempted to avoid embrittlement of wood. No significant properties improvement was noticed.

iv. Tannins / (poly)glycerols – bio-based acids

Because tannin powder was insoluble in the bio-based acids, water-based blend containing more than 50% of tannin and bio-based acids were necessary. The polymerization didn't occur because water hindered the esterification. The attempt of pre-reacting tannins with polyesters monomers (lactic/citric acid, citric acid-(poly)glycerol) was carried out to include the tannin unit in the pre-polymer to be crosslinked into wood. Those formulations led to high leaching and limited biological resistance.

c. Critical observation of some tests, reliability evaluation

i. Biological resistance methods for chemically modified wood

All along the project run, biological resistance evaluation was discussed because there is no standardized test available for rapid and discriminant characterization of chemically modified wood. Fungal screening tests were set up and performed the same way by one partner only, for all wood treatments. The results allowed to select some treatments, for which standardized EN113 tests were applied. The results obtained supported the screening test methods validation, as well as a more refined selection for biological performance. Due to the very discriminating character of those biological tests, the fact that several treatments fulfilled the EN113 efficiency criteria is a very promising result.

ii. Long term performance

As usually observed in research projects dealing with wood treatment for applications where very long-lasting life cycle is expected, there is no possibility to simulate in a perfectly reliable way a 25 year-exposure outdoors in ground contact. All resistance tests carried out (leaching resistance, natural/artificial weathering, durability) allowed very good comparative selection of variants but must be consolidated with real scale exposure in real conditions. This part will be taken in charge by exposure of several real size railway sleepers in ground contact for years with regular evaluation. The implementation of that work will be reported in an annex report, provided by the coordinator to the WoodWisdom Secretariat before end of November 2017.

2. Technical results

a. Process definition

The treatment process had to be always considered as a limiting parameter in order to ensure the up-scaling ability of treatments. This could be quite guaranteed by the global concept of impregnating and curing, which is a classic process for chemically modified wood.

i. Impregnation

For most treatments developed, the impregnation was easily carried out. Vacuum/pressure, or simple vacuum cycles allowed sufficient diffusion of treatments in wood structure (either water

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9 Agreed by e-mail the 16.06.2017 (Marion Noël / Mika Kallio)
based or in the melt). The main limitation is the necessity of using stainless steel for all parts of the industrial process, because of treatments acidity.

ii. Heat treatment
Thermal treatment represents a challenge for up-scaling because of the high temperature needed to reach outstanding performance. Industrially, this would be no problem for the implementation of a new industrial process, but none of the 2 industry partners are equipped for such high temperature treatment. Pre-tests on real scale treated railway sleepers will be carried out in the thermal treatment chamber of Corbat Holding, even though the chamber is not perfectly suitable: sensitivity of sensors which might be damaged by acidity, need of degassing in order to keep the internal relative humidity low enough. The implementation of that work will be reported later on as well.

b. Development of pilot scale treatment process

i. Pongauer Jägerzaun
The renovation of an impregnation chamber (2.3m³, 6m long, 63cm diameter) was carried out by the Austrian research partner. An external, universally connectable and transportable impregnation device allowing 10 bar pressure and 0.1 bar vacuum was built. This machine allows the impregnation from pilot (30/50L) to industrial (2/3 m³) scale. Wood elements 1.30m-long, of different section shape and size, were impregnated with tannin-based solutions: retention and diffusion have been evaluated and showed very good feasibility, however the drying process must be slow and controlled to avoid cracks. Evaluation of performance is being carried out.

ii. Corbat Holding SA
Because the impregnation in Corbat’s autoclave was impossible due to treatment acidity, real size beech wood railway sleepers (0.13 x 0.26 x 2m) are being impregnated at the Swiss research partners facilities. The thermal treatment will take place in the company’s thermal treatment chamber end of August 2017. Some pieces will be evaluated in terms of product diffusion, extent of curing and durability, while others will be long-term exposed in ground contact with regular observations.

3. Market positioning

a. Raw material supply for implementation
The mimosa tannin used in this project is abundantly available in the austral hemisphere and is commercially available. Studies of feasibility are under evaluation in other institutes for using spruce extract to make condensed tannins more sustainable for European needs. One local producer of bio-based lactic acid has been contacted and is interested to take part to any further development. The company is now official partner of a follow-up Swiss project together with Corbat Holding SA.
b. Market analysis

Two market analyses have been carried out and showed that the lactic acid- and the polyesters-based treatments would potentially be very price competitive for applications as high-end wood for outdoors, comparable to Accoya® or Kebony®. However, the necessary investments and the product cost make it hardly conceivable for railway sleepers market.

4. Environmental considerations

The purpose of BioCoPol was the development of bio-based material with outstanding properties. The importance of energy consumption has always been taken in consideration, as well as the leaching potentiality of treatment into the environment.]

1.3 Conclusions
The most important contributions to the state-of-the-art, derived from the results and discussion.

[The target of combining formulations was unsuccessful but unnecessary, because single-treatments optimization led to outstanding properties. The selection of variants was facilitated by very conclusive results. Thanks to the economical evaluation, the implementation seems feasible at mid-term. Some partners have already started follow-up projects with this goal. Real size wood pieces could be treated and will be analysed on the long term. BioCoPol will provide interesting knowledge and know-how in the field of wood bio-based chemical modification.]

1.4a Capabilities generated by the project

Knowledge generated in the project / outcomes of the project, such as unpublished doctoral theses, patents and patent applications, computer programs, prototypes, new processes and practices; established new businesses; potential to create new business opportunities in the sector.

[The main outcomes are fully described wood treatment procedures with bio-based chemicals, reported in 2 doctoral theses, 2 MSc. theses, scientific peer reviewed papers and national scientific reports. Very important and useful knowledge was acquired in terms of durability assessment of chemically modified wood. Thorough comparison between screening biological resistance test and standardized durability test could be done and will facilitate future research in the field.
Real scale pieces could be produced for evaluation, because of the development of pilot scale facilities: impregnation chamber, impregnation container and adaptation of the thermal treatment chamber.
Even though no new business was established before the project end, there is a clear potential to create new business opportunities in the sector, competitive to chemically modified wood on the market.]
1.4b Utilisation of results

Give a brief description of how the results of the research and development have been used and/or what is the exploitation plan or plans for transferring the results into practice.

[Results were regularly presented and peer-reviewed articles were submitted. Two doctoral theses will be defended in 2017 and 2018. One follow-up project on marketing study has started in 2017 in Switzerland. Depending on the outcome, the industry partners will decide about a launch on the market. A number of field tests were initiated within BioCoPol and will continue to generate information for future developments.]

1.5 Publications and communication

a) Scientific publications

For publications indicate a complete literature reference with all authors and for articles a complete name. Indicate the current stage of the publishing process when mentioning texts accepted for publication or in print. Abstracts are not reported. Indicate the five most important publications with an asterisk.

1. Articles in international scientific journals with peer review


2. Articles in international scientific compilation works and international scientific conference proceedings with peer review


3. Articles in national scientific journals with peer review

[]

4. Articles in national scientific compilation works and national scientific conference proceedings with peer review

[]
5. Scientific monographs


6. Other scientific publications, such as articles in scientific non-refereed journals and publications in university and institute series


1.6 National and international cooperation

Give a brief description of the cooperation/networking (partnership between the project participants and how this has developed; industrial involvement; synergies of industrial and research expertise; Has the project collaborated with similar projects in the WW-Net countries or other regions, or established new links with/ between local or international organisations involved in the respective research field? Describe how these partnerships have supported the project.

National vs. transnational aspects in the project; added value for the project and its impacts which result from transnational cooperation.

The cooperation/networking between project participants, either research or industry partners, was a success. The exchange of expertise, ideas and facilities was highly beneficial to the project run. In particular, the centralization of the durability evaluation at the CIRAD had a significantly positive impact on the global function of the project.

A cooperation with researchers of the BIO4ever project (SIR/MIUR call) has been developed. Many samples have been sent and exposed in several conditions for later evaluation. The exchange of know-how and knowledge with this team was very valuable in terms of analysis during the project.

Moreover, BioCoPol partners have participated to many conferences providing ideas and leading to scientist exchanges in the frame of other projects.

In the frame of BioCoPol, a very motivated and interested raw material producer was contacted and is now official partner of a follow-up project in Switzerland.

Besides, the BioCoPol consortium is preparing to apply for further research within an extended research and implementation group, under the ForestValue call, dedicated to the direct application of the knowledge and know-how gained.