# Wood-based aerogels - AEROWOOD

## FINAL REPORT

### Title of the research project
Wood-based aerogels – AEROWOOD

### Coordinator of the project
Maija Tenkanen

## BASIC PROJECT DATA

### Project period
01.05.2014 - 30.06.2017

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### URL of the project
http://blogs.helsinki.fi/aerowood-project/

## FUNDING

### Total budget in EUR
1 343 698 EUR

### Public funding from WoodWisdom-Net Research Programme:
Total funding granted in EUR by source:

**Austria**
Federal Ministry of Agriculture, Forestry, Environment & Water Management (BMLFUW)
184 782 EUR

**Finland**
Academy of Finland (AKA)
404 600 EUR

**France**
Ministry of Agriculture, Fisheries and Forestry Resources (MAAF)
163 123 EUR

**Germany**
Agency for Renewable Resources (FNR)
208 869 EUR

**Slovenia**
Ministry of Education, Science and Sport (MIZS)
208 924 EUR
Other public funding:
University of Helsinki, Finland 173 400 EUR

Other funding:

**PROJECT TEAM (main participants)**

<table>
<thead>
<tr>
<th>Name, degree, job title</th>
<th>Sex (M/F)</th>
<th>Organization</th>
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<tr>
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<td>Kirsi Mikkonen, docent</td>
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### DEGREES
Degrees earned or to be earned within this project.

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<tr>
<th>Year</th>
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<td>Bojana Gracanac, 1989,</td>
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PROJECT SUMMARY REPORT

The AEROWOOD project studied ways to prepare aerogel materials derived from all major wood components. The aim was to find new possibilities for valorisation of lignocellulosics to value-added advanced functional materials. The special emphasis was given on systematic structure-function relation studies to understand the mechanisms affecting aerogel formation and characteristics. New ways of introducing reinforcements, bioactive compounds, functional packaging constituents, quantum dots, and sensing moieties to the aerogel matrixes were explored. The processes were conducted in aqueous and environmentally compatible green systems. Materials were tested in intelligent and active packaging and biomedical applications. The main outcomes were:

- Wood components – cellulose, hemicellulose, lignin – as well as milled wood were all successfully reformulated into new lightweight materials with high specific surface area, aerogels.
- Substitution of hazardous epoxides by safer cyclic organic carbonates was shown possible for the derivatization of hemicelluloses to improve gelation and enable crosslinking.
- The produced transparent aerogels from cellulose open new fields of applications in biosensing, bioimaging, photovoltaics, thermal superinsulation, and true volumetric displays.
- Lignosulfonate-alginate composite aerogels are promising eco-friendly materials for thermal insulation applications due to their facile preparation, mechanical robustness and near-superinsulating properties.
- Cellulose and hemicellulose aerogels were characterized as biocompatible drug release and cell growth media for wound healing and tissue engineering.
- Hemicellulose aerogels showed potential as part of active packaging to extend the shelf-life of packed fruit or in health care applications.
- The AEROWOOD project resulted in new insights in utilizing the most significant wood biorefinery products in new lightweight materials.
- Four short term scientific visit were carried out and four doctoral students and three post docs were trained during the project.
1.1 Introduction

1.1.1 Background

The forestry industry has the opportunity to play a major role in the future bioeconomy as it can deliver both renewable energy and new materials. This is envisaged to lead also to a more profitable forest industry as a whole, by broadly combining knowledge ranging from forestry to foods and medicine. Establishing forest-based biofuel production requires simultaneous development of fractionation processes followed by manufacturing of high-value wood-based products. The future biorefineries will strongly depend on the development of diversified and innovative applications for all wood components (cellulose, hemicelluloses, lignin) to secure economic sustainability of the whole forest-based industry. Emerging potential value-added future products, namely, highly porous and lightweight aerogel materials, were explored in this project.

1.1.2 Objectives

The AEROWOOD project aims were to study ways to prepare aerogel materials derived from on all major wood components, as well as on whole wood and unbleached pulp. The objective was to find new possibilities for valorisation of lignocellulosics to value-added advanced functional materials. The special emphasis was given on systematic structure-function relation studies. New ways of introducing reinforcements, bioactive compounds, functional packaging constituents, quantum dots, and sensing moieties to the aerogel matrixes were explored and exploited. The key target was to carry processes using smart (bio)technologies, integrating safety and possible toxicity aspects, finding sustainable solutions for a better use of wood-based materials in aqueous and environmentally compatible systems. The project aimed to establish proof-of-concepts, to understand the mechanisms affecting aerogel formation and characteristics, and to show diversified application prospects. The main emphasis was put on intelligent and active packaging and biomedical applications. The AEROWOOD project resulted in new insights in utilizing the most significant wood biorefinery products.

1.2 Results and discussion

The work was divided in four work packages (WP). The key results in each of them is presented below.

**WP1 Material collection, isolation and modification**

Cellulose, lignin and wood samples were either commercial samples or provided by P4. Xylans were isolated from beech wood, hardwood pulp and oat spelts. Galactoglucomannans were obtained from the spruce thermomechanical pulping water. Pure cellulose was microcrystalline cellulose, cotton linters with various molecular weights, bleached pulp or nanofibrillated cellulose. Lignosulfonate and pine kraft lignin were studied lignins. Materials were used as such or after chemical or enzymatic modification.
For detailed analysis of all products new analytical methods were developed: reductive amination followed by HPAEC-UV for hemicellulose; reductive amination followed LC-fluorescence for xylan derivatives; HR/MAS-NMR for characterisation of insoluble products and gels. For xylans the derivatisation with cyclic organic carbonates was established. Reactions with propylene carbonate were investigated under homogeneous and heterogeneous conditions leading to hydroxypropyl xylans with different substitution levels, substituent distributions, solubilities and rheological properties. In homogenous reaction soluble products and in heterogeneous conditions insoluble but swellable products were obtained. The homogeneous reaction of xylan with vinylenecarbonat enabled the introduction of vinyl bonds. These double bonds could be used for radical induced covalent crosslinking and subsequent production of aerogels.

**WP2 Cellulose- and wood-based aerogels**

Cellulose of various molecular weights and dissolved at different concentrations was used to prepare aero-, cryo- and xerogels via drying with supercritical CO₂, lyophilisation and low-vacuum drying, respectively. A systematic characterisation was performed (density, porosity, specific surface area, morphology and mechanical properties) allowing correlating molecular parameters and processing conditions with final material properties. Mechanical properties of aero- and cryocellulose were analysed using new (for these materials) approach. Overall, this work makes a background for the understanding of cellulose II based porous materials’ morphology and properties.

Aero-, cryo- and xerogels from wood (poplar) were prepared: they showed morphology and properties similar to those of cellulose-based counterparts. The results are very promising showing that depending on the application, non-pure cellulose may be used to make aerogels and cryogels.

Based on oxidatively modified and subsequently nanofibrillated cellulose transparent aerogels reaching the transmission of silica aerogels could be obtained. As the latter feature large internal surfaces they are regarded promising matrices for true volumetric displays. It was shown that both 6-carboxyl cellulose and 2,3-dicarboxyl cellulose aerogels can be homogeneously equipped with physically or chemically immobilized photoluminescent upconverting nanoparticles (UCNP), including amino functional carbon dots (self-prepared) and lanthanide-doped NaYF₄ nanocrystals. Uniaxial densification of aerogels from oxidatively modified cellulose was furthermore found to be an efficient means to afford mechanically very robust aerogels. Simultaneous pore size harmonization was demonstrated to afford superinsulating aerogels whose resilience and mechanical characteristics are very promising with regard to real-world super-insulation applications.

**WP3 Hemicellulose derived hydrogels and aerogels**

Aerogels from hemicelluloses were prepared applying enzymatic, chemo-enzymatic and chemical crosslinking techniques. The processes were conducted in aqueous and
environmentally compatible systems. Spruce galactoglucomannans and birch glucuronoxylans were successfully crosslinked to form hydrogels with nanofibrilated cellulose. Lightweight and strong aerogels with sponge properties were obtained by freeze-drying. Enzymatically crosslinked galactomannan – nanocellulose gels in solvent were scCO$_2$ dried to obtain mesoporous aerogels with high specific surface area. Synchrotron x-ray microtomography was used for the first time to reveal the 3D inner structure of freeze-dried aerogels. Addition of nanocellulose decreased the pore size, and adjusting the freezing direction aligned the pores. New ways of introducing reinforcements, bioactive compounds, and functional packaging constituents to the aerogel matrixes were also explored.

**WP4 Lignin-based aquogels, aerogels and carbon aerogels**

Free-standing lignin-based aquogels were prepared from ammonium lignosulfonate and sodium alginate by physical cross-linking in acidic aqueous media. Subsequent neutralization and solvent exchange (to CO$_2$ miscible organic solvent) followed by scCO$_2$ drying afforded nanoporous lignin alginate composite aerogels (beads, discs, cylinders) of an average bulk density of 70-75 mg cm$^{-3}$. While higher alginate contents increased the internal surface area of the composite aerogels, enhanced lignin contents had a positive impact on dimensional and mechanical stability. Along with the excellent thermal insulation performance of 24.7–25.4 mW m$^{-1}$ K$^{-1}$, the novel type of lignin-rich composite aerogels can be considered a promising candidate for real world insulation applications. Slow carbonization of these lignin/alginate composite aerogels up to a final temperature of 1300°C turned out to afford carbon aerogels of well-preserved nanomorphology.

Lignin organogels, cryogels and carbon aerogels were also prepared from kraft pine lignin by chemical cross-linking using DMSO as solvent and methylene diphenyl diisocyanate (MDI) as cross-linking agent. Dynamic rheology revealed that gel formation occurs at MDI:lignin molar ratios exceeding 2:1. Respective cryogels obtained after freeze-drying featured good mechanical performance as evident from the Young’s moduli which exceeded considerably that of lignin/alginate composite aerogels.

Beyond the work dedicated to lignin-based aquogels, aerogels and carbon aerogels, some strong UV light blocking transparent and mechanically very robust composite films and discs with a glass like texture were prepared from lignosulfonates and poly(vinyl pyrrolidone). Respective materials are currently tested for eye protection from sun light.

**WP5 Application potentials of aerogels in packaging and health care**

Hemicellulose aerogels showed potential as part of active packaging to extend the shelf-life of packed fruit or in health care applications (wound healing, tissue engineering). Spruce galactoglucomannan-based aerogels were characterized as packaging materials for control release of hexanal, which extends the shelf life of fruit and vegetables. Sunflower oil was emulsified and entrapped in gel matrix together with lipase and lipoxygenase enzymes. These enzymes catalyzed the formation of hexanal. According to the amount of released hexanal, 1-2
g of the developed aerogels is estimated to yield the desired preservative effect in a fruit packaging of 1.5-2 L in volume.

Polysaccharides are not new in drug delivery. Here aerogels were developed from cellulose and hemicelluloses with different tailorable properties (e.g. porosity, physic-chemical properties) that could be fine-tuned to control various drug delivery performances to the need of the patient. Results obtained show, that the release of different drugs can be tailored using different base polysaccharide materials. If novel material is to be used in applications in contact with humans, safety and efficiency testing is one of the most important steps in the material development. Thus one of the important efforts was to develop in vitro testing platforms, based on human derived cells that can be used for full safety and efficiency assessment of novel aerogel materials. These tests are the foundation for possible future clinical testing and further commercialization. Platforms from human skin derived cells and bone derived cells were developed and tested. Cellulose and hemicellulose aerogels were characterized as biocompatible drug release and cell growth media for wound healing and tissue engineering.

1.3 Conclusions

The main project outcomes were:

- Wood components – cellulose, hemicellulose, lignin – as well as milled wood were all successfully reformulated into new lightweight materials with high specific surface area, aerogels.
- Substitution of hazardous epoxides by safer cyclic organic carbonates was shown possible for the derivatization of hemicelluloses to improve gelation and enable crosslinking.
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- The AEROWOOD project resulted in new insights in utilizing the most significant wood biorefinery products in new lightweight materials.
- Four short term scientific visit were carried out and four doctoral students and three post docs were trained during the project.
1.4a Capabilities generated by the project

The main outcomes of the project have been published in peer-reviewed scientific articles (see 1.5.). Several manuscripts are also under preparation. The project results have been disseminated actively by the partners in several international conferences. In total 35 talks and several poster presentations were given during years 2015-2017. All publications and presentations can be found on the project www-pages, which is still regularly up-dated after the project: http://blogs.helsinki.fi/aerowood-project/publications/

In addition to already published papers, several manuscripts are in progress:


Plappert S, Quraishi S, Pircher N, Mikkonen K, Rosenau T, Liebner F, Transparent, flexible and mechanically strong 2,3-dialdehyde cellulose films with excellent oxygen barrier properties, manuscript in preparation.


One dissertations is expected by the end of 2017 (Gafar) and three in 2018 (Akil, Quraishi, Lorenz).
1.4b Utilisation of results

The project showed successfully that aerogels can be prepared from all wood components as well as from whole wood without separating cellulose, hemicelluloses and lignin. Depending on the raw materials(s) and gelling and drying processes used, aerogels with different morphology, structure and mechanical durability were obtained which opens vast application potentials for these wood-derived light-weight materials. Freeze-dried hemicellulose-based materials had interconnected macroporous structure highly suitable for cell growth in tissue engineering applications whereas some cellulose- and lignin-based aerogels dried with supercritical carbon dioxide possessed very high specific surface area and near-super insulating properties The transparent aerogels from cellulose, in which nanoparticles such as carbon dots can be entrapped, are promising in biosensing, bioimaging, and for true volumetric displays. Slowly hexanal releasing aerogels have great potential as novel packaging materials to obtain extended self-life of fruits, berries and vegetables. Crosslinked aerogels which absorbed water 30-40 times their initial weight and showed reversible sponge property, may find use for example in water purification. These application potentials are further exploited in the follow-up projects by partners, some of which are carried out in collaboration with industry.

1.5 Publications and communication

1. Articles in international scientific journals with peer review


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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


The project results have been disseminated actively by the partners in several international conferences:


Sven Plappert, Sakeena Quraishi, Thomas Rosenau, Falk Liebner. 31- Photoluminescence in highly ordered transparent cellulose aerogels imparted by surface-grafted carbon dots. 251st ACS National Meeting. March 13-17, 2016, San Diego, California, USA.


Jose Martin Ramos-Diaz, Tatiana Budtova, Kirsti Parikka, Kirsi Mikkonen, Maija Tenkanen. Tannic acid crosslinking enables formation of birch xylan-NFC-based hydrogels and aerogel


1.6 National and international cooperation

Samples have been exchanged between all partners. Three short term researcher visits from P1, P2 and P4 were also conducted in P3 laboratory. A joined MSc thesis was performed in cooperation between P3 and P4. A particular strength of the consortium was the development of analysis methodology and testing different wood-based samples produced by the project partners with the developed methodology. One common article (P3 and P4) is submitted and two more (P1 and P3, P1 and P2) are under the preparation, several joint presentations at conferences were made and are planned.

P1 established a link with the research group of Prof. Irina Smirnova, Institute of Thermal Separation Processes, Hamburg University of Technology (TUHH), Germany. A highly successful research visit for 3 month in 2015 was conducted from P1 to this group to obtain know-how on the aerogel formation by supercritical CO₂ drying. In the late phase of the project, P4 started a collaboration with this group on aerogels from hydroxyvinylethylated xylan. This will be continued with funding from a PhD scholarship.

Hemicellulose and nanocellulose samples were obtained from Åbo Akademi University, Finland and UPM, Finland, respectively. Aerogel 3D inner structures were analysed in Paul Scherrer Institut, Switzerland using synchrotron radiation beamtime at the TOMCAT beamline.