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
Contact information of the coordinator	Department of Food and Environmental Sciences University of Helsinki Agnes Sjöbergin katu 2 FI-00014 Helsinki Tel. +358-2941 58410 E-mail: Maija.tenkanen@helsinki.fi
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)

Name, degree, job title	Sex (M/F)	Organization	Country
Maija Tenkanen, Professor	F	University of Helsinki	Finland
Kirsi Mikkonen, docent	F	University of Helsinki	Finland
Kirsti Parikka, docent	F	University of Helsinki	Finland
Suvi Alakalhunmaa, PhD student	F	University of Helsinki	Finland
Abdul Ghafar, PhD student	M	University of Helsinki	Finland
Jose Martin Ramos Diaz, post doc	M	University of Helsinki	Finland
Tatiana Budtova, “Directeur de recherche"	F	MINES ParisTech/Armines/CEMEF	France
Nela Buchtova, post-doc	F	MINES ParisTech/Armines/CEMEF	France
Gerrit Spiess, trainee	M	MINES ParisTech/Armines/CEMEF	France
Bodo Saake, Professor	M	University of Hamburg	Germany
Dominic Lorenz, PhD student	M	University of Hamburg	Germany
Youssef Akil, PhD student	M	University of Hamburg	Germany
Falk Liebner, Privatdozent	M	Universität für Bodenkultur Wien	Austria
Sakeena Quraishi, PhD student	F	Universität für Bodenkultur Wien	Austria
Silvo Hribernik, post-doc	M	University of Maribor	Slovenia
Uroš Maver, Assist. Prof.	M	University of Maribor	Slovenia

DEGREES

Degrees earned or to be earned within this project.

Year	Degree	Sex	Name, year of birth	University	Supervisor of thesis,
2015	M.Sc.	M	Bojana Gracanac, 1989,	University of Helsinki	Kirsi MIkkonen University of Helsinki
2016	M.Sc.	M	Gerrit Spiess, 1991,	University of Hamburg	Tatiana Budtova, MINES ParisTech
2017	M.Sc.	F	Ida Nikkilä, 1987,	University of Helsinki	Kirsti Parikka University of Helsinki
2017	PhD	M	Abdul Ghafar, 1985,	University of Helsinki	Kirsi Mikkonen Kirsti Parikka Maija Tenkanen University of Helsinki
2018	PhD	M	Dominic Lorenz, 1989,	University of Hamburg	Bodo Saake University of Hamburg
2018	PhD	M	Youssef Akil, 1990	University of Hamburg	Bodo Saake Univeristy of Hamburg
2018	PhD	F	Sakeena Quraishi, 1990	BOKU, Wien	Falk Liebner BOKU, Wien

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 microcrystallinen 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 vinylethylencarbonat 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 CO_2, 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 $NaYF_4$ 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.
- 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.
- Cellulose and hemicellulose aerogels were characterized as biocompatible drug release and cell growth media for wound healing and tissue engineering.
- 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:

Lorenz D, Knöpfle A, Akil Y, Saake B, Quantitative investigations of xylose and arabinose substituents in hydroxypropylated and hydroxyvinylethylated arabinoxylans, submitted.

Akil Y, Castellani R, Lehnen R, Budtova T, Saake B, Hydroxyalkylation of xylan using propylene carbonate: Comparison of products from homo- and heterogeneous synthesis by HRMAS NMR and rheology, submitted.

Ramos-Diaz MJ, Budtova T, Kilpeläinen P, Mikkonen K, Tenkanen M, Birch xylan-based aerogels, manuscript in preparation.

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.

Quraishi S, Plappert S, Schäfferling M, Mitterer C, Liebner F, Transparent nanocellulose hydrogels and aerogels equipped with covalently bonded photoluminescent carbon dots, manuscript in preparation.

Plappert S, Taupe P, Quraishi S, Nedelec J-M, Rennhofer H, Lichtenegger H, Liebner F, Transparent moisture resistant NFC/PMMA nanocomposite aerogels of nematic liquid-crystalline skeletal structure, manuscript in preparation.

Quraishi S, Plappert S, Taupe P, Ungerer B, Wang H, Rosenau T, Liebner F**,** Photo-luminiscent BNC/quantum dot hybrid membranes and aerogels, manuscript in preparation.

Quraishi S, Halbauer P, Requejo-Silva A, Ilbizian P, Rigacci A, Liebner F, Ligno-sulfonate-alginate hybrid aerogels: A facile route towards biopolymer-based thermal insulation materials at the boundary of superinsulation, manuscript in preparation.

Liebner F, Nano Cellulose and Bacterial Cellulose Based Aerogels: Processing and Morphology. In: Sabu T, Laly A P, Rubie M-S (editors), Biobased Aerogels **–** Polysaccharide and Protein-based Materials, Green Chemistry Series. Royal Society of Chemistry, 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

Ghafar A, Parikka K, Sontag-Strohm T, Österberg M, Tenkanen M, Mikkonen KS (2015). Strengthening effect of nanofibrillated cellulose is dependent on enzymatically oxidized polysaccharide gel matrices. *European Polymer Journal* 71: 171-184. *http://doi.org/10.1016/j.eurpolymj.2015.07.046*

Lorenz D, Erasmy N, Akil Y, Saake B (2016). A New Method for the Quantification of Monosaccharides, Uronic Acids and Oligosaccharides in partially Hydrolyzed Xylans by HPAEC-UV/VIS. *Carbohydrate Polymers* 140: 181-187. *http://doi.org/10.1016/j.carbpol.2015.12.027*

*Akil Y, Lorenz D, Lehnen R, Saake B (2016). Safe and non-toxic hydroxyalkylation of xylan using propylene carbonate. *European Polymer Journal* 77: 88-97. *http://doi.org/10.1016/j.eurpolymj.2016.02.010*

*Stergar J, Maver U (2016). Review of aerogel-based materials in biomedical applications. *Journal of Sol-Gel Science and Technology* 77: 738-752. *http://doi.org/10.1007/s10971-016-3968-5*

*Buchtová N, Budtova T (2016). Cellulose aero-, cryo- and xerogels: towards understanding of morphology control. *Cellulose* 23: 2585–2595. *http://doi.org/10.1007/s10570-016-0960-8*

*Alakalhunmaa S, Parikka K, Penttilä PA, Cuberes T, Willför S, Salmén L, Mikkonen KS (2016). Softwood-based sponge gels. *Cellulose* 23: 3221–3238. *http://doi.org/10.1007/s10570-016-1010-2*

Akil Y, Lehnen R, Saake B (2016). Novel synthesis of hydroxyvinylethyl xylan using 4-vinyl-1,3-dioxolan-2-one. *Tetrahedron Letter* 57: 4200–4202. *http://doi.org/10.1016/j.tetlet.2016.08.009*

*Ghafar A, Gurikov P, Raman S, Parikka K, Tenkanen M, Smirnova I, Mikkonen KS (2017). Mesoporous guar galactomannan based biocomposite aerogels through enzymatic crosslinking. *Composites Part A* 94: 93-103.
http://doi.org/10.1016/j.compositesa.2016.12.013

Guo J, Liu D, Filpponen I, Johansson L, Malho J, Quraishi S, Liebner F, Santos H, Rojas O (2017). Hybrids of cellulose nanocrystals and carbon quantum dots as cytocompatible probes for bioimaging. *Biomacromolecules* 18: 2045−2055.
http://doi.org/10.1021/acs.biomac.7b00306

Ghafar A, Parikka K, Haberthür D, Tenkanen M, Mikkonen KS, Suuronen J-P (2017). Synchrotron microtomography reveals the fine three-dimensional macroporosity of composite polysaccharides aerogels. *Materials* 10: 871-890.
http://doiorg/10.3390/ma10080871

Parikka K, Nikkilä I, Pitkänen L, Ghafar A, Sontag-Strohm T, Tenkanen M (2017). Laccase/TEMPO oxidation in the production of mechanically strong arabinoxylan and glucomannan aerogels. *Carbohydrate Polymers* 175: 377-386.
http://doi.org/10.1016/j.carbpol.2017.07.074

Plappert S, Nedelec J-M, Rennhofer H, Lichtenegger H, Liebner F (2017). Strain hardening and pore size harmonization by uniaxial densification: A facile approach towards superinsulating aerogels from nematic nanofibrillated 2,3-dicarboxyl cellulose. *Chemistry of Materials*, in press.
http://doi.org/10.1021/acs.chemmater.7b00787

Lorenz D, Janzon R, Saake B (2017). Determination of uronic acids and neutral carbohydrates in pulp and biomass by hydrolysis, reductive amination and HPAEC-UV/VIS. *Holzforschung*, in press.

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

Gracanac Bojana, Polysaccharide-based aerogels as water absorbent and oxygen scavenger in meat packaging (2015), Master Thesis, University ofHelsinki, EKT Series 1705.
https://helda.helsinki.fi/handle/10138/157467

Nikkilä Ida, Uudentyyppiset polysakkaridipohjaiset hydro- ja aerogeelit TEMPO/lakkaasi-katalysoidulla hapetuksella (2017) Master Thesis,University of Helsinki, EKT Series 1777.
https://helda.helsinki.fi/handle/10138/178546

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

Mikkonen K, Parikka K, Ghafar A, Tenkanen M (2014). Enzymatic oxidation technology enables manufacturing of novel lightweight and stiff polysaccharide-based aerogels, 13th European

Workshop on Lignocellulosic and Pulp (EWLP), Sevilla, Spain, 24-27 June 2014, 99-102. (ISBN 978-84-616-9842-4).

Alakalhunmaa, S, Parikka K, Penttilä PA, Cuberes TM, Willför S., Salmén L, Mikkonen KS (2015). Softwood-based sponge-like composite aerogels. *Proceedings of the 10th Biennial Johan Gullichsen Colloquim – New Business Opportunities from Wood:* pages 31-34. Wanha Satama, Helsinki, Finland. November 19, 2015.

Plappert S, Liebner F, Cellulose-based photoluminescent nanocomposites. In: Peresin, S., Filpponen, E., Nypelö, T. (eds.), Lignocellulosics: Renewable feedstock for (tailored) functional materials and nanotechnology. Elsevier 2017, Chapter 10, 49 pages, accepted.

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

Kirsti Parikka, Abdul Ghafar, Kirsi S. Mikkonen, Maija Tenkanen. Polysaccharide aerogels by enzymatic crosslinking with galactose oxidase**.** *International Seminar on AEROGELS – 2014.* October 6-7, 2014. Hamburg, Germany.

Abdul Ghafar. Three-dimensional imaging of polysaccharide aerogels by synchrotron radiation microtomograph. *International Seminar on AEROGELS – 2014.* October 6-7, 2014. Hamburg, Germany. (poster)

Cyrielle Rudaz, Arnaud Demilecamps, Nela Buchtova, Richard Bardl, Romain Sescousse, Roxane Gavillon, Tatiana Budtova. Bio-aerogels. *GDR Synthons et Matériaux Biosourcés SYMBIOSE.* April 8-10, 2015. Nantes, France.

Nela Buchtová, Tatiana Budtova. Highly porous cellulose: aerogels vs cryogels. *249th ACS National Meeting & Exposition*. March 22-26, 2015. Denver, CO, United States.

Falk Liebner, Huiqing Wang, Sven Plappert, Sakeena Quraishi, Nicole Pircher, Thomas Rosenau. Photoluminiscent and transparent cellulose-based aerogels and films carrying covalently immobilized core-shell quantum dots. *249th ACS National Meeting & Exposition*. March 22-26, 2015. Denver, CO, USA.

Abdul Ghafar, Kirsti Parikka, Tuula Sontag-Strohm, Maija Tenkanen, Kirsi S. Mikkonen. Enzyme-mediated gelation of polysaccharides yields bio-based aerogels. *18th Gums & Stabilisers for the Food Industry Conference*. Glyndwr University, Wrexham, UK. June 23-26, 2015.

Nela Buchtová, Christophe Pradille, Lidija Gradišnik, Janja Stergar, Karin Stana Kleinschek, Uroš Maver, Tatiana Budtova. Highly porous cellulose aerogels and cryogels for biomedical applications. *Polymer Processing Society Conference (PPS) 2015*. September 21-25, 2015. Graz, Austria.

Sakeena Quraishi, Sven Plappert, Philip Taupe, Bernhard Ungerer, Thomas Rosenau, Falk Liebner. Transparent aerogels from liquid-crystalline TEMPO-oxidised nanocellulose reinforced with PMMA and equipped with evenly distributed, covalently immobilized, highly photoluminiscent carbon dots. *18th ISWFPC.* September 9-11, 2015. Vienna, Austria.

Sakeena Quraishi, Sven Plappert, Nicole Pircher, Huiqing Wang, Thomas Rosenau, Falk Liebner. Fluorescent BNC/quantum dot aerogels reinforced with biocompatible polymers. *2nd Symposium on Bacterial NanoCellulose*. September 9-11, 2015. Gdansk, Poland.

Falk Liebner, Nicole Pircher, A. Russler, E. Haimer, Thomas Rosenau. Tailoring of ultra-lightweight biopolymer-based aerogels for high-performance applications using multiple $scCO_2$ technologies. *11th International Symposium on Supercritical Fluids*. October 11-14, 2015. Seoul, South-Korea.

Youssef Akil, Dominic Lorenz, Ralph Lehnen, Bodo Saake. Save and Non-toxic Hydroxyalkylation of Xylan using Propylene Carbonate. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland.

Suvi Alakalhunmaa, Kirsti Parikka, Paavo A. Penttilä, Teresa M. Cuberes, Stefan Willför, Lennart Salmén, Kirsi S. Mikkonen. Preparation and characterization of softwood-based sponge gels. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland.

Nela Buchtová, Christophe Pradille, Jean-Luc Bouvard, Tatiana Budtova. Cellulose aerogels and cryogels: morphology and mechanical properties. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland.

Dominic Lorenz, Youssef Akil, Bodo Saake. Detailed Characterization of Xylans by HPAEC-UV/VIS after Labeling by Anthranilic Acid. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland.

Kirsti Parikka, Abdul Ghafar, Kirsi S. Mikkonen, Maija Tenkanen. Production of polysaccharide aerogels by crosslinking with galactose oxidase –catalyzed oxidation. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland.

Abdul Ghafar. Synchrotron microtomography reveals the three-dimensional morphology of polysaccharide aerogels. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland. (poster)

Nicole Pircher, Sakeena Quraishi, Markus Bacher, Leticia Carbajal, Jean-Marie Nedelec, Harald Rennhofer, Helga Lichtenegger, Thomas Rosenau, Falk Liebner. Impact of selected cellulose solvents on chemical, morphological and mechanical properties of cellulose II aerogels. *4th EPNOE International Polysaccharide Conference*. October 19-22, 2015. Warsaw, Poland.

Maija Tenkanen, Abdul Ghafar, Suvi Alakalhunmaa, Kirsti Parikka, Kirsi S. Mikkonen. Aerogels from mannans. *2nd Symposium on Lignin and Hemicellulose Valorisation*. November 3-4, 2015. Lund, Sweden.

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.

Kirsti Parikka, Ida Nikkilä, Maija Tenkanen. Polysaccharide hydro- and aerogels by chemo-enzymatic oxidation. *Nordic Polymer Days/Nordicc Rheology Conference*. May 30-June 1, 2016, Helsinki, Finland.

Maija Tenkanen, Abdul Ghafar, Suvi Alakalhunmaa, Kirsti Parikka, Kirsi Mikkonen. Light-weight load-bearing aerogels from plant-derived mannans. *XIVth Cell Wall Meeting.* June 12-17, 2016, Chania, Crete.

Sven Plappert, Thomas Rosenau, Falk Liebner. Transparent birefringent monolithic aerogels from liquid-crystalline nanofibrillated TEMPO-oxidized cellulose**.** *European Workshop on Lignocellulosic and Pulp*. June 28-30, 2016. Grenoble, France. (poster)

Sakeena Quraishi, Sven Plappert, Thomas Rosenau, Falk Liebner. Transparent nematic cellulosic aerogels covalently equipped with carbon dots of high quantum yield: First steps towards true volumetric 3D displays. *European Workshop on Lignocellulosic and Pulp*. June 28-30, 2016. Grenoble, France. (poster)

Dominic Lorenz, Bodo Saake. Simultaneous determination of monosaccharides, oligosaccharides and uronic acids in partially hydrolyzed pulp and biomass. *14th European Workshop on Lignocellulosics and Pulp.* June 28-July 1, 2016, Autrans, France.

Maija Tenkanen, Abdul Ghafar, Ida Nikkilä, Kirsti Parikka, Kirsi Mikkonen. Polysaccharide-derived aerogels by chemo-enzymatic oxidation. *OxiZymes 2016.* July 3-6, 2016, Wageningen, The Netherlands.

Sven Plappert, Sakeena Quraishi, Thomas Rosenau, Falk Liebner. Transparent aerogels from nematic nanofibrillated carboxyl celluloses covalently equipped with carbon dots of high quantum yield: First steps towards bio-based true volumetric 3D displays. *Advances in Functional Materials*. August 11-18, 2016. Jeju Island, South-Korea.

Nela Buchtova, Tatiana Budtova. Highly porous cellulose: towards morphology control. *From Nano to Macrostructures. Design and Characterization of Soft Materials.* August 24-26, 2016, Strömstad, Sweden.

Falk Liebner, Sven Plappert, Sakeena Quraishi, Thomas Rosenau. First steps towards bio-based true volumetric 3D displays: Transparent liquid-crystalline cellulose aerogels equipped with carbon dots of high quantum yield. Keynote Lecture. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France.

Nela Buchtova, Tatiana Budtova. Cellulose aerogels and cryogels: structure-properties correlations. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France.

Sonja Kekäläinen, Mari Lehtonen, Kirsi S. Mikkonen. Hexanal-releasing polysaccharide aerogels for extending the shelflife of fruit. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France.

Abdul Ghafar, Pavel Gurikov, Kirsti Parikka, Maija Tenkanen, Irina Smirnova, Kirsi S. Mikkonen. Solvent compatibility for hydro- to aerogel pathway of guar galactomannan. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France.

Sakeena Quraishi, Sven Plappert, Ana Requejo Silva, Maryem Rezki, Thomas Rosenau, Falk Liebner. Preparation of monolithic, stiff and transparent aerogels from solutions of 2,3-dialdehyde cellulose in non-derivatizing ionic liquids. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France.

Sven Plappert, Jean-Marie Nedelec, Falk Liebner. 2,3-Dicarboxyl nano cellulose: a novel source material for transparent birefringent aerogels. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France.

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

materials. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France. (poster)

Kirsti Parikka, Ida Nikkilä, Maija Tenkanen. Chemo-enzymatic oxidation in the production of polysaccharide cryogels. *International Seminar on AEROGELS – 2016. September* 22-23, 2016. Sophia Antipolis, France. (poster)

Falk Liebner, Sven Plappert, Sakeena Quraishi, Thomas Rosenau. First steps towards bio-based static true volumetric 3D displays: Transparent cellulose scaffolds equipped with photon upconverting rare earth metal doped nanophosphors (*uc*-NP). 253rd ACS National Meeting. April 2-6, 2017. San Francisco, CA, USA.

Sven Plappert, Jean-Marie Nedelec, Falk Liebner. 2,3-Dicarboxyl nano cellulose: a novel source material for transparent birefringent aerogels. 253rd ACS National Meeting. April 2-6, 2017, San Francisco, CA, USA.

Maija Tenkanen. Oxidative enzymes – route to functional polysaccharides. 253rd ACS National Meeting. April 2-6, 2017. San Francisco, CA, USA.

Sakeena Quraishi, Sven Plappert, Thomas Rosenau, Falk Liebner. First steps towards bio-based static true volumetric 3D displays: Transparent cellulose scaffolds covalently equipped with photon up-converting $NaYF_4$:Er,Yb nanocrystals. *Material Research Society, Spring Meeting & Exposition*. April 17-21, 2017. Phoenix, AZ, USA.

Maija Tenkanen, Abdul Ghafar, Ida Nikkilä, Kirsti Parikka, Kirsi S. Mikkonen. Enzymatic oxidation enable prodiction of novel light-weight polysaccahride aerogels. *12th CBM.* April 23-26, 2017. Vienna, Austria.

Kirsti Parikka, Ida Nikkilä, Leena Pitkänen, Abdul Ghafar, Tuula Sontag-Strohm, Maija Tenkanen. Polysaccharide aerogels by TEMPO/laccase -mediated oxidation. *19th Eurocarb.* July 2-6, 2017. Barcelona, Spain. (poster)

Maija Tenkanen. Abdul Ghafar, Ida Nikkilä, Jose Martin Ramos-Diaz, Kirsti Parikka, Kirsi S. Mikkonen, Making aerogels from hemicelluloses. *5th EPNOE International Polysaccharide Conference*. August 20-24, 2017. Jena, Germany.

Youssef Akil. Cyclic organic carbonates as hydroxyalkylating reagents for the formation of sophisticated materials from xylan. *5th EPNOE International Polysaccharide Conference*. August 20-24, 2017. Jena, Germany.

Falk Liebner, Sven Plappert, Sakeena Quraishi. Transparent *nf*-2,3-dicarboxyl cellulose aerogels equipped with up-converting lanthanide-doped cubic $NaYF_4$ nanocrystals: New developments towards bio-based true volumetric displays. *19th International Symposium on Wood, Fiber and Pulping Chemistry*. August 30 September 1, 2017. Porto Seguro, Brazil.

Falk Liebner, Sven Plappert, Jean-Marie Nedelec, Harald Rennhofer, Helga Lichtenegger. Strain hardening and pore size harmonization by uniaxial densification: A facile approach towards thermal superinsulating cellulosic aerogels. *19th International Symposium on Wood, Fiber and Pulping Chemistry*. August 30 September 1, 2017. Porto Seguro, Brazil. (poster)

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 CO_2 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.