WoodWisdom-Net Research Programme – Joint Call 4 (2013)

FINAL REPORT

Title of the research project	Tunable lignocellulose-based responsive films (TunableFilms)
Coordinator of the project	Maria Soledad Peresin

BASIC PROJECT DATA

Project period	10.03.2014-09.03.2016
Contact information of the coordinator (institute/unit, address, telephone, fax, e-mail)	VTT Technical Research Centre of Finland Ltd. Biologinkuja 7 P.O.Box 1000, FI-02044 VTT +358 40 720 7047 +358 20 722 7001 soledad.peresin@vtt.fi
URL of the project	N/A

FUNDING

Total budget in EUR	745 837 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)	129 453,62 EUR
Finland Tekes – the Finnish Funding Agency for Innovation Academy of Finland (AKA)	186 192 EUR (100 708 EUR for VTT and 85 484 EUR for Aalto Univ.)
Sweden Swedish Governmental Agency for Innovation Systems (VINNOVA)	150 574.57 EUR
Other funding:	
EcoPlus, Austria	7 191.87 EUR

Berndorf Band, Austria	3 000.00 EUR

PROJECT TEAM (main participants)

Ilari Filpponen, PhD, Docent	M	Aalto University	Finland
Eero Kontturi, Dr., Associate professor	M	Aalto University	Finland
Henniges, Ute, Dr., Assistant professor	F	BOKU University	Austria
Nypelö, Tiina, Dr., researcher	F	BOKU University	Austria
Zweckmair, Thomas, Dr., researcher	M	BOKU University	Austria
Tekla Tammelin, Docent, Princip.scientist	F	VTT Research Centre of Finland, Ltd.	Finland
Maria Soledad Peresin, Dr. Senior scientist	F	VTT Research Centre of Finland, Ltd.	Finland
Christiane Laine, Dr. Senior scientist	F	VTT Research Centre of Finland, Ltd.	Finland
Hannes Orelma, Dr. Senior scientist	M	VTT Research Centre of Finland, Ltd.	Finland
Lars Wågberg, Dr. Professor	M	KTH University	Sweden
Per Larsson, Dr., researcher	M	KTH University	Sweden
Monica Ek, Dr. Professor	F	KTH University	Sweden
Josefin Illergård, Dr. researcher	F	KTH University	Sweden
Jonatan Henschen, researcher	M	KTH University	Sweden

DEGREES (if relevant)
Degrees earned or to be earned within this project.

2016	PhD	F	Elina Niinivaara, year of birth 1984, and year of earning MSc. 2012		Eero Kontturi, Aalto University
2016	Licenciate	M	Jonatan Henschen, year of birth 1989, year of earning MSc. 2013		KTH University Lars Wågberg, Per Larsson, Josefin Illegård, KTH University
2015	BSc	M	Leo Jocher	BOKU University BOKU University	Ute Henniges, Tiina Nypelö,

PROJECT SUMMARY REPORT

The objective of the VTT-coordinated EU-financed Wood Wisdom-net project 'Tunable lignocellulose-based responsive films -Tunable films' was to demonstrate the potential of nanocellulosic and hemicellulose films in relevant packaging solutions and also go beyond the state-of-the-art by exploring the possibilities for completely new materials emerging from the lignocellulosic feedstock. These solutions include novel functional materials such as humidity sensors and smart and bioactive films. The ultimate goal is to construct smart and intelligent packaging solutions, where high oxygen and moisture barrier properties and excellent mechanical performance are combined with antimicrobial feature.
The project ran between February 2014 and May 2016 and the partners involved are well-known research institutions from Finland (VTT Technical Research Centre of Finland and Aalto University, Department of Forest Products Technology), Austria (BOKU University of Natural Resources and Life Sciences, Department of Chemistry, Chemistry of renewable resources) and Sweden Department of Fiber and Polymer Technology). The Finnish partners were financed by the Finnish Academy while BMLFUW and VINNOVA financed the Austrian and Swedish partners, respectively. National and international industrial partners and organizations were CH-Polymers Oy, Picosun Oy, HeiQ, PulPaper Machinery Dick Carrick AB, EcoPlus, Metsä Fibre Oy, and Berndorf Band GmbH.
The project resulted in several scientific highlights. One is a newly developed method, applied for the study of the submicron structure of cellulose nanofibril (CNF) films containing other carbohydrate-based components. It was demonstrated that a uniform chemical composition within the film matrix has positive impact on physical features of the formed films and therefore phenomena behind differences in barrier and strength properties were explained. The method uses PeakForce quantitative nanomechanical mapping (QNM) that is an Atomic Force Microscope (AFM) mode. (VTT/BOKU cooperation)
Another highlight is the detailed investigation of two dimensional assemblies of cellulose-based materials and their response to various external stimuli. Ultrathin films of nanocellulosic materials were constructed on inorganic solid substrates and their response towards humidity were examined using quartz crystal microbalance with dissipation monitoring and environmental ellipsometric porosimetry. These fundamental findings on water/vapour sensitivity ultimately facilitate the exploitation of wood-based materials as water/vapour barriers and sensor elements. The results were included in the doctoral dissertation of Elina Niinivaara. (Aalto/VTT cooperation)
The project also studied the introduction of bioactive components to CNF materials. As an example, bioactivity was demonstrated by conjugating antibodies onto the oxidized films and to carboxymethyl cellulose modified bacterial cellulose tubes. These substrates were shown to selectively capture the target antigens. Moreover, development of the patterned CNF surfaces for microfluidic applications was demonstrated (Aalto). Furthermore, polymer coating methods to embed contact-active antimicrobial polymers in CNF materials were investigated. By proper structural design and polymer adsorption, materials were made that could remove more than 99.9% of the bacteria present in a bacterial suspension could be removed. (KTH)
The project yielded numerous high impact publications as well as results relevant for application in the field of cellulose-based films.

1.1 Introduction

1.1.1 Background

The European forest-based sector is actively seeking innovative product concepts in order to valorise the under-used potential of renewable resources and to create new markets which can support the renewal of the forest-based industry. Several other industrial sectors, including packaging and immunodiagnostics, are searching for sustainable and non-petroleum based material alternatives to substitute e.g. synthetic plastic films. The overall aim of this project is to explore efficient and feasible routes for **extraction**, **fractionation** and **functionalisation** of hemicelluloses and cellulose nanofibrils (CNF) to develop **value-added** materials by exploiting the inherent features (film formation tendency, high oxygen barrier properties, moisture sensitivity and hydrophilicity) of selected plant cell wall components. These pave the way towards new advanced materials such as smart and tunable films with controlled response upon exposure to external stimulii.e. moisture, UV, temperature, presence of biomolecules. Even though the overall aim of the project was to conduct research with very fundamental approach the technological relevance of the research is covered by the contribution of numerous collaborators from small and medium-sized enterprises (SMEs) and industry ranging from material suppliers to machinery and technology suppliers.

1.1.2 Objectives

The objective of the TunableFilms was to demonstrate the potential of film-like structures of wood-derived nanoscaled cellulosic materials and hemicelluloses not only in highly relevant packaging purposes but to go significantly beyond state-of-the-art to explore possibilities for completely new materials solutions from **lignocellulose-based compounds**, including novel functional materials such humidity sensors, and bioactive films for rapid diagnostics and immunoassays. The ultimate goal was to combine the specifically developed **new functionalities** to construct **smart and intelligent packaging solutions** where high oxygen and moisture barrier properties and excellent mechanical performance are combined with antimicrobial, mouldable and responsive features.

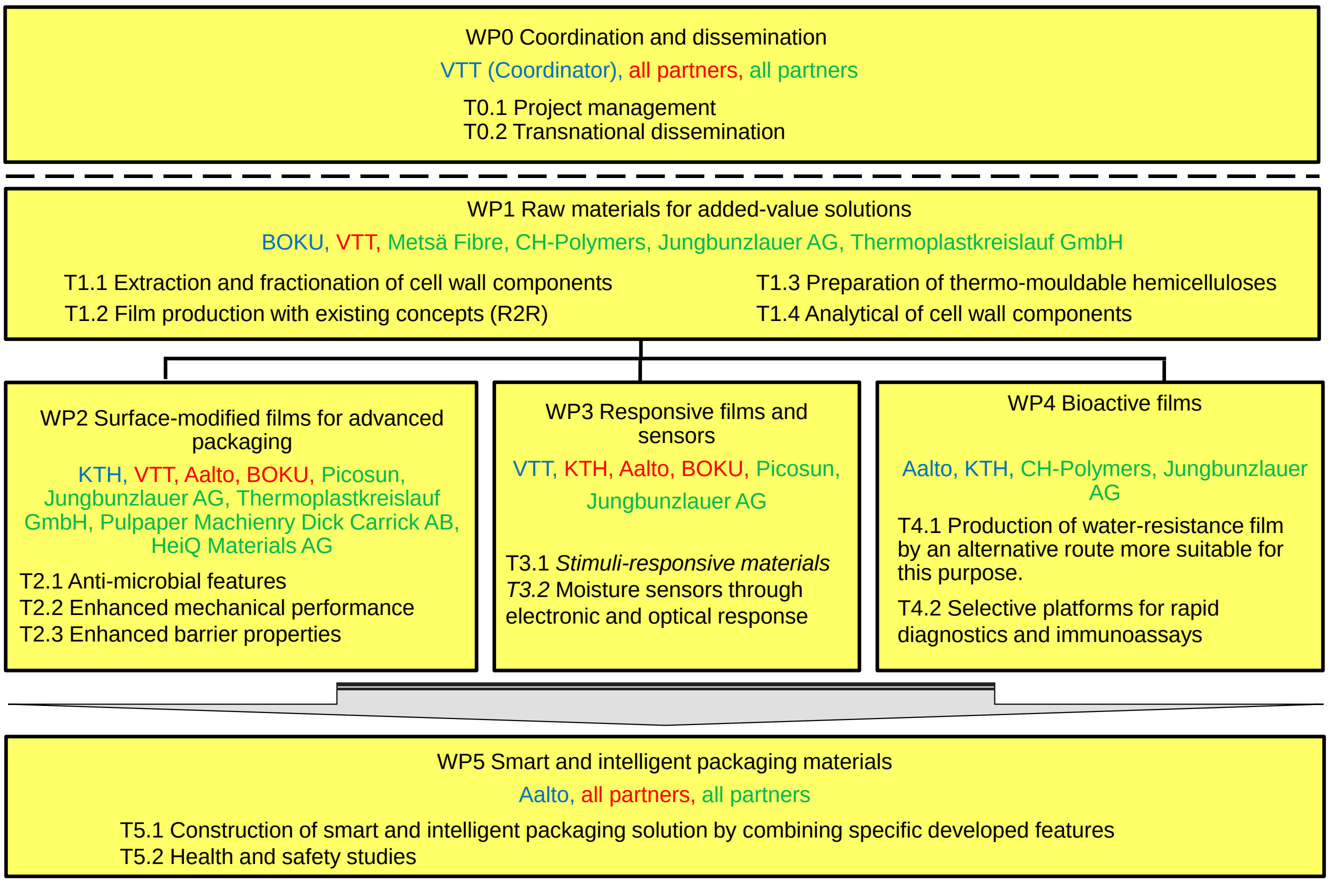
Specific objectives set for this projects were:

- To explore efficient and feasible routes for extraction, fractionation and functionalisation of hemicellulose and CNF in order to develop wood-based value added materials;
- to combine a series of appropriated analytical tools for a thorough and quick characterization of raw materials their functionalisations and link the findings with their mechanical and barrier performance.
- to establish analytical techniques for in-depth characterization of polysaccharide films (FTIR and multivariate data analysis) (WP1)
- to prepare and exploit the films from the selected raw materials utilizing existingtechnologies (VTT SutCo concept and vacuum filtration)
- To develop new functional materials such as responsive films, humidity sensors and bioactive films which could potentially be combined in order to produce smart and intelligent packaging solutions.

1.2 Results and discussion

All raw materials (i.e. cellulose nanofibrils and hemicelluloses; native and modified) were distributed among the partners and films were produced according to the different methodologies. A comprehensive characterization of CNFs and hemicelluloses as well as films thereof was performed (Nuclear Magnetic Resonance, Size Exclusion Chromatography, Atomic Force Microscopy, UV-Vis, contact angle and Infra-Red), combining adhesion and interaction findings to their physical performance. Mechanical, oxygen barrier and light transmission properties of CNF films together with hydroxypropylated hemicellulose derivatives and sorbitol were contrasted to the submicron hierarchy of the films. AFM adhesion mapping was shown to be an efficient tool for investigating the nanostructure of the films according to the distribution of the additives into the nanocellulose film matrix. It was concluded that a uniform chemical composition within the film matrix has positive impact on physical features of the formed films (WP1) (see work packages structure in Figure 1). In order to confer functionality to the films (antimicrobial, fire retardant properties, etc.) while improving their mechanical properties, with the aim of producing advanced packaging solutions, the films surface were functionalized by polymer adsorption, chemical modification, ALD and a combination of those. The challenge of this approach lies in overcoming the rather poor wet strength resistance of CNF films, due to their inherent hydrophilicity. To this end, several approaches were used in order to embed the antimicrobial polymer in the films, such as deep-, spin-, Langmuir-Blodgett, spray-coating (WP2). Increase on thermal stability of the films upon very thin (nanometer scale) ALD coating was demonstrated. The thickness of those ALD layers was characterized using Multi-Parameter Surface Plasmon Resonance. Finally, bioactivity was also demonstrated by conjugating antibodies onto oxidized films (WP4). Ultrathin films of nanocellulosic materials were constructed on inorganic solid substrates and their response towards humidity were examined using quartz crystal microbalance with dissipation monitoring and spectroscopic environmental ellipsometric porosimetry (WP3). A significant mass uptake of water vapor by the films was detected using the QCM–D upon increasing relative humidity. In addition, thickness changes proportional to changes in relative humidity were detected using EEP. Quantitative analysis of the results attained indicated that in preference to being soaked by water at the point of hydration, each individual CNC in the film became enveloped by three monolayers of adsorbed water vapour, resulting in the detected thickness response. These fundamental findings on water/vapour sensitivity ultimately facilitate the exploitation of wood-based materials as water/vapour barriers and sensor elements. UV-responsive films of carboxymethylated CNFs were prepared by incorporating photoluminescent carbon dots (CDs) onto the film's structure. It is noteworthy, that the photoluminescence can be tuned by varying the size of the CDs (WP3). Finally, bioactivity was demonstrated by conjugating antibodies onto the oxidized films and to carboxymethyl cellulose modified bacterial cellulose tubes. These substrates were shown to selectively capture the target antigens (WP4). Moreover, elegant chemistries (thiol-ene and thiol-yne reactions) for creating superhydrophobic CNF surfaces were investigated. It was demonstrated that a controlled patterning of CNF surfaces could lead to the development of microfluidic channels which are desirable in many diagnostic applications (WP4). Ongoing efforts are focused on building project demonstrators, integrating polyelectrolyte adsorption and ALD coating on CNF films in order to improve the films barrier properties, at the time of imparting antimicrobial properties. Simultaneously, we expect to improve CNF film wet strength to certain extent. Compared to the original project plan, due to restrictions on local EU financing, Prof. Markus Biesalski (Darmstard University, Germany) did not became a full partner of the consortium of TunableFilms. However, as planned a freshly graduated D.Sc. from Aalto (Dr. Hannes Orelma) spent a year as a post-doc in his group, and results related to bioactive films will be disseminated as achievements in WP4.

Figure 1. TunableFilm Project Structure (where: **WP Leader**, Research Partner & *SME or Industrial Collaborator*)



First set of trials on combination of ALD-coated, crosslinked nanocellulose films with antimicrobial activity and high barrier performance was performed (WP5). Although preliminary results were promising, due to limited resources towards the end of the project, completion of this task was not fully achieved and it is contemplated to be continued in subsequent projects.

Additionally, the concept was applied to lignocellulosic substrates, beyond the scope of films, and successful antibacterial functionalisation of lightweight aerogels as well as commercial cellulose-based non-wovens were achieve during the project. To show industry relevance, about 15 m of non-woven was also modified roll-to-roll in a pilot machine. By utilising this water-based non-leaching functionalisation technique, companies producing packaging materials, absorbents and non-wovens/wovens can gain competitiveness, or possibly facilitate development of new products.

Health and safety studies of nanocellulosic materials were decided to carry out by intensively following the developments in the state-of-art in this specific research area. This was realised by involving the expertise and views of VTT senior scientists Heli Kangas and Marja Pitkänen in order to evaluate the CNF materials risks in the applications. According to their recent review paper on environmental, health and safety aspects of cellulose nanomaterials and products, no immediate safety threats was not revealed. However, for example chemical modifications have been shown to have influence on nanocellulose toxicity and some indications on the dose-dependent toxicity and inflammatory effects have been detected. It was concluded that the risk assessment for processes and products must be carried out in case-by-case manner.[(*)]

The innovativeness of this project is a result of the combination of modern material science, advanced characterization, surface chemistry and organic chemistry of nanoscaled biomaterials as well as the connections and involvement of industry to address their major technological needs in order to develop novel and cost-effective routes to process and functionalize wood components for suggested value-added products
TunableFilms shed light into the feasibility of lignocellulosic materials as sensor, bioactive, antimicrobial and barrier films, thus further broadening the scope of uses of the next generation multiproduct biorefinery material streams. This is of significant impact as every material fraction of a biorefinery will need to find a feasible enough end use for the whole biorefinery concept to be worthwhile. On the lines of biorefineries, it is noteworthy to mention the forecasted rise in dissolved pulp production in the future, which would also need complementary usage of non-cellulosic materials, such as hemicelluloses. Furthermore, the production of CNF or hemicellulose films, for whichever use, would run the cause of replacing synthetic oil-based films by bio-based ones. Impact on industrial competitiveness and growth is expected to be significant since the project acted along the full width of the value chains. Simultaneously the efficient utilisation and separation processes were exploited (raw material level) and both innovative materials (smart and intelligent packaging materials and (bio)responsive films) and products (humidity sensors and biosensors) were introduced (end-product level). SMEs and industrial partners worked in close collaboration with the research groups and therefore the know-how related to process optimisation and efficient product functionalisation can be expected to increase their turn over and drive the forest industry to utilise their raw materials and sidestreams more efficiently and economically in the future. Linking the research, not only to the traditional pulp and paper applications, but also to novel application areas, can be expected to attract new companies to work with plant-based materials.
Environmental concerns and the requirements for energy and carbon efficiency together with the trend to reduce dependency on fossil feed stocks lead to a necessity to develop new materials that support sustainable development and create novel possibilities to boost bioeconomy. Efficient technological solutions (R2R production and functionalisation of lignocellulosic-based hybrid films) developed in the project can be expected togenerate more value from plant-based materials through new high added value functional materials.. The substitution of non-renewable resources by renewable forest-based solutions lead to the reduction of carbon emissions and waste and simultaneously assure more biodegradability and recyclability (Green and environmental friendly solutions). Nanocellulose and hemicelluloses can be considered as either sidestreams or completely novel raw material alternatives for the forest industry and therefore the utilisation of these natural resources will lead to value added for the forest sector and will have a positive impact on the economy of this industry sector. Breakthrough technological solutions also for other market sectors addressedare diagnostics and sensors. By the achievements generated in the TunableFilms project we expect to see novel breakthrough business opportunities for completely new business sectors. which may even improve the rate of employment which definitely has a positive societal impact.

[(*)] Heli Kangas and Marja Pitkänen. Environmental, Health & Safety (EHS) aspects of cellulose nanomaterials (CN) and CN-based products. Nordic Pulp&Paper Research Journal. 31, 2, 2016, 179-190.

1.3 Conclusions

Among the most important contributions to the state-of-the art from TunableFilms project, we can count the development of a comprehensive characterization of CNFs and hemicelluloses as well as films thereof method. Combining a set of traditional spectroscopic and highly advanced microscopic techniques, it was possible to correlate materials properties to their mechanical and barrier performance, concluding that a uniform chemical composition within the film matrix has positive impact on physical features of the formed films. Such kind of linkage between submicron architecture in the biomaterial film structure has not been previously shown.
It was shown that by direct surface modification of the nanocellulosic film, the moisture sensitivity can be improved. Simple chemical modification via APTES-chemistry generated a cross-linked surface structure which prevented the diffusion of oxygen molecules at high humid conditions and whereby improved the oxygen barrier performance of the free-standing nanofibrillar cellulose film at high humid conditions.

The fundamental findings related to the effect of supramolecular structure of cellulose thin films on water vapour interactions/sensitivity are promising and they facilitate the exploitation of wood-based materials in the sensing field as water/vapour barriers and sensor elements.

Thin inorganic layers deposited via ALD method improved the CNF film thermal stability and thermal tolerance (up to 400 ˚C) which is a required feature in many electronics applications e.g. in thermoelectric materials.

In terms of lignocellulosics modifications, green methods (aqueous reaction media) for the selective surface modification of CNF films were developed. For instance, materials capable to selectively capture target antigens from a solution were prepared. Furthermore, it was shown that click chemistries based on the UV activation (thiol-ene and thiol-yne) could be utilized for designing of the patterned CNF surfaces with microfluidic properties that are prerequisite in many diagnostic applications. Additionally, it was learned that basically any cellulose-based material can be made antibacterial by adsorption of an antibacterial polymer. However, the exact performance of a functionalised material is delicately controlled by material properties such as charge density and structure. The concept of water-based modification can be scaled up.

1.4a Capabilities generated by the project

Even though the project outcomes are still conceptual and findings, especially high end application related findings are yet demonstrated only at the laboratory (highly fundamental TRL stage), all of them are equally relevant to be technologically exploited by the stake-holders, since potential of these applications have been successfully evidenced. Through Ecoplus Network, Bendorf Band (Austria) got involved in TunableFilms, recognizing new business opportunities for machinery manufacturers. Upon incorporation to the advisory board, Bendorf Band gave useful input to the project on viable solutions for bio-based films manufacturing processes and upscaling of those.

1.4b Utilisation of results

The characterization methodology developed in this project is of potential interest for raw materials providers since it gives a good and fast analytical solution to control the quality and potential uses of their materials.
There is both a potential and an interest for antibacterial surfaces, and, from an environmental point of view, contact-active surfaces is a significant improvement from today's commercially available systems that leach some active component. The research conducted as a part of this WoodWisdom project has not only improved the understanding of contact-active systems, but also demonstrated that the functionalisation technique can be used in larger-scale processes. The plan is to continue to pursue a partner who is willing to invest in a process, and obviously take the risk associated with this investment, to further develop the technology from a small pilot scale to an intermediate or full scale.
What it comes to functionalization, developed mild and generic methods for the selective modification of CNF surfaces towards bioactive and responsive films will be further explored in our ongoing projects. It is anticipated

that the findings gathered under this WoodWisdom project will lead to a construction of a CNF-based diagnostic assays that are exploiting the developed concepts for the selective binding and introducing the microfluidic property.

1.5 Publications and communication

a) Scientific publications

1. Articles in international scientific journals with peer review

Example of the format:
Puhakainen T, Li C, Boije-Malm M, Kangasjärvi J, Heino P, Palva ET (2004). Short-day potentiation of low temperature-induced gene expression of a C-repeat-binding factor-controlled gene during cold acclimation in silver birch. Plant Physiol. 136: 4299-4307.

Nypelö, T, Laine, C, Aoki, M, Tammelin, T, Henniges, U (2016). Etherification of Wood-Based Hemicelluloses for Interfacial Activity. Biomac. 17(5): 1894-1901.

Niinivaara, E., Faustini, M., Tammelin, T. and Kontturi, E. Mimicking the Humidity Response of the Plant Cell Wall by Using Two-Dimensional Systems: The Critical Role of Amorphous and Crystalline Polysaccharides, Langmuir, 2016, 32, 2032–2040. DOI: 10.1021/acs.langmuir.5b04264.

Niinivaara, E., Faustini, M., Tammelin, T. and Kontturi, E. Water vapor uptake of ultrathin films of biologically derived nanocrystals: quantitative assessment with quartz crystal microbalance and spectroscopic ellipsometry. Langmuir, 2015, DOI: http://dx.doi.org/10.1021/acs.langmuir.5b01763.

Orelma H, Morales L, Johansson L-S, Hoeger I, Filpponen I. Castro C. Rojas O, Laine J. (2014). Affibody conjugation onto bacterial cellulose tubes and bioseparation of human serum albumin. RSC Advances. 4(93): 51440-51450.

Henschen J, Illergård J, Larsson PA, Ek M, Wågberg L (2016). Contact active aerogels from cellulose nanofibrils. Under revision Colloids Surf., B.

Orelma H., Vuoriluoto M., Johansson L.-S., Campbell J., Filpponen I., Biesalski M., Rojas O. Preparation of photoreactive nanocellulosic material via benzophenone grafting. Submitted RSC Advances 2016.

Nypelö, T, Laine, C, Henniges, U, Tammelin, T. Submicron hierarchy of cellulose nanofibril films with etherified hemicelluloses Ready for submission to Carbohydrate Polymers

Peresin, M.S., Vartiainen, J., Kammiovirta, K., Heikkinen, H., Johansson, L-S., Österberg, M. and Tammelin, T. Strategy for enhanced nanofibrillated cellulose film surface modification. Ready for submission to Carbohydrate polymers.

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

Nypelö T, Laine C, Henniges U, Tammelin T. Interactions of cellulose nanofibrils and modified hemicelluloses in films, 18th ISWFPC Vienna 2015

Nypelö T, Laine C, Henniges U, Konnerth J, Tammelin T. ACS CELL: Division of Cellulose and Renewable Materials 174 - Structure-property relation established by chemical mapping of cellulose nanofibril films containing renewable additives 251th American Society National Meeting and Exposition, San Diego, CA 2016

Henschen J, Illergård J, Larsson P, Ek M, Wågberg L. Antibacterial aerogels from cellulose nanofibrils. 251th American Society National Meeting and Exposition, San Diego, CA 2016

Henschen J, Illergård J, Larsson P, Ek M, Wågberg L. Antibacterial surface modification of nanocellulosic materials. 249th American Society National Meeting and Exposition, Denver, CO 2015

Niinivaara E, Faustini M, Tammelin T, Kontturi E. Water vapor adsorption of 2D polysaccharide films to mimic the plant cell wall International. 251st ACS National meeting and Exposition, San Diego, California, USA, 13.-17.03.2016.

Niinivaara E, Faustini M, Tammelin T, Spirk S, Ehmann H, Kontturi E. Flexibility of cellulose nanocrystal networks in response to water vapor. Annual Seminar of the Department of Forest Products Technology, Espoo, Finland, 12.06.2015.

Niinivaara E, Faustini M, Tammelin T, Spirk S, Ehmann H, Kontturi E. Flexibility of cellulose nanocrystal networks in response to water vapour International 249th ACS National meeting and Exposition, Denver, Colorado, USA, 22.-26.03.2015.

Niinivaara E, Faustini M, Tammelin T, Ehmann H, Kontturi E. Humidity response of thin films consisting of alternating layers of amorphous and crystalline cellulose Forest Products Technology Aalto University Department Seminar, Espoo, Finland, 06.06.2014.

Niinivaara E, Faustini M, Tammelin T, Spirk S, Ehmann H, Kontturi E. Tuning the swelling behaviour of ultrathin cellulose films by controlling the ratio of amorphous and crystalline cellulose. 5th International Colloids Conference, Amsterdam, the Netherlands, 21.-24.6.2015.

Niinivaara E, Faustini M, Tammelin T, Spirk S, Ehmann H, Kontturi E. Flexibility of cellulose nanocrystal networks in response to water vapour. EU Cost Action FP1105 6th Workshop, San Sebastian, Spain, 26.-27.5.2015.

Peresin MS, Nypelö T, Putkonen M, Tammelin T, Rojas O Local thermal characterization of nanocellulose films coated with inorganic thin films, deposited by atomic layer deposition. EU Cost Action FP1105 6th Workshop, San Sebastian, Spain, 26.-27.5.2015.

Tammelin, T. Modified xylan as CNF film softener – a promising material?, Invited talk in Nanocellulose2015, Round Table of Ideas –Workshop, Vienna, Austria, 26-28 September, 2015.

Tammelin, T., Niinivaara, E., Kontturi, E. Quantitative assessment of water interactions of cellulose nanocrystals. 251st ACS National meeting and Exposition, San Diego, California, USA, March 13-17, 2016.

Tammelin, T., Assessment of surface accessibility of nanocellulosic structures using surface sensitive methods, Invited talk in A. Payen Symposium, 251st ACS National Meeting & Exposition, San Diego, CA, United States, March 13-17, 2016.

Jiaqi Guo, Karoliina Junka, Ilari Filpponen, Janne Laine, Orlando J. Rojas. ”Luminescent biohybrid nanomaterials from nanocellulose and carbon dots (CDs)”. 18th International Symposium on Wood and Pulping Chemistry (ISWPC), Vienna, Austria, 2015. Proceedings, pp. 237-240.

Jiaqi Guo, Ilari Filpponen, Orlando J. Rojas. Carbon dot (CD) modified cellulose nanocrystals (CNC) for biosensing and –imaging. 249th American Society National Meeting and Exposition, Denver, CO 2015

Hannes Orelma, Luis O. Morales, Leena-Sisko Johansson, Ingrid C. Hoeger, Ilari Filpponen, Cristina Castro, Janne Laine, Orlando J. Rojas. Affibody functionalized bacterial cellulose tubes for biofiltration applications. 249th American Society National Meeting and Exposition, Denver, CO 2015

Hannes Orelma, Luis O. Morales, Leena-Sisko Johansson, Ingrid C. Hoeger, Ilari Filpponen, Cristina Castro, Janne Laine, Orlando J. Rojas. "Affibody functionalized bacterial cellulose tubes for bioseparation applications". 3rd Iberoamerican Congress on Biorefineries (CIAB), 4th Latin American Congress on Biorefineries and 2nd International Symposium on Lignocellulosic Materials, Concepción, Chile, 2015. Proceedings, pp. 116-117.

Orelma H. UV-crosslinkable nanocellulose with benzophenone grafting. NPD2016, Kumpula, Helsinki

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

Henniges, U, Nypelö, T
Nanofibrillierte Cellulose/modifizierte Hemizellulose – Tunable Films
Biobased Future- Mitteilungsblatt über Biomasse für Energie und Industrie in einer nachhaltigen Wirtschaft Nummer 5 – Jänner 2016

a) Other dissemination

TunableFilms results were featured with a contribution to the "Clusterland Award 2015" (Austria) (May 2015), and also at the VTT ForestTech Newsletter (to be published August 2016)
Upon request visits to some of the industrial partners were arranged in order to discuss project results. Two visits from VTT to Metsä Group were arranged. Additionally, research partners held separate meetings with Bendorf Band (BOKU and VTT), HeiQ Materials, PulPaper Machinery Dick Carrick AB (KTH) and PicoSun (VTT)

1.6 National and international cooperation

Cooperation with project partners
Cooperation with project partners have run smoothly, a good response was obtained when needed and different means of communication have been implemented in order to fulfil a satisfactory communication. Several official Project Group meetings have been held, starting with a kick-off meeting where all the partners and industrial collaborators (also part of the Industrial Advisory Board) were present (Espoo, Mar 2014). Additionally, all the partners have met on two occasions for Project Group meetings: Stockholm Sept 2014, where the attendance of the Industrial Advisory Board was significant, and Denver, USA - Mar 2015, arranged in conjunction with ACS conference). Two other meetings were held between partners and Berndorf Band (VTT and BOKU, Dec 2014 and BOKU, Mar 2015); several teleconferences have been held between Aalto, BOKU, VTT and KTH (Jun-Nov 2014); and also, some working in person-meetings took place in Helsinki (Jun 2014 and Mar 2015) when personnel from BOKU visited VTT to exchange samples and discuss experimental plans. Working meeting to sketch the research plan for WP5 was held in Stockholm (Jun 2015) in conjunction with SWE-FIN workshop "New materials from trees".

In addition, numerous informal meetings were held at different all three locations (Espoo, Vienna and Stockholm) within the different institutions, supported by mail exchange and email/phone contact with other partners when needed.
A final meeting was held at Aalto University in Espoo (Apr 2016) with the participation of all research partners, some of the industrial advisory board members and a representative of the Finnish funding agency (Academy of Finland).
Despite the fact that this project has been considered highly relevant from the fundamental science point of view, the industrial collaborators have been extremely cooperative and involved from the very beginning of the project. MetsäBoard had delivered the starting materials for the project and Picosun and CH-Polymers have been be fully included when integrating all planned features on the films, at the latest ongoing stage of the project (during the execution of the WP5). In addition the involvement of BerndorfBand will bolster up the film manufacturing development.

Cooperation and networking with non-partners
Within BOKU, this project is embedded in an active research environment concerned with polysaccharide modification and analysis that contributes and enables to networking with non-partners. Through EcoPlus (Austria), dedicated to networking, further outreach was achieved, e.g. contribution to the "Clusterland Award 2015" where "Tunable Films" was not nominated, but listed in the category "Research and Development, Innovation". Additionally, Berndorf Band (Austria) started to follow the project.The meeting between VTT, BOKU and Berndorf Band (Dec 2014) was followed by visit of BOKU representatives to Berndorf Band facilities in Berndorf, where common interests and main achievements on the CNF field were discussed. It is worthwhile to mention the research collaboration with Université Pierre et Marie Curie, Laboratorie Chimie de la Matiere Condensée – Collège de France (Prof. Marco Faustini) in the area of water vapour uptake investigations utilising spectroscopic environmental ellipsometric porosimetry. This cooperation resulted in thorough fundamental knowledge on water/vapour sensitivity of wood-based materials which facilitate their exploitation as water/vapour barriers and sensor elements. Two joint publications are ongoing.[*] In collaboration with TECNALIA (Spain), strategies for imparting intumescent properties to CNF films by depositing different compounds via layer-by-layer assembly and atomic layer deposition (ALD) were studied. Additionally, direct evidence on ALD thickness development was investigated using surface plasmon resonance in cooperation with Bionavis Oy. A collaboration (3 months student research visit) with Karlsruhe Institute of Technology (KIT) resulted in an improved knowledge in UV-induced click chemistries that were utilized for the creation of patterned CNF surfaces.