HEMICELL

FINAL REPORT

Title of the research project	**Wood based chemicals, in particular chemical modified hemicellulose, used as functional additives to enhance the material properties of cellulose esters**
Coordinator of the project	Thomas Wodke

BASIC PROJECT DATA

Project period	01.04.2014-31.03.2017
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URL of the project	http://www.hemicell-project.com

FUNDING

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Public funding from WoodWisdom-Net Research Programme:	Total funding granted in EUR by source:
Austria Federal Ministry of Agriculture, Forestry, Environment & Water Management (BMLFUW)	-

<u>Finland</u> Tekes – the Finnish Funding Agency for Innovation Academy of Finland (AKA)	 -
<u>France</u> Ministry of Agriculture, Fisheries and Forestry Resources (MAAF) French Environment and Energy Management Agency (ADEME)	 - 261 871 EUR
<u>Germany</u> Agency for Renewable Resources (FNR)	 452 713 EUR
<u>Ireland</u> Department of Agriculture, Food and the Marine (DAFM - CoFoRD Programme)	 -
<u>Norway</u> The Research Council of Norway (RCN)	 -
<u>Slovenia</u> Ministry of Education, Science and Sport (MIZS)	 -
<u>Sweden</u> Swedish Governmental Agency for Innovation Systems (VINNOVA)	 343 .223 EUR (3 299 732 SEK)
<u>Switzerland</u> The Commission for Technology and Innovation (KTI; in the Federal Department of Economic Affairs FDEA)	 -
<u>United Kingdom</u> The Forestry Commissioners (FC)	 -

Other public funding:

There was no other public funding in the HEMICELL project.

Other funding:

Södra Innovation, Sweden 60 638 EUR (582 975 SEK)

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

Year	Degree	Sex (M/F)	Name, year of birth and year of earning M.Sc., D.Sc., etc. Degree	University	Supervisor of thesis, supervisor's organization
2015	M.Sc.	F	Karin Sahlin 2015	Chalmers University of Technology, Sweden	Fredrik Berthold, Innventia Espen Ribe, Södra
2015	M.Sc.	F	Li Hong Chew, 2015	INSA Lyon, France	Fredrik Berthold, Innventia
2015	M.Sc.	M	Christophe Berto, 2015	Université de Nice Sophia Antipolis, France	Dr. Patrick Navard, Dr. Tatiana Budtova, Dr. Thibault Cousin, Mines
2016	M.Sc.	M	Otto Lintunen, 2016	Aalto University, Finland	Prof. Jukka Seppälä, Aalto University Instructors: Dr. Tatiana Budtova, Dr. Patrick Navard, Mines

PROJECT SUMMARY REPORT

Cellulose esters were among the first developed plastics. With increasing awareness about the benefits of bio-based feedstock and the regional added value, these materials have come into the market focus again. Some of the current drawbacks of cellulose esters are the need for plasticizers, the low bio-based content and their high melting point. The main goal of the HEMICELL project was the use of wood-based chemicals, in particular chemically modified hemicellulose, as plasticizers and also the use of functional additives to enhance the material properties of cellulose esters.

A study of pulping process conditions for an optimal extraction of hemicellulose from wood was conducted. As a result, two different hydrolysates were produced for preliminary tests. Difficulties in the scale-up of the process were overcome. A higher amount of hardwood hemicellulose was produced and used for further chemical modifications to increase the compatibility of the hemicellulose with cellulose esters.

Different routes for acetylation of the hemicellulose were tested. The method using DABCO/acetic anhydride was identified as the most promising one. For scale-up the DABCO method was modified to successfully produce acetylated hemicellulose. Beside the acetylated hemicellulose, benzoylated, aminated and levulinated hemicelluloses were produced in laboratory scale.

The samples of modified hemicellulose were compounded in different proportions with glycerol triacetate (GTA) and cellulose acetate (CA) or cellulose acetate butyrate (CAB) in mini-extruder and internal mixer, respectively. The samples of CA with 10% of acetylated hemicellulose produced on the mini-extruder showed a lower glass transition temperature (T_g 144 °C) than pure CA (T_g 200 °C). Due to thermal degradation of the acetylated hemicellulose, it was not possible to compound it with CA and CAB in the internal mixer. Tests with benzoylated hemicellulose on the mini-extruder were promising. This modified hemicellulose acts as plasticizer in CA (T_g 121 °C). Due to the small amount of material the tests on internal mixer or compounding line were not possible. More research to identify possible application fields for modified hemicellulose is necessary.

The calculated prices for dried and modified hemicelluloses are within normal ranges for fine chemicals. The cost estimation is based on assumptions made by the project partners for water and energy demand. Higher demands or higher energy costs for drying steps would increase the costs.

1.1 Introduction

1.1.1 Background

There is an increasing demand for bio-based materials in our societies. The shortage of oil and the political uncertainties regarding the control of oil resulting in fluctuating prices as well as the increasing levels of carbon dioxide resulting in the greenhouse effect and global warming are the two main societal driving forces. The decreased use of printing paper resulting in the closure of paper mills and unemployment is another driving force. The forest industry needs to find new markets for its raw material. The pulp and fibre industry has recently started developing new pulp qualities and new energy efficient processes, pursuing new side streams in the pulp mills. Some of those side streams are used mainly for energy production or fermentation to alcohol and may contained hemicellulose, hence could be use in the HEMICELL project to prepare new materials.
Among the first developed plastics were the cellulose esters i.e. cellulose acetate (CA). Their development stopped in the late 1960s when fossil based polymers were coming on the market with low prices, wide variety, ease of processability and good properties. Still CA is an excellent plastic and with the above mentioned discussions about bio-based feedstock and regional added value, it comes in the market focus again. Some of the current drawbacks of CA and other cellulose esters are the need of plasticizers, the low bio-based content, and their high melting point. By developing and using new chemically modified hemicellulose and other wood-based chemicals, the HEMICELL project team wanted to overcome several of these disadvantages.

1.1.2 Objectives

The aim of the research project is the use of wood-based chemicals, in particular hemicelluloses, as functional additives to improve the properties of cellulose esters. It is also intended to decrease the melting point of cellulose acetate (CA) to allow the use of CA as a matrix material of wood or natural fibre reinforced plastics.
Hemicelluloses are side stream molecules from wood pulping and are converted into higher quality products within this project. The hemicelluloses dissolved in the wood hydrolysate are fractionated by ultrafiltration. The influence of the process conditions in the hydrolysis and the ultrafiltration on the molecular properties of the hemicelluloses is the main difficulty in this project. The molecular weight of hemicellulose decreases with process time and temperature. The aim of the HEMICELL project is to isolate and modify hemicellulose. Several modified hemicelluloses are tested as plasticizers in CA. Thus, the most suitable hemicelluloses are to be found to produce new, improved CA compounds.

1.2 Results and discussion

At the beginning of the project a study of raw materials and pulping process conditions for an optimal extraction of hemicellulose from wood was conducted by Södra. The aim was the understanding of how hemicellulose content, composition and form vary with different prehydrolysis condiditions and raw materials (spruce, pine and birch) in order to supply optimal hemicellulose containing liquors for further processing by other partners. As an example of the main results Figure 1 depicts the change of total xylan content and monomer content in birch prehydrolysis liquor with time and temperature during prehydrolysis at liquor to wood ratio of 6:1.

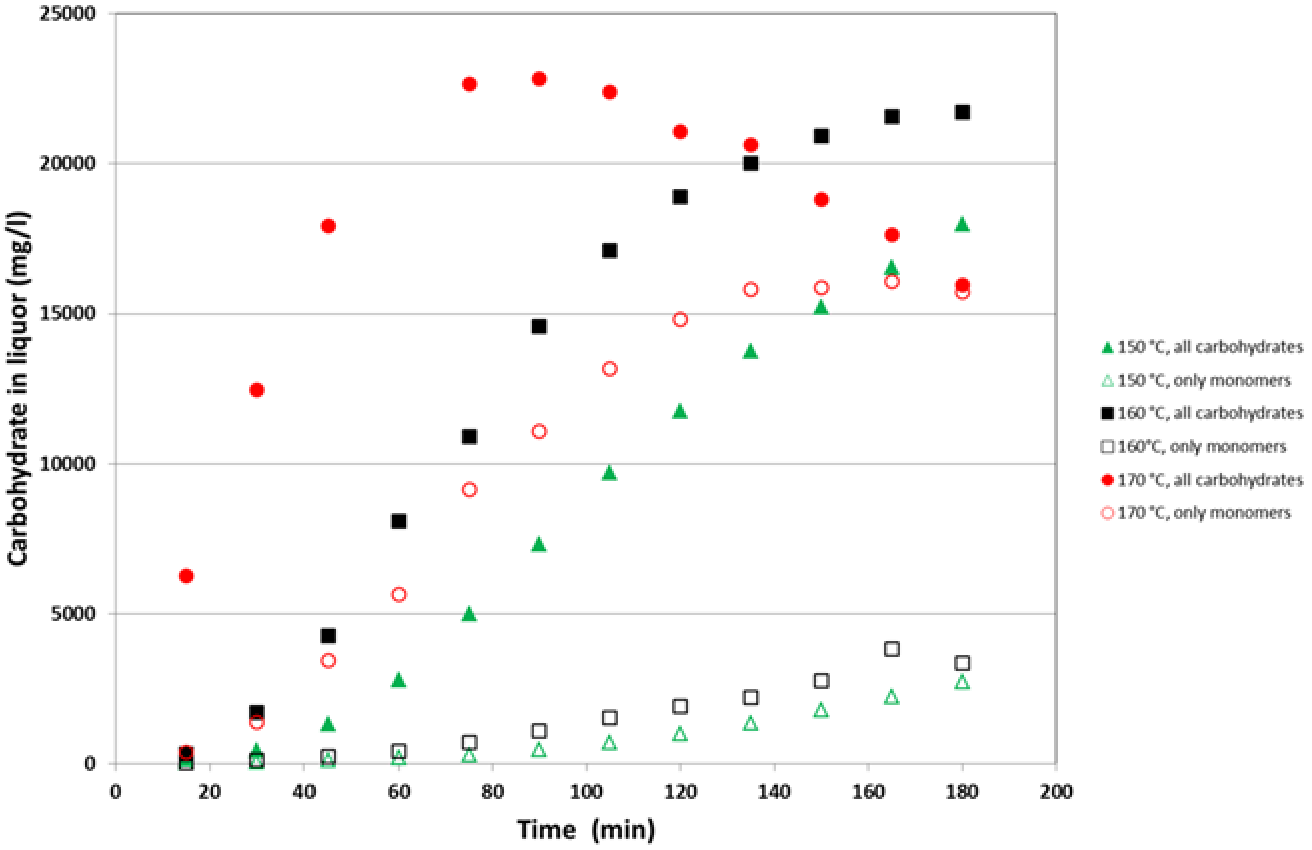

Figure 1: Xylan content in prehydrolysis liquor at different temperature and residence time.

As a result, Södra produced two different optimized hydrolysates for the chemical modification and send them to Innventia and OrganoClick.

The hemicellulose containing hydrolysate had to be dried before the modification. Innventia tested several methods for drying. A combination of evaporation, rotary evaporation and vacuum oven turned out as the most effective way. For acetylation of the hemicellulose different routes were tested by Innventia. The method using DABCO/acetic anhydride was identified as the most promising one.

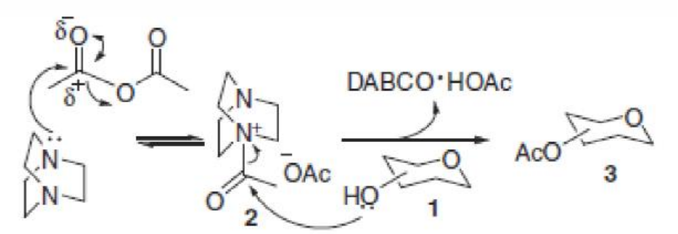

Figure 2: Acetylation of hemicellulose with DABCO/acetic anhydride

Small amounts of acetylated hemicellulose were produced by Innventia in the first year and sent to Mines and UMSICHT. For the scale-up the DABCO method cannot be used due to safety risks. Innventia modified the DABCO method together with SP Process Development, a research institute with focus on scale-up verification. After overcoming several problems Innventia and SP Process Development produced higher amounts of acetylated hemicellulose in the last year of the project.

At OrganoClick three different functionalities (alkylamine functionality, vinyl functionality and biopolymer based functionality) were linked to hemicellulose, but the results were inconclusive. Despite this, the fractioned low molecular weight hemicellulose produced within the project was interesting due to its potential as plasticizer, considering the required melting point and the possibility to have molecular diffusion of the modified hemicellulose through the polymeric matrix. Therefore, OrganoClick focussed on other functionalities: amination, benzoylation and levulination.

Amination of the low molecular weight fractioned hemicellulose hydrolysate was performed using APTES in alkaline conditions.

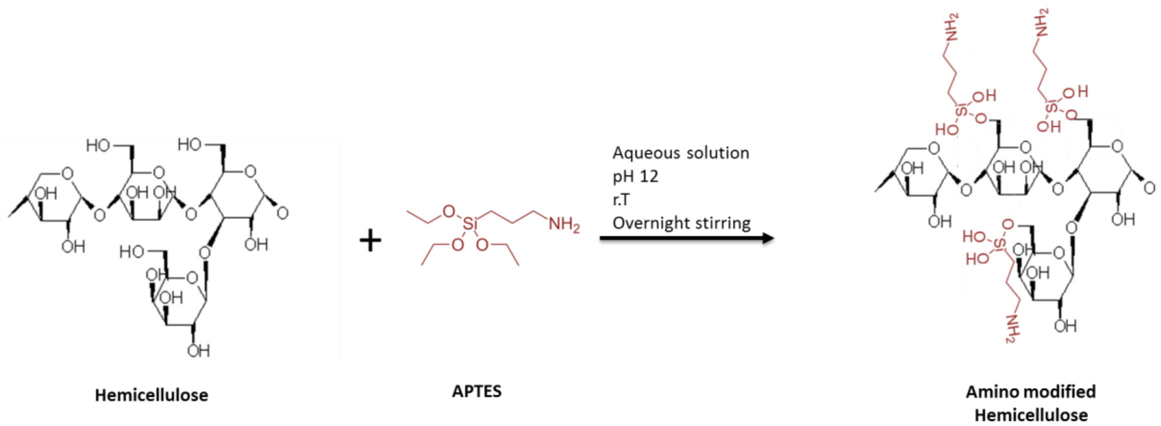

Figure 3: Amination of the hemicellulose using APTES at alkaline condition

The product obtained from this reaction was a viscous black liquid with rather hydrophilic character (moderate solubility in water and not soluble in acetone).

Benzoylation and levulination was also successfully performed. Levulination was performed via dehydration/esterification reaction under the conditions illustrated in Figure 4.

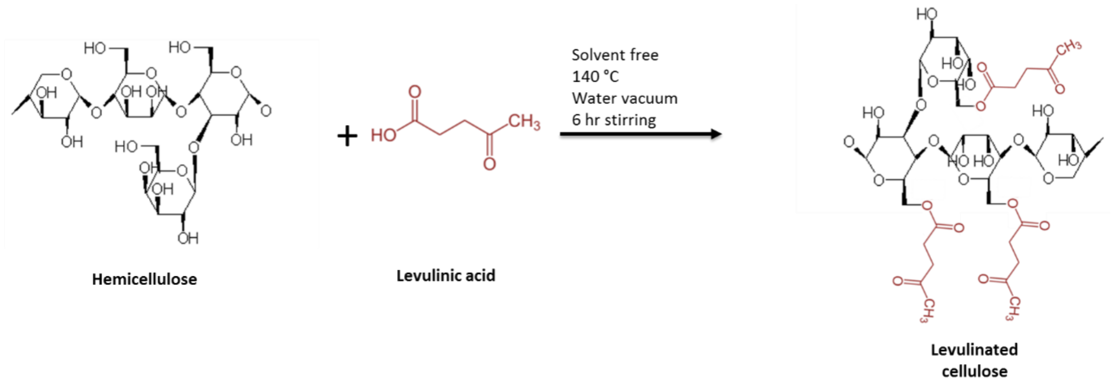

Figure 4: Schematic representation of the levulination reaction

Purified/dried levulinated hemicellulose was a viscous dark brown liquid at room temperature with hydrophobic character. Samples of the aminated, benzoylated and levulinated hemicelluloses were sent to Mines for compounding tests.

Before the compounding tests, the influence of the scale and type of processing tool on plasticization of CA was tested by Mines and Fraunhofer UMSICHT. Four processing tools (two twin-screw extruders, one being a mini-extruder, and two mixers) were used to prepare plasticized CA with 20 wt% of glycerol triacetate (GTA). The goal was to deduce if the scale of the processing tool influences the dispersion of the plasticizer as estimated by the thermal, rheological, and mechanical properties of the obtained materials. The amount of polymer used ranged from 5 g for mini-extruder to a 10 kg/h for pilot-scale extruder. The specific mechanical energy was used to compare the thermal, rheological, and mechanical properties of CA obtained with the four processing tools using different processing conditions. No differences were found in the glass transition temperature between the compounds processed with different tools. The rheological studies showed differences in terms of specific mechanical energy rather than as of the tool size. It was found, that the larger was the tool, the higher were the Young's moduli. This was ascribed to an overall better distribution and dispersion of the plasticizer. However, these variations were not significant, showing that small laboratory processing machines can prepare thermoplastic compounds with similar properties as pilot scale extruders, at least in what concerns CA.

At Mines all the modified hemicelluloses were studied first by differential scanning calorimetry (DSC) to assess their stability. After the measurements, the modified hemicelluloses were mixed with cellulose acetate. The decrease of the glass transition temperature in the compounds was studied by DSC. The test specimens were prepared from processable modified hemicellulose CA compounds and their mechanical properties were investigated.

The materials received in the first year (fractionated hemicelluloses) were suitable as plasticizers but were difficult to process. The samples sent in the second year were used to prepare formulations with up to 20 % acetylated hemicellulose. However, it was not possible to inject materials with high amounts of acetylated hemicellulose. Compounds with acetylated hemicellulose had a higher Young's modulus but were more fragile and had a higher glass transition temperature (T_g). Acetylated hemicellulose was a less efficient plasticizer than the ones typically available.

Tests with the benzoylated hemicellulose on mini-extruder were promising. This modified hemicellulose acts as plasticizer in CA (T_g 121 °C). Levutinated hemicellulose could also be a potential plasticizer when dissolved in a common solvent (acetone) with CA.

At Fraunhofer UMSICHT, the first amounts of acetylated hemicellulose from Innventia were compounded with CA and CAB in various proportions in a rolling mill. The CA samples show a drop in the T_g from 162 °C (reference sample) to 151 °C with the addition of 10% acetylated hemicellulose and to 141 °C. with 20% compounds. According to these results acetylated hemicellulose can be classified as an additive with softening effect. In contrast to the CA samples, acetylated hemicellulose has no significant effect on the T_g of the CAB compounds.

The acetylated hemicellulose supplied by Innventia from the scale-up was thermally unstable and therefore not suitable for compounding with CA (see Figure 5). Compounding with CAB and polylactic acid (PLA) was successfully due to the lower processing temperatures. However, a softening effect of the hemicellulosic derivatives was not observed for these polymers.

Figure 5: Thermal degradation during compounding of CA/GTA with acetylated hemicellulose in the internal mixer

Because of the thermal instability of the acetylated hemicellulose, FKuR Kunststoff GmbH was unable to carry out the scale-up compounding tests and the production of the demonstrators.

The partners decided to use CA fibers as reinforcement of CA (with GTA as plasticizer), so called “all cellulose based composites”, as alternative solution in the project. The objective was to prepare all-cellulose acetate composites. Two routes were studied by Mines. The first one is the solvent route, in which CA fibers were exposed to different acetone and water combinations to make all CA composites. This route had several challenges and the hardest to overcome was the physical barrier that the fibers made. The solvent was not able to penetrate inside the material leaving the inner part intact without a proper matrix. To overcome this challenge, vacuum processing and stirring were tried, both attempts without success. The second approach for making all-cellulose acetate composites was by melting a matrix. In this approach the matrix was CA plasticized with triethyl citrate or GTA and then mixed with aligned CA fibers and compacted with a hot press. . With fiber contents larger than 20%, impact strength is enormously increased, up to 37 kJ/m^2 from 2-5 kJ/m^2 for the neat matrix. All other mechanical properties are left as the ones of the matrix.

FKuR ordered regenerated cellulose fibres for scale-up tests because CA fibres were not available in sufficient amounts. The results of the compounding of CA compounds with regenerated cellulose fibres (Figure 6) show that no technical or economic value could be generated. In addition, the optics and haptics of the material were not appealing (no natural fibre optics, only brown colouring). The high material price of the fibres (~ 3.00 €/kg) and the difficulties by compounding increased the cost of fibres compounds. A certain added value was generated by the increased bio-based content.

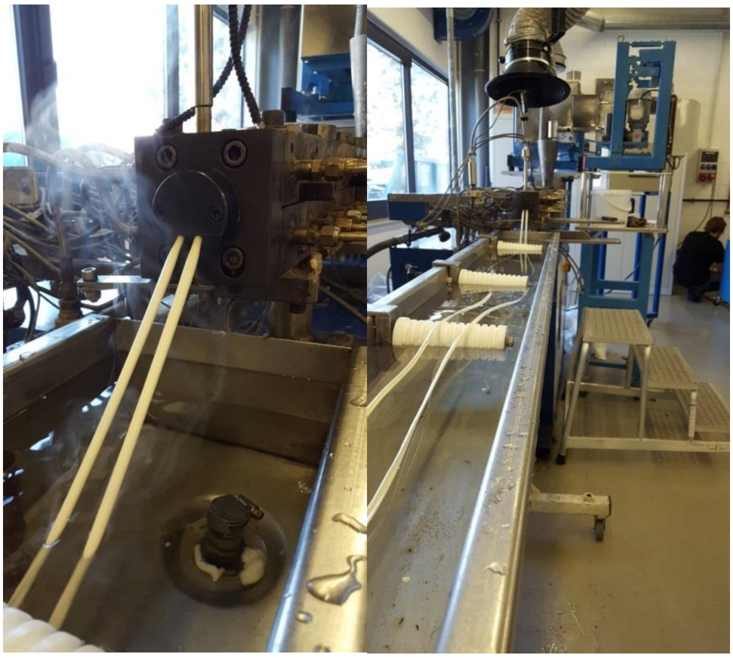

Figure 6: Compounding of CA/GTA with 10 % regenerated cellulose fibre

The development process was framed into an ecological and techno-economic assessment and a market study.

Scenarios to be included in the study were determined and checked. Data collection was completed regarding the environmental aspects of the effects on the pulp mill when extracting hemicellulose, instead of incinerating it in the recovery boiler,. Due to thermal degradation of the acetylated hemicellulose, compounding with CA and CAB on internal mixer was not successful. Compounding tests with benzoylated and levulinated hemicellulose could not be performed. Both did affect the LCA studies, the collection of environmental data from the processes implemented in the other work packages and the analysis of the environmental performance in different scenarios.

In the market research, nova Institute identified the following possible applications for unmodified and modified hemicelluloses:

- Hemicellulose: The market prices for hemicelluloses currently lie at 1 to 35 €/kg (glucomannan). The higher the price, the higher purities. Potential markets are the use as emulsifier, thickener, appetite suppressant and as absorbent. Further options are in the chemical industry, such as in furan chemistry, but for these applications lower prices need to be achieved.
- Acetylated hemicellulose: Possible applications are as additives in the field of paints and lacquers.
- Levulinated and alkyaminated hemicellulose: Areas of application are hitherto unknown.

The prices for dried and modified hemicelluloses calculated in the technical-economic evaluation are in the normal range for fine chemicals.

- Dried hemicellulose: 1 600 €/t
- Dried acetylated hemicellulose: 7 800 €/t
- Dried acetylated and levulinated hemicellulose: 7 900 €/t
- Dried acetylated and alkyaminated hemicellulose: 3 400 €/t

The market price for glycerol triacetate (GTA), which is typically used as a plasticizer in CA, is 1 500-2 000 €/t and thus in a range which is achievable for the dried hemicellulose. The cost estimation is based on assumptions made by the project partners for water and energy supplies. However, with higher energy costs and a higher energy requirement, the costs can be considerably higher and in individual cases exceed the amount of 10 000 €/t.

1.3 Conclusions

Several acetylated and modified hemicellulose samples were synthesized and analysed. The using of acetylated hemicellulose as plasticizer for CA as main goal was not achieved. Acetylated hemicellulose could not be compounded with CA due to thermal degradation. Compounding with CAB and PLA was successful due to the lower processing temperatures. However, no softening effect of the acetylated hemicellulose was observed in these polymers.

Other modifications of hemicellulose like the prepared functionalized low molecular weight derivates using benzoyl chloride and levulinic acid have shown promising results, meaning that they are no longer water soluble, still liquid at room temperature and could hence be use as potential plasticizers in a hydrophobic matrix.

1.4a Capabilities generated by the project

This project has generated know-how to functionalize hemicellulose. It has shown that transformations are indeed possible using quite conventional synthetic procedures. Nevertheless, scale-up is required to determine the feasibility of the transformation from an economical and environmental point of view.

The results from the comparison of the different processes from mini-extruder to pilot-scale twin-screw extruder can be used in other research projects. Beside this, the collected experience in the processing of powdery unmodified and modified hemicellulose will help to develop other compounds with powdery raw materials.

Nova Institute gained experience in the application of the New Methodology for Techno-Economic Evaluations of Innovative Industrial Processes (nTEE) developed at the institute, which can be used in subsequent projects and connection projects.

1.4b Utilisation of results

The results of the project are interesting and some of the partners intend to continue the exploration of wood-based chemicals as performance chemicals in cellulosic esters. Albeit the HEMICELL project did not result in market ready additives, the results are encouraging and the estimated production cost is reasonable. More time needs to be spent on scale-up and further analyses of the effects of functionalized hemicellulose in polymer matrices. The overall approach still fits well into the strategy of a wood-based biorefinery, but financing for further research has to be organized.

On the basis of the work within the project, contacts were made with companies from different branches of industry. In addition, networks with different research facilities have been set up. Further joint research projects are conceivable here.

Due to the technical difficulties within the project and since the goals were not achieved completely, the project partners from industry took a stand against detailed publication of the project results.

1.5 Publications and communication

a) Scientific publications

1. Articles in international scientific journals with peer review

Cousin, T.; Berto, C.; Budtova, T.; Kurek, J.; Navard; P. (2016): Influence of the Scale and Type of Processing Tool on Plasticization of Cellulose Acetate. Polymer Engineering and Science. 57, 563–569 (2017) DOI: 10.1002/pen.24452

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

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3. Articles in national scientific journals with peer review

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

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5. Scientific monographs

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

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a) Other dissemination

Presentation in international conferences:

Cousin, T.; Berto, C., Budtova; T.; Navard, P.: Biocomposites based on plasticized cellulose acetate and short miscanthus stem fragments. EPNOE 2015 Conference, Varsovie (Pologne) 19-22 October 2015

Lintunen, O.; Budtova; T.; Navard, P.: All cellulose acetate composites", XIIth French-Romanian Polymer Meeting, Sophia Antipolis, France, 5-7 September 2016

Launch of project website (www.hemicell-project.com) on 2nd March 2015.

Distribution of the project flyer on:
- European Bioplastics Conference (Berlin, October 2015)
- EFIB – European Forum of Industrial Biotechnology (Brussels, October 2015)
- Bioeconomy Investment Summit (Brussels, November 2015)
- BMEL-Konferenz „Innovative biobasierte Produkte: Chancen für einen verstärkten Einsatz erneuerbarer Ressourcen“ (Berlin, November 2015)
- Microplastic in the Environment – Sources, Impacts and Solutions (Cologne, November 2015)
- 6th WPC and NFC Conference (Cologne, December 2015)
- CLIB International Conference 2016 (Düsseldorf, January 2016)
- 9th International Conference on bio-based Materials (Cologne, April 2016)
- Bio-based Start-up Day (Cologne, April 2016)
- BIO World Congress on Industrial Biotechnology (San Diego, April 2016)
- BioBased Products / Bio-based Chemicals World (Amsterdam, Mai 2016)
- European Bioeconomy Congress Lodz (Lodz, October 2016)
- K-Messe (Düsseldorf, October 2016).

Discussions with potential stakeholders, for example on kick-off events of various national and international projects.

1.6 National and international cooperation

The project partners met every 6 months to discuss technical and administrative matters. For the exchange of files and information between the partners the project coordinator created an internal website. The partners exchanged information and discussed technical tasks at the meetings and in addition during bilateral meetings between some of the partners, in telephone conferences, and via e-mail. The needs of the different processing technologies were communicated and broadened the expertise of the partners. It can be concluded that the HEMICELL project was not only bringing together partners from three European countries; it has to be emphasized that partners from very different industries worked together aim-orientated sharing information and experiences on their raw materials and processing technologies.

For the trials several material samples were shipped between the partners. The needed information about material data and test results were exchanged via e-mail or phone so that the whole consortium was continuously informed about the advance of the project. Intense discussions about the intermediate results were held in the meetings. The experimental plan was adapted and the next tasks were defined. The cooperation between the partners during the project was efficient and aim-orientated.

Innventia modified the acetylation process together with SP Process Development, a research institute with focus on scale-up verification. After some successful pre-trials SP Process Development carried out the scale up of the acetylation of hemicellulose.

The technical efforts that the project required could not have been taken by one of the members alone or a smaller group of participants, even if they had been supported by national funding. Involving renowned R&D centers and industrial partners from several disciplines contributing highly qualified technicians and scientists was necessary to pursue the project. The Scandinavian partners had special knowledge in wood and pulp. The French partner is one of the leaders in cellulosic materials processing in Europe and the German partners are experts in compounding and in market studies.

Each partner has its own large national and international network that will be activated to develop follow-up projects, in particular between the industrial sectors and the regions involved in the project.