Processes for nanocellulose composite manufacturing (PRONANOCELL)

Processes for nanocellulose composite manufacturing, PRONANOCELL

Title of the research project	**[Title]**
Innventia	Göran Flodberg
Coordinator of the project	[Full person name]

BASIC PROJECT DATA

Project period	01.01.1914-07.31.1917
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URL of the project	http://[-]

FUNDING

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Sweden Swedish Governmental Agency for Innovation Systems (VINNOVA)	280338 EUR

PROJECT TEAM (main participants)

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PROJECT SUMMARY REPORT

The PRONANOCELL project has aimed at developing new environmentally friendly and light-weight nanocomposites by utilizing water based processing methods with no harmful chemicals being used. This is of course a great challenge since the nanocomposite should constitute a blend of hydrophobic polypropylene or polyethylene blended with the hydrophilic character of cellulose which has low compatibility with hydrophobic polymeric matrices. Another challenge was how to get rid of water to perform hot extrusion of the composite. Dewatering was solved by the processes used, the Wet Web comingling process, the DEVO process and the modified Kyoto process by Innventia. Agglomeration occurred verified by microtomography, but not in all cases. The mechanical test results show that nanocellulose composites can be an alternative to glass fibre reinforced composites. It was also shown that it is possible to perform foam injection moulding with good results.

1.1 Introduction

1.1.1 Background

The PRONANOCELL project aims at developing new light-weight nanocomposites derived from green resources. The main components will be nanofibrillated cellulose (NFC) with excellent mechanical properties from wood fibres and traditional plastics such as polyethylene (PE) and polypropylene (PP). The fibrils have a width in the nano scale, 5-60 nm and a length up to several µm. This result in a very high aspect ratio and together with the high stiffness (140 GPa) and light-weight character due to the low density (1.5 g/cm^3). Consequently, nanocellulose is emerging as one of the most promising sustainable building blocks for future biocomposites in sectors like rigid packaging, automobiles and building/construction.

1.1.2 Objectives

- A new extrusion method for *in situ* formation of NFC from wet pulp in an extruder, which is subsequently compounded into a composite material and pelletized for further processing with injection moulding.
- A process for comingling of NFC, wood fibre and plastics during wet conditions, followed by a paper-based process, where a composite sheet is formed for further processing with compression moulding.
- A uniform dispersion of NFC in the polymer matrix must be obtained
- The mechanical properties of the composite should be maximized
- The interfacial strength between NFC and the matrix should be optimal
- Suitable chemical adjuvants for the enhancement of the compatibility between NFC and the matrix will be investigated

1.2 Results and discussion

Initially, there was no method set-up for processing nanocellulose composites either at Elastopoli or Innventia or any place in the world. The only serious paper in this field was published by Kyoto University and Suzuki et al. However, after several experiments it was possible to test a Wet Web comingling process and a devolatilization process (DEVO (Table 1, figure 1-2) and (Table 2, figure 3, 5-6). To become an alternative to glass fibre filled polypropylene used today in inner doors for Volvo Cars the target for Youngs modulus was 5 GPa. Was this possible to reach? During the autumn 2016, new batches reach the target of 5 GPa for Young modulus and it was approved by Volvo Cars. This was a kind of quality index set up by Volvo Cars. Concerning the third method, more suitable for small particles of granular material and for mixtures too difficult to dewater, this method is more suitable. Another positive feature of this method, it need only on extruder, or two extruders connected in series. However, it was found out by following Suzukis method it did not work out at all. A modified process was necessary to develop at Innventia (patent will be investigated) and it worked out very well with good mechanical test results obtained (Table 3). The granular material obtained was not free from agglomerates as visible in figure 7.

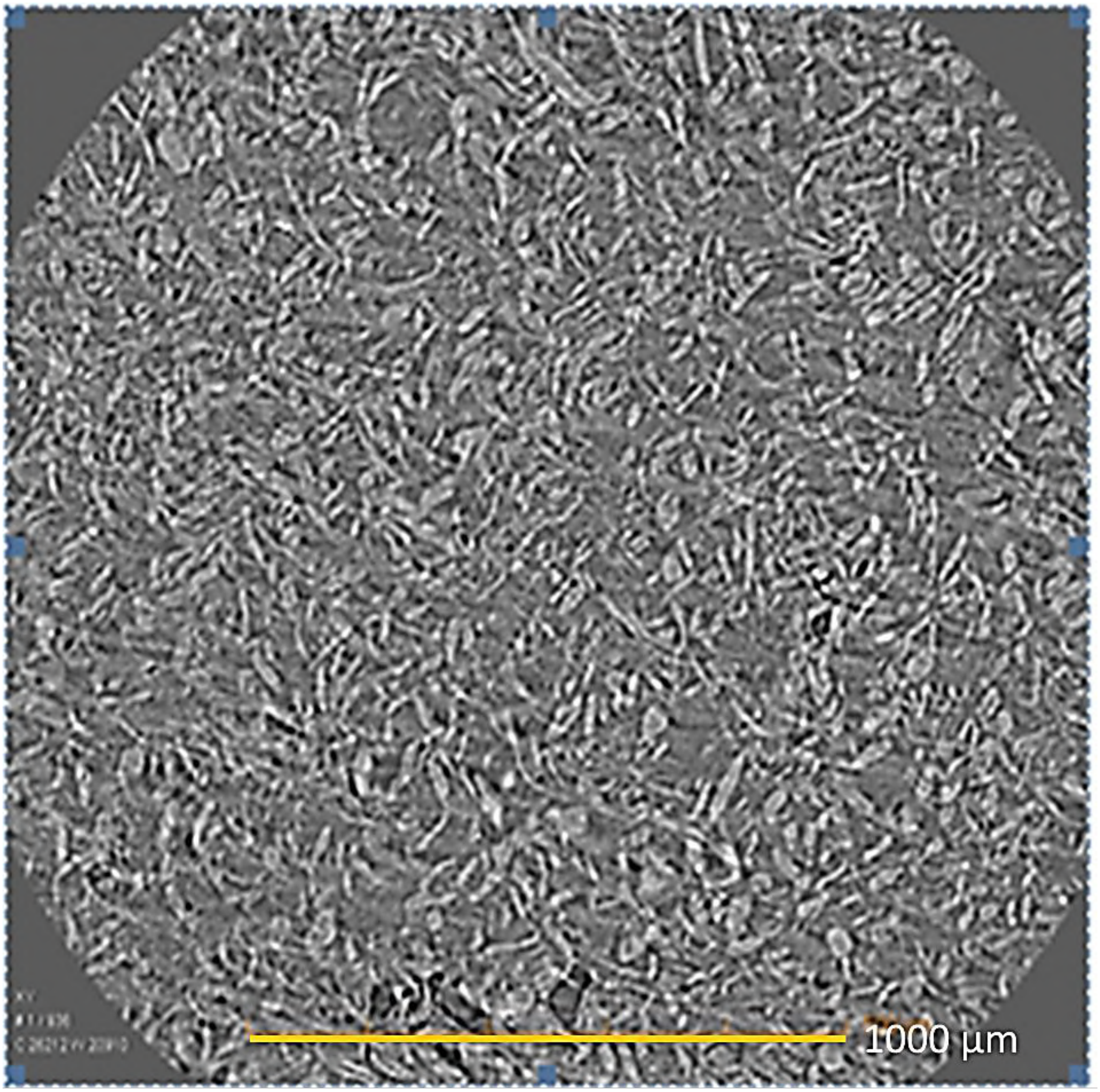


Figure 1. Composite Q1A. XY plane from microtomography (20x). Wet web comingling process followed by extrusion. Composite Q1A: Granular PP 47%, NFC 25%, pulp fibre 25%, SCONA TPPP8112FA 3%. Cellulose pulp fibres are well distributed in this part in PP. No agglomerates are visibile of pulp fibres or NFC.

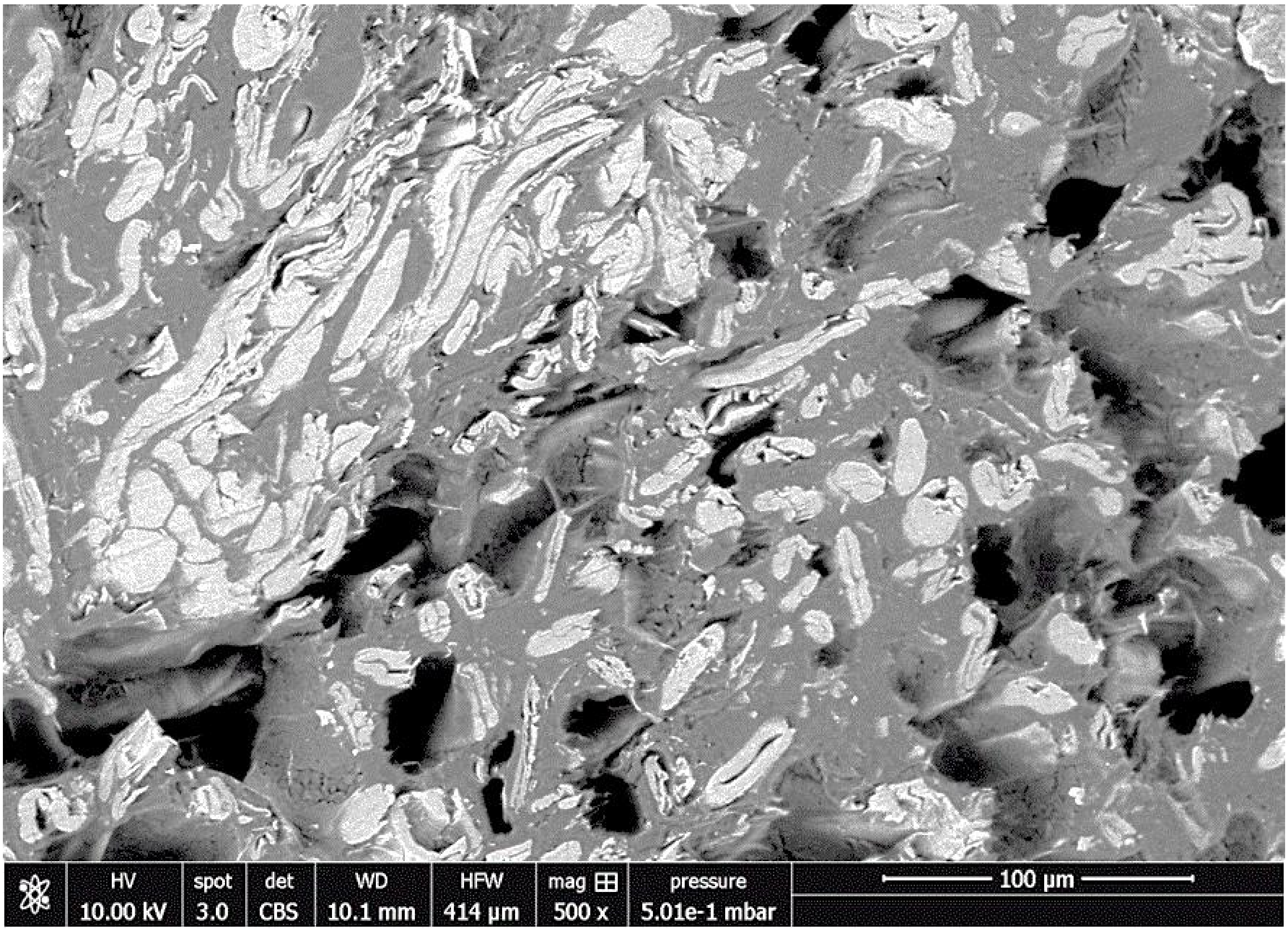


Figure 2. Composite Q1A. SEM micrograph of fracture surface (500x). Wet web comingling process followed by extrusion. Composite Q1A: Granular PP 47%, NFC 25%, pulp fibre 25%, SCONA TPPP8112FA 3%. Cellulose material distributed in PP. Pulp fibres and holes from pull-out of fibres are visible.

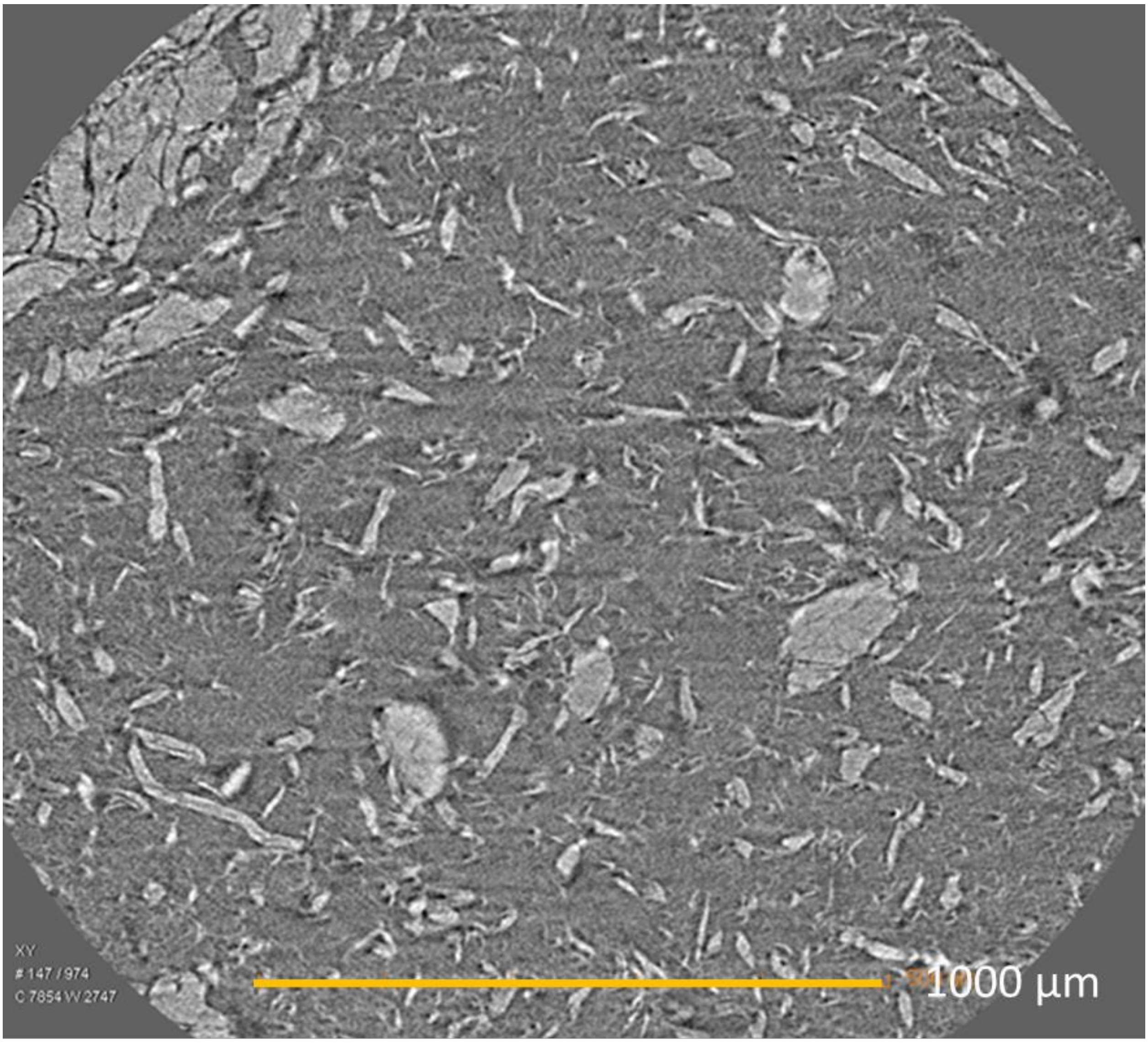


Figure 3. Composite Q2B. XY plane from microtomography. DEVO process. Composite Q2B: Granular PP47%, NFC 36%, pulp fibre14%, SCONA TPPP8112FA 3%. Agglomerates are visible.

In the DEVO process agglomerates of NFC in the PP matrix became visible in figure 3. It can be observed that both composite Q1A and composite Q2B was not processed during optimal conditions e.g. were wrong vira used which caused problem with dewatering. However, further experiments with exchange of vira and technical improvement of the head box lead to improved processing and the agglomerates disappeared. This is shown below in figure 5-6 together with mechanical test results.

Table 1. Tensile testing and flexural testing. Concerns composite Q1A Wet web comingling (Granular PP47%, NFCF25%, pulp fibre25%, SCONA TPPP8112FA 3%) and composite Q2B DEVO process (Granular PP 47%, NFC 36%, pulp fibre 14%, SCONA TPPP8112FA 3%).

Sample no.	Tensile Test [DIN EN ISO 527-1*]						Flexural test					
	E	s	σM	s	εM [%]	s	E(b)	s	σfM	s	εfM	s
	[MPa]	[MPa]	[MPa]	[MPa]	[%]	[%]	[MPa]	[MPa]	[MPa]	[MPa]	[%]	[%]
NP	1639,7	8,6	35,2	0,12	7,7	0,1	1690,8	29,6	45,66	0,06	6,82	0,09
Q1A-CM	3089,1	131,2	27,05	1,28	1,1	0,08	3146,7	178,8	39,23	7,12	1,83	0,43
Q1A-IM	3689,9	109,7	48,41	1,65	3,68	0,16	4001,9	84,6	65,5	1,55	4,72	0,15
Q2B-CM	2439	87,6	25,05	1,64	1,5	0,15	2502,9	64,4	38,31	2,97	2,5	0,26
Q2B-IM	2780,3	58,7	40,33	1,76	3,41	0,51	2798,8	76,8	59,21	0,56	6,09	0,16

NP in table 1 refers to the original polypropylene not blended with cellulose. CM means compression molding and IM refers to injection molding. The best result was obtained for Q1A-CM and Q1A-IM which was produced with the wet web comingling method. In this case no agglomeration of NFC was visible. Concerning Q2B-CM and Q2B-IM, produced by the DEVO process agglomeration was discovered. This can be attributed to a higher cellulose content and the DEVO processing method.

Furthermore, by studying the micrographs from Fraunhofer-ICT, concerning Q1A and Q2B and their fracture surfaces from mechanical testing it is verified by sample Q2B that good adhesion is obtained by the SCONA TPPP8112FA coupling agent and the Ico polymer HJ40XI polypropylene surface (See figure 4).

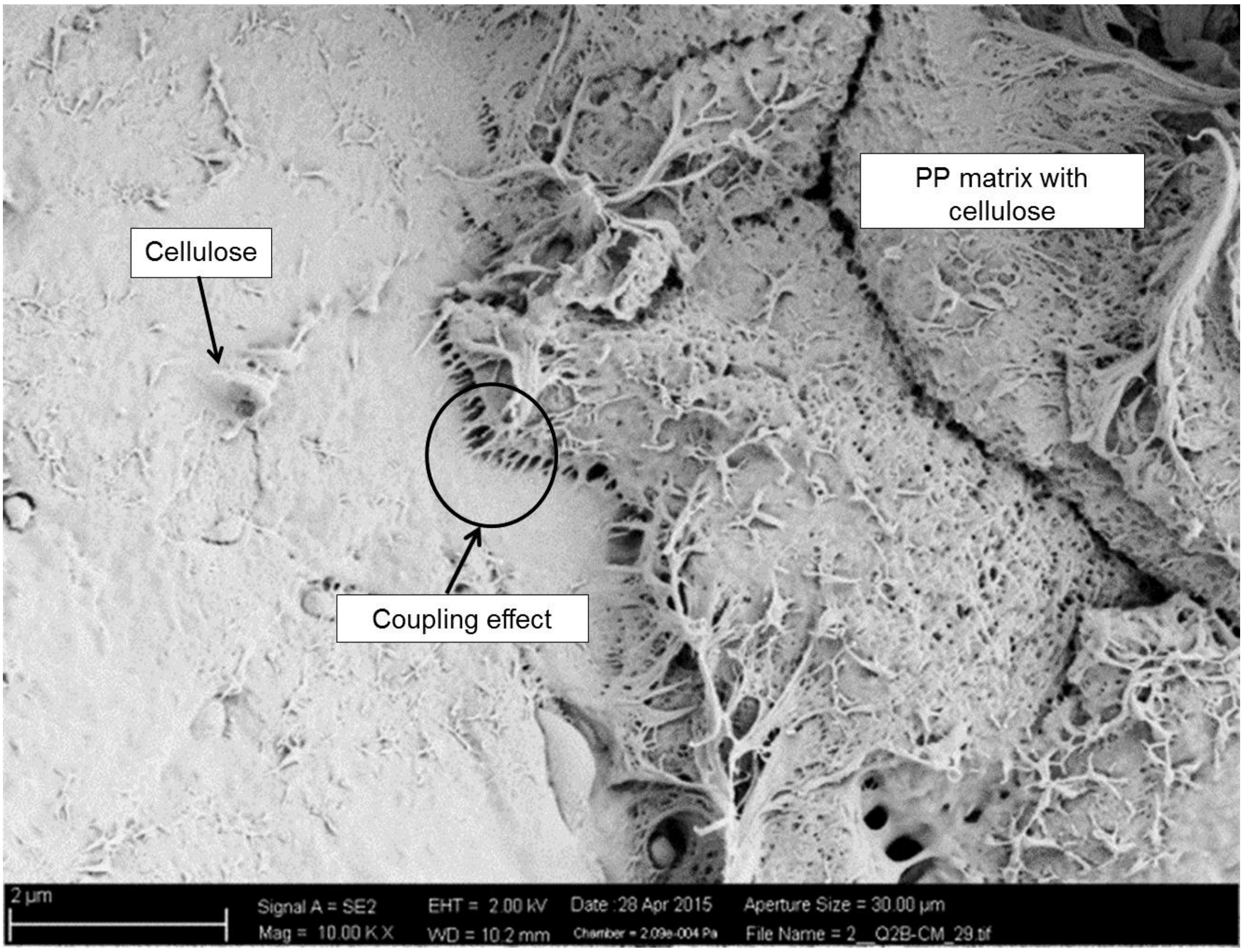


Figure 4. Fracture surface of Q2B by Fraunhofer-ICT that shows coupling effect between PP-MAPP- cellulose surface. Composite Q2B (Granular PP47%, CNF36%, pulp fibre14%, SCONA TPPP8112FA 3%)

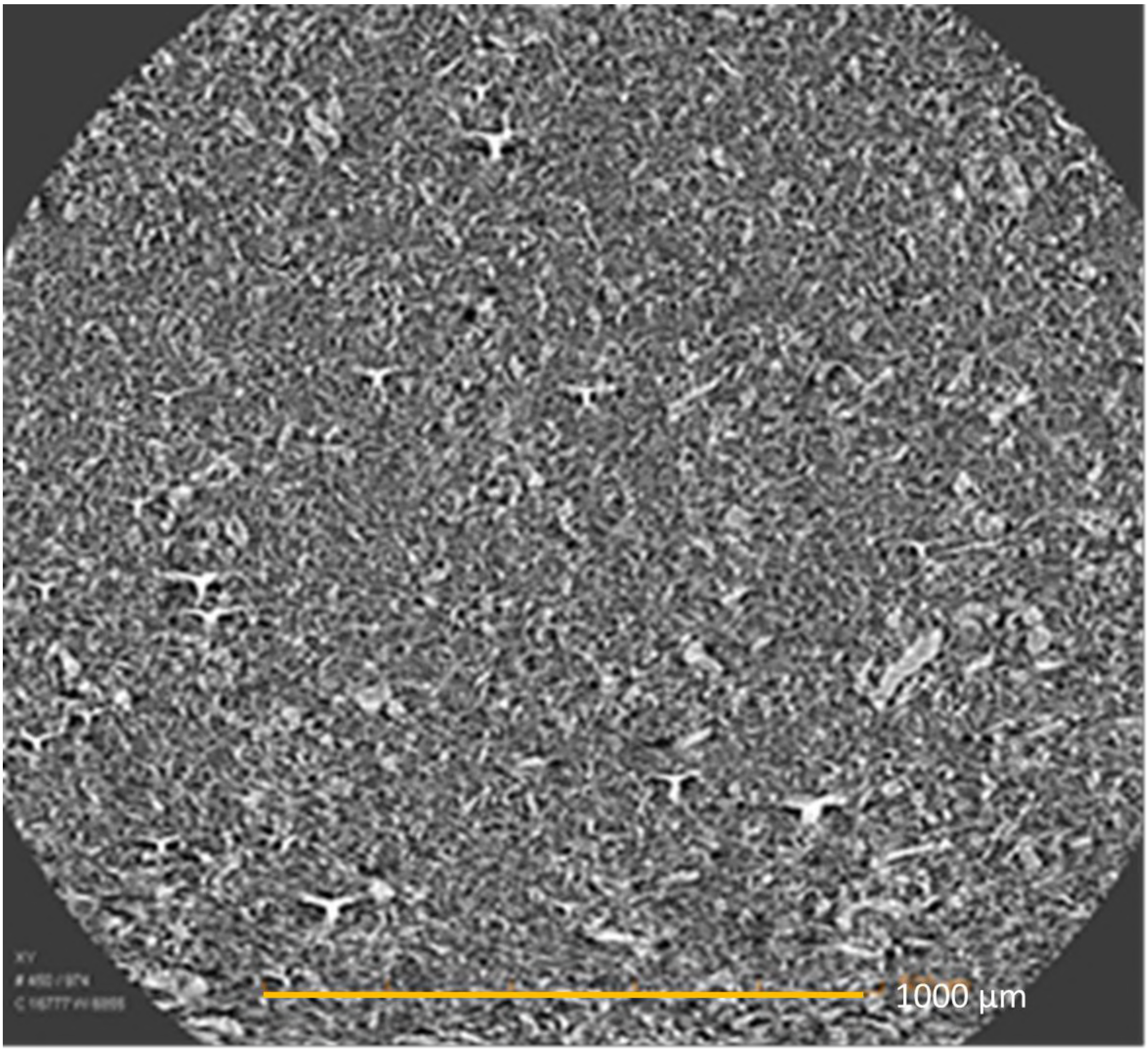


Figure 5. XY plane from microtomography. DEVO process. 50 % PP and 50 % CNF. No agglomerates and voids are visible.

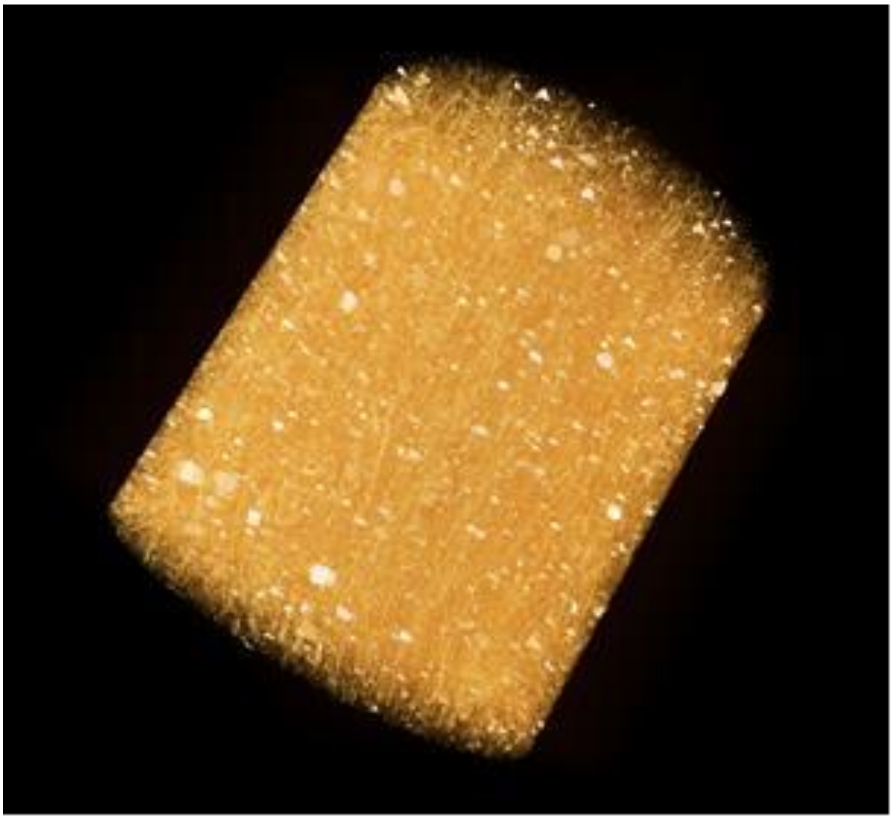


Figure 6. Rendered 3D volume of Sample PP-CFN 50:50 in different orientation using microtomography. The volume dimensions are: 1mm diameter and 1 mm length. DEVO process. 50 % PP and 50 % NFC. Homogenous sample, no agglomerates and voids are visible.

Table 2. DEVO process. Polypropylene 50% reinforced with 50% NFC. Density 1,11 g/cm^3. MFI (g/10 min) 57. In parenthesis are values obtained from table 1.

Tensile strength	Tensile modulus	Strain	Flexural strength	Flexural modulus
MPa	GPa	%	MPa	GPa
52 (35,2)	4,2 (1,6)	1,7 (7,7)	76 (45,7)	4 (1,7)

Figure 5 shows that the mechanical test results shown in table 2 were free from agglomerates. In this case was the DEVO process used. So, this shows that it is possible to obtain agglomerate free granular samples using a water based process with a hydrophobic matrix.

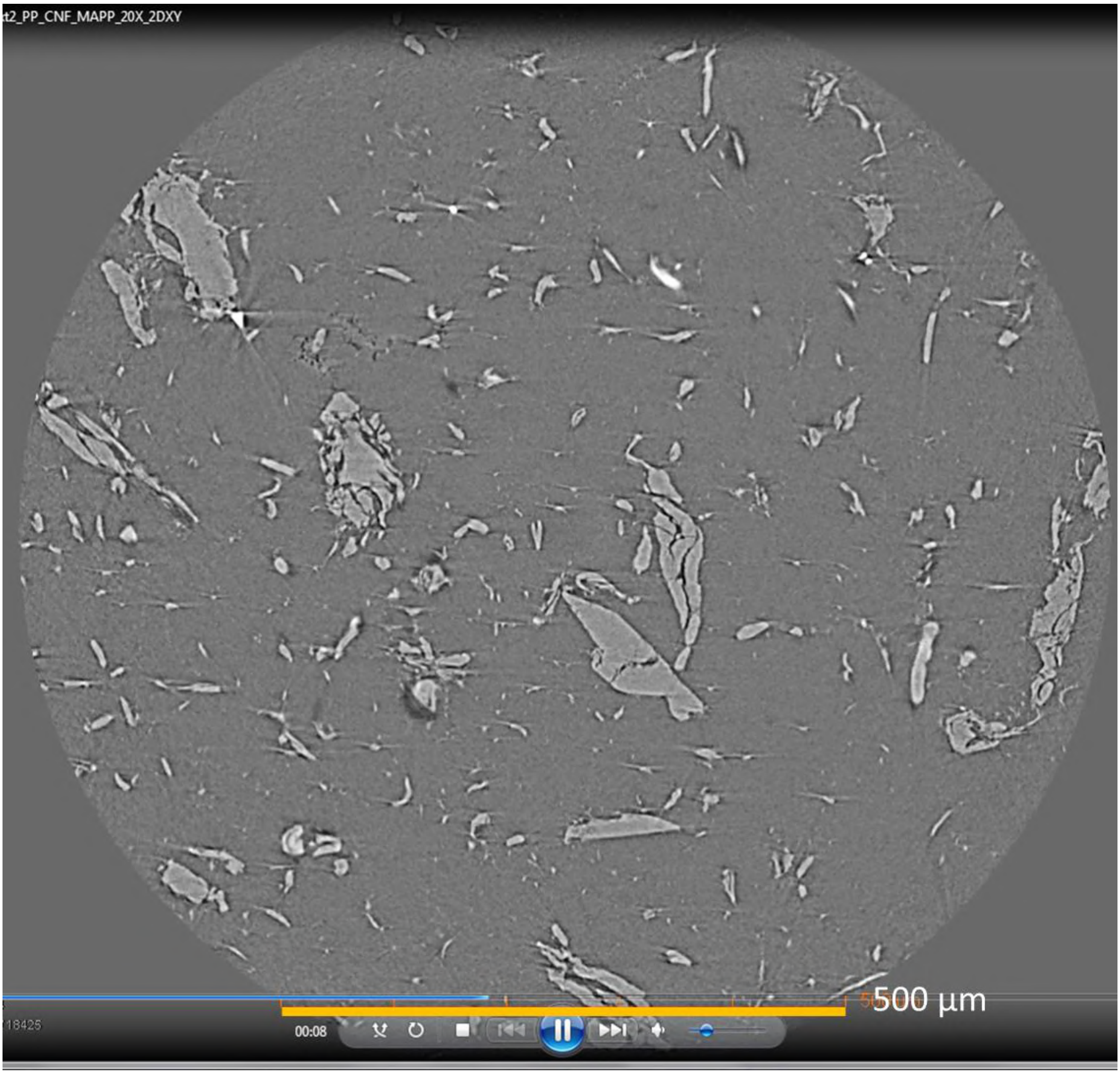


Figure 7. Modified Kyoto process by Innventia. Granular PP 81%, NFC 14%, SCONA TPPP8112FA 5. Some agglomerates of cellulose are visible.

Table 3. Modified Kyoto process by Innventia. PP is polypropylene. NFC is nano fibrillated cellulose and SCONA is maleic acid-grafted-polypropylene or MAPP

Specimen	Tensile strength	Tensile modulus	Strain	Charpy Notch test
	MPa	GPa	%	KJ/m^2
PP (A. Schulman)	33,2 (0,5)	2 (0,05)	22,7 (2,4)	2,3 (0,4)
PP/NFC/SCONA 81:14:5	35,7 (0,2)	2,6 (0,03)	6 (0,3)	2,2 (0,2)
PP/NFC/SCONA 67:29:4	39,6 (0,2)	3,3 (0,07)	4,6 (0,5)	2,3 (0,1)
PPNFC/SCONA 47:47:6	46 (0,4)	4,4 (0,05)	3,8 (0,2)	2,7 (0,1)

The mechanical test results in table 3 are at the same level as in table 2 (DEVO process) even though agglomeration occurred. The results in table 2 are free from agglomeration. However, since the results are at the same level the question is how critical is agglomeration? A new project has too answer this question. Finally, it is not possible yet to judge if PP/NFC or PP/NFC/Pulp fibre should be the choice. More experiments are necessary.

Fraunhofer-ICT has worked with process developments for advanced nanocomposites Generic injection moulding process development and has written a process guide for injection moulding of Pronanocell materials based on DOE analysis.

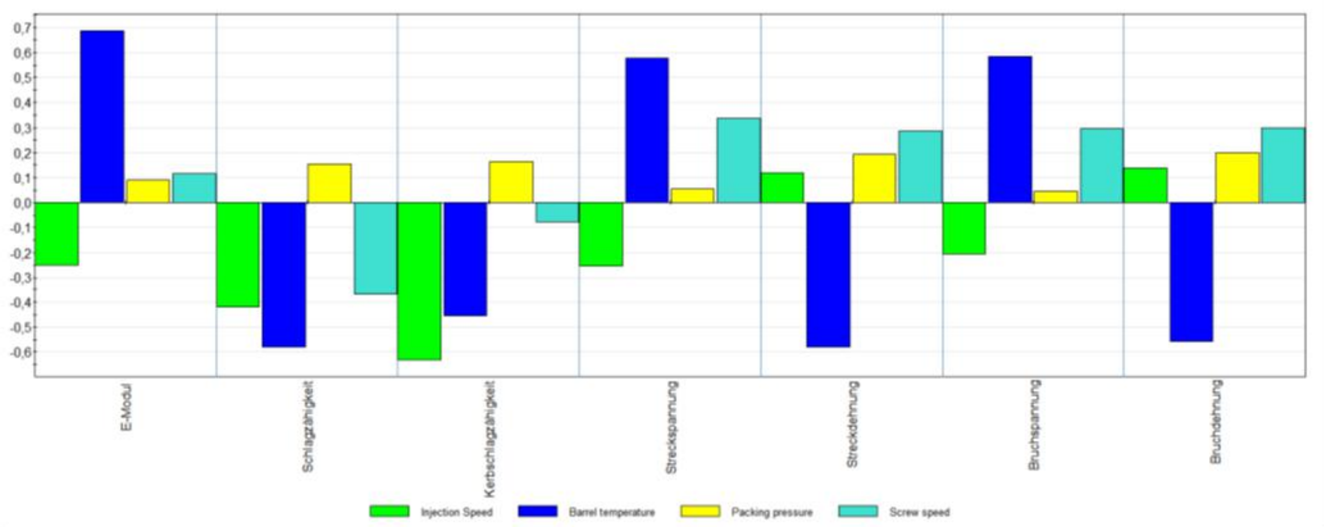


Figure 8. DOE analysis for process handbook.

•Process parameters (in the choosen frame) have only a negligible effect on the mechanical properties.

•The max. derivation in the properties can be investigated in the Charpy impact strength for unnotched and notched samples.

•Increase in the injection speed results in a reduction of the Youngs modulus, yield strength, impact strength and elongation at break. Instead, an increase in elongation at yield and elongation at break was obtained.

•An increase in the barrel temperature clearly resulted in an increase of the Youngs modulus properties, stress at yield and stress at break.

•However, an increase in the barrel temperatures leads to reduced impact, yield stress and elongation at yield properties.

•The investigation of the break surfaces of the PP-NFC samples has been carried out in order to analyze the influence of the processing conditions on fibre damage, e.g. fibre length reduction.

•Different magnification levels have been investigated in order to get a general view on the break surface and detailed view of individual representative sections.

•The SEM images show that there is an increased screw speed results in increased fibre damage, due to the increased shear rates (N1=50 rpm, N13=250 rpm). This is also indicated in the resulting impact properties, which are declining if screw speed is increased.

•Additionally if the screw speed and the injection speed is increased at the same time (N3=80 cm^3/s, and N16=160 cm^3/s) it can be observed that fibre damage is increased and smaller fibre fragments can be found in the break surface.

•The images made from break surface gives a clear hint of interrelation of the measured mechanical properties and calculated trends of the DOE and thus help to understand the results.

Another process that was developed by Fraunhofer-ICT was foam injection moulding of NFC-composites. Supercritical N_2 or CBA, chemical blowing agents (A. Schulman's Polybatch CBA and Clariant's Hydrocerol ITP 817) were tested. Both foam processes can be used at Fraunhofer-ICT, what is the best is not possible to judge yet.

The results from use of chemical blowing agent Hydrocerol ITP 817 is presented below:
•The mechanical properties are at a comparable level to those of commercially available products.
•Embrittlement still occurs with increasing fibre content / density reduction: The impact strength of PP 45% Nano is 20% below the value of the commercial product.
•Reduction of the mechanical performance in a expected range, due to foaming
•High injection speeds result in a good surface appearance, figure 11, but the effect is limited. High injection speed damage the fibres

Innovativeness, industrial relevance and contribution to competitiveness
ProNanoCell can be considered as a very high innovative project where nanocellulose composites has been produced for the first time in pilot scale (Wet Web comingling and DEVO process). The modified Kyoto process by Innventia will make it possible to run very small granular material less than 100 µm and using nanocellulose that are too difficult to dewater and cannot be run with the two other processes. Industrial relevant demonstrators have been produced and are presented in part 1.4 below.

Environmental and societal impact
The forest industry constitutes a large renewable resource for production of sustainable materials as NFC. The life cycle cost for the products becomes low, which increases the sustainability. No harmful chemicals are used in NFC production and the composite manufacturing processes used where all water based. The composites produced can be an alternative energy source when the materials are recycled or transformed into granular material again and reprocessed. The concept of a Sustainable Society is a key issue today. This kind of society needs high quality and renewable materials with a low carbon footprint. NFC, extracted from the wood fibres with low energy consumption processing (Innventia process) represents such a raw material and when incorporated into composites, it becomes more sustainable than if glass fibres or carbon fibres are used. ProNanoCell will therefore also promote a biobased future for the European bio-economy sector, which already accounts for 22 million jobs

1.3 Conclusions
When higher mechanical strength is a prerequisite it is necessary to replace WPC materials or mineral filled plastics with a reinforcement that has higher aspect ratio. If it should be only nanocellulose or a combination of pulp fibre and nanocellulose with a plastic matrix, it is too early to judge. More experiments are necessary. The mechanical test results showed that it was possible to increase the flexural properties more than 50% even up to 135%. It was also possible to increase the Youngs modulus well above the values for WPC material. Recent experiments have shown values up to 5 GPa. Advanced injection moulding as foam injection moulding resulted in lower density and a material comparable to commercial material. The mechanical test results are in same level as for glass fibre reinforced polypropylene, however further optimization is necessary if less nanocellulose is going to be used to obtain liighter nanocomposite materials. On the other hand, a more environmentally nanocellulose composite

material is obtained since 45% of fossil based polypropylene was replaced with nanocellulose. Even higher levels of nanocellulose can be tried out.

1.4a Capabilities generated by the project

Volvo Cars has shown interest in the outcome of the project and All-Plast would like to fabricate different prototypes by injection moulding with a moulding machine adopted for cellulose composites. Stora Enso has also shown interest in the outcome of this project.

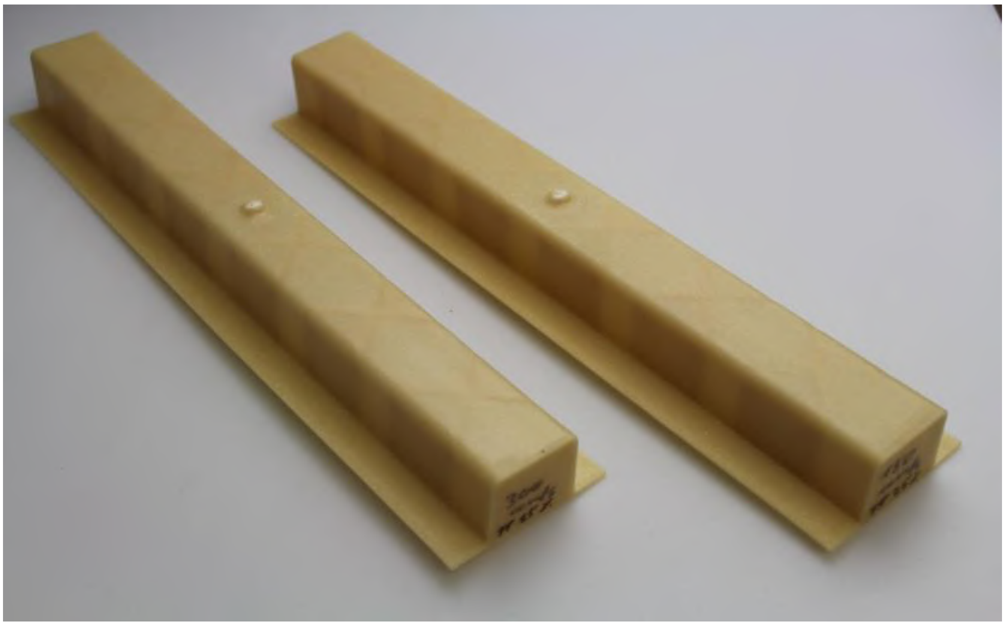
Prototypes

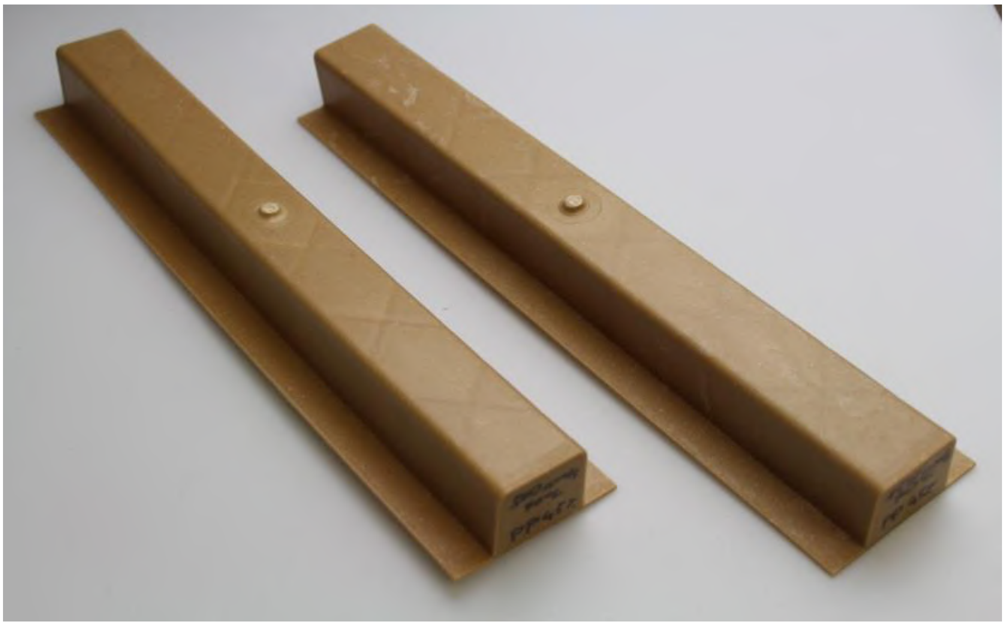
Figure 9. Wrist support produced by All-Plast. Process: Injection moulding
Material: Left NFC/PP (50/50), right 30 % NFC/5 % Carbon fibre/65 % PA 6.

Working prototypes in figure 11. The black one contains also carbon fibre and nylon instead of PP and this makes it stiffer than the PP/NFC composite.

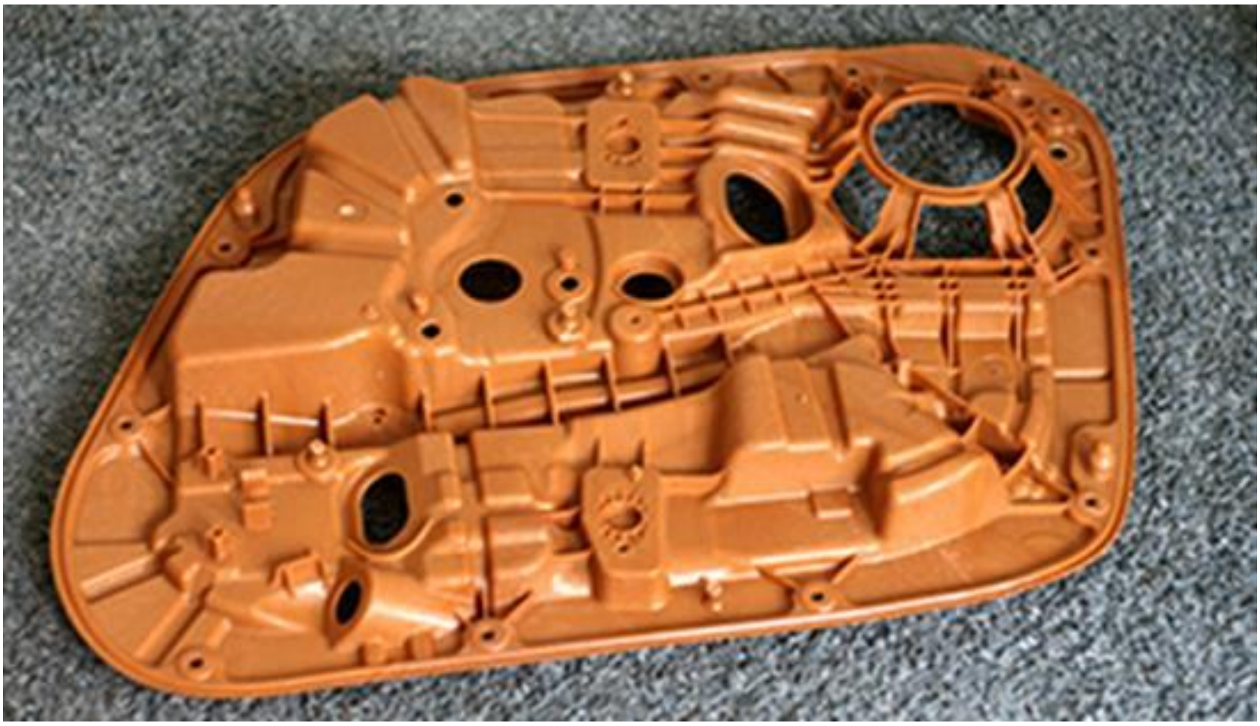
Figure 10. Produced by All-Plast. Process for Stora Enso: injection moulding. Material: NFC/PP (50/50.)

The coffee mugs in figure 12 works well and can be washed in a dish washing machine without any problem and this has been tested.





Figur 11a and 11b. By Fraunhofer-ICT. Scope of the optical investigations: Variation of mold temperature photo above in figure 13a 50°C up to 70°C photo below in figure 13b and injection speed 150 ccm/s figure 13a up to 600 ccm/s in figure 13b to improve the surface appearance. High speed more dark brown. As figure 13b shows.



Fiigure 12a. Volvo Cars demonstrator part an inner door module for XC90 produced of PP/NFC 55:45.

Figure 12b. Volvo Cars demonstrator part an inner door module for XC90 produced of PP/NFC/pulp fibre, 50:25:25.

The inner door in figure 12a was somewhat more brittle than the inner door that contains also pulp fibre in figure 12b.

Figure 13. A droner shell was produced by Ljungby Komposit AB. Material PP/NFC 55:45.

The market asks for droner shells made of environmentally friendly material, and nanocellulose composites constitutes one way.

1.4b Utilisation of results

It is of course not possible to get out optimal mechanical strength from nanocellulose composite materials within a short time period as 3 years. However, by reaching high flexural and Young modulus in this project it can be stated that the nanocomposite material is good enough for many applications concerning rigid packagings, construction details and automobile parts. Concerning exploitation of this project Stora Enso has shown great interest and a special meeting will be held. For Volvo Cars, a meeting will be held about further testing of the nanocellulose composite material. Volvo Cars has many special tests they would like to perform before saying yes to a new material since it will be used in their cars for 15 years.

1.5 Publications and communication

a) Scientific publications

None. If there wilkl be a publication, the industry decides about it. At the moment the experimental details are confidential.

1. Articles in international scientific journals with peer review

Confidential work details

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

Confidential work details

3. Articles in national scientific journals with peer review

Confidential work details

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

Confidential work details

5. Scientific monographs

Confidential work details

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

Confidential work details

a) Other dissemination

WoodWisdom Net+ Seminars in Stockholm 9-10 April 2014, Zürich 14-15 September 2015 and Edinburgh 4-5 April 2017

1.6 National and international cooperation

Consortium: Innventia (Coordinator), Elastopoli Oy, Fraunhofer-ICT, Ljungby Komposit AB, Volvo Cars, Stora Enso Pulp & Paper Asia AB, All-Plast Oy, A. Schulman

Without Elastopoli success concerning nanocellulose composite manufacturing using Stora Enso special grade of nanocellulose this project would have been impossible to perform. Nanocellulose composites are not commercial and is still on the research level. A. Schulman provided special graded quality of polypropylene. This grinding took place in their facility in France. Without this grinding, it would not have been possible to get such good mechanical results from the nanocellulose composites. The Kyoto process did not work out in accordance with the scientific paper by Suzuki et al. and after modification by Innventia it was possible to get out good results, but the extruder is at lab. scale and could not produce enough material for any of the partners involved in ProNanoCell. Fraunhofer-ICT used very advanced injection moulding techniques, even foam injection moulding maybe not possible to perform in any other place. All-Plast performed injection moulding with a re-built injection moulding machine for cellulose composites with great success. Volvo Cars performed also a very advanced injection moulding using a machine for inner door moulding for XC90. Finally, Ljungby Komposit AB, fabricated a droner shell which is of great interest, since it can be made environmentally friendly. Important if lost in nature. Very good synergies developed between the industry and the research institutes Innventia and Fraunhofer-ICT. Innventia coordinated the experimental work and transferred their knowledge about nanocellulose as a new material in composites and also knowledge about dewatering of nanocellulose to all partners. Fraunhofer-ICT provided a process handbook to the industry for injection moulding of nanocellulose composites. This was transferred to all the industrial partners. Several meetings have been held for networking and for exchange of information. Reports and newsletter has been written. No collaboration with other projects in the WW-Net countries has been done, and no new links to with/between local or international organizations have been done. The ProNanoCell project could not have been accomplished without transnational cooperation, this was really necessary as described above.