

PROJECT FINAL REPORT



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Final publishable summary report

1. Executive summary

The strategic objective of CARBOPREC project is to develop low cost precursors from renewable materials widely available in Europe (lignin and cellulose) and doped by carbon nanotubes in order to produce cost-effective carbon fibers with medium performance for mass-market applications (automotive, wind blade energy...).

Both high purity cellulose- and lignin-based formulations will be defined in order to provide:

- a homogeneous dispersion of carbon nanotubes into polymer blend,
- a satisfactory spinning processability,
- an acceptable cost/performance ratio of the carbon fiber.

The (pre)carbonization and (post)carbonization process of carbon fiber will be optimized in order:

- to increase the yield of carbonization process up to 35% for cellulose route and up to 50% for lignin route,
- to make the manufacturing process simpler by adding a plasma treatment step instead of the oxidation step.

The final objective of CARBOPREC project is to provide a global life cycle analysis (LCA) and technical-economical assessment of renewable source nanostructured carbon fibers for mass-market applications (automotive, wind blade energy...).

The consortium is composed of 14 partners:

- ARKEMA
- FRAUNHOFER CBP / IGB
- LLC BCP
- ADERA / CANOE
- RENAULT
- SIGMATEX
- PLASTINOV
- UNIVERSITY OF HAMBURG
- MDP
- ALBERT LUDWIGS UNIVERSITY OF FREIBURG
- AVANA
- CTAG
- AYMING
- CETI

2. Summary description of project context and objectives

a) Technical specifications

The objective was to accurately define the specification of the materials and parts according to industrial applications foreseen. Once done, it should allow to select the prototypes/components and the drawings, the criteria and type of tests for characterizing and benchmarking the materials and parts made.

b) Bio-based precursor development

For lignin-based materials, high-purity lignin was to be produced by the organosolv process at the pilot plant located at FRAUNHOFER CBP in Leuna. With the aim to optimise the lignin quality for melt spinning through the adoption of the process conditions and raw material choice for ethanol-water pulping in the pilot-scale, several pulping cycles were carried out in order to provide various grades of lignin to the consortium. In addition, Kraft lignin was provided. Based on the results from compounding and fibre spinning, process parameters were chosen for production of lignin and approx. 130 kg have been provided as precursor for demonstrator parts. A detailed analytical characterization of lignin- and cellulose-based materials was carried out throughout the whole project and detailed reports were provided. Furthermore, lignin was functionalized by acylation to enable plasma induced stabilization of lignin containing carbon fibres. Experiments for lignin derivatization were supported with studies based on model compounds. A synthesis route was selected for scale-up into 100-L scale. The procedure was further optimised during pilot scale trials and several kilograms of acylated lignin could be provided.

For cellulose-based materials, a purification process for upgrading low-cost cellulose material based on paper grade pulp to dissolving pulp was developed. The process is based on the extraction with sodium hydroxide and provides pulp with high cellulose content. The purification was optimised in lab-scale to provide the basis for pilot-scale experiments. Trials in pilot scale were successfully carried out to provide 120 kg of purified cellulose precursors. In addition, an alternative tailor made dissolving pulp precursor was manufactured by prehydrolysis soda AQ pulping and subsequent bleaching, which was also delivered for dissolution and spinning trials.

A detailed analytical characterization of lignin- and cellulose-based materials was carried out throughout the whole project and detailed reports were provided.

c) Dispersion

A big challenge of CARBOPREC project was to obtain precursor fibers with a homogenous distribution of carbon nanotubes (CNT) inside the bio-based matrix (lignin or cellulose). Because the spinning process for both precursors is not the same, the strategy to add the CNT also differs. For cellulose route, the fiber are produced by wet-spinning process. This means, the spinning dope is liquid, the coagulation solution is also liquid and by injection of the dope inside the coagulation bath, it forms a gel fiber that will be solid after drying. Therefore, the CNT must be dispersed in the liquid spinning dope containing the cellulose. The main challenge was the acidic media. It is well known how to obtain a stable dispersion of CNT in water, but we performed lot of trials to find the good surfactant that allow to remain stable even at pH < 3. SEM characterizations did not show aggregates in the cellulosic precursor fibers. Concerning the lignin, as it is spun by extrusion, the use of CNT masterbatch was obvious. Different carrier matrices were possible and were investigated to find the one the most compatible with lignin. For each way, different kind of nanotubes were tested (as produced, high purity, oxidized) and different concentration.

d) Spinning

The objectives was to produce bio-based precursor fibers. Two different spinning technologies are used: wet spinning process for the cellulose precursor and melt spinning process for the lignin based precursor. For the cellulose approach, a new reactor, spin pump and spin pack was developed and installed at CANOE facilities to enable the dissolution of the cellulose in phosphoric acid with carbon

nanotubes. Lot of work was done on the optimization of the dissolution and spinning process to obtain cellulose fibers with a thin diameter and mechanical performances suitable for carbonization. For the lignin route, as it was not possible to spin fibers using only lignin, lot of formulations were done to obtain blends suitable for multifilament spinning. The key factors are nature of additives, concentration, viscosity extrusion temperature profiles... In addition, thanks to the spinning process optimization, around 40kg of homogeneous lignin fibers doped with CNT have been prototypes.

At the same time, discontinuous carbonization at lab scale were done to acknowledge the potential of the different precursors.

e) **Bio-based carbon process**

The physical and mechanical properties of the fibers to be processed in the carbon materials should conform to the requirements to precursors; besides these fibers should not be melted while carbonization and should ensure the high yield of the carbon fiber. The obtained carbon fiber should have the high physical and mechanical properties.

In the frame of the project the following studies have been done:

Cellulose route

- influence of the plasma treatment on the precursors characteristics being obtained with the different production methods (commercial PAN fiber, hydrated cellulose fiber TENCEL, LENZING, hydrated cellulose yarn CORDENKA® 700 Super 3, the samples of the hydrated cellulose modified fiber, lignin fiber) and on the properties of the carbon fiber based on them.
- evaluation of the possibility to obtain the carbon fiber based on the hydrated cellulose fiber, being modified and not modified with the carbon nanotubes (CNT), compared to the commercial hydrated cellulose fiber TENCEL, LENZING and hydrated cellulose yarn CORDENKA® 700 Super 3.
- influence of the CNT introduced into the precursor structure while its preparation for the carbonization process, on the carbon fiber properties.

It was worked through the process of carbonization and graphitization of the hydrated cellulose precursor in the form of non-woven fabric and yarn as modified with CNT, as not modified with CNT, compared to the commercial precursors.

Lignin route

- evaluation of the possibility to obtain the carbon fiber using as precursor the commercial hydrated cellulose fiber TENCEL and hydrated cellulose yarn CORDENKA with the preliminary application of the organosolv lignin on their surface.

f) **Demonstrators of composite parts from bio-based carbon fibres**

This part of the project aimed at implementing industrially and validate at demonstrator scale of the CARBOPREC carbon fibers. It also worked on the establishment of appropriate process tests methodologies and the unitary production of semi-products with new carbon fibers.

g) **Fundamental understanding of interactions**

The aim of this work package was twofold; On the one hand, the interfacial interactions between lignin (alternatively cellulose) polymers and carbon nanotubes shall be unravelled and the impact of the molecular structure of the wood biopolymers on their miscibility and adhesion with carbon nanotubes deciphered. Additionally, this part aimed at determining the impact of shear rate, as relevant to the production of the precursor fiber, on the morphology of the wood biopolymer. This first goal was thus considered as a guide to select the optimum wood polymer attributes for producing high performance precursor fibers. On the other hand, this transverse work package focused on assessing the interface

properties of demonstrators based on bio-based carbon fibers and compare those to commercial petroleum-based carbon fibers.

h) LCA, recycling, safety issues & economic analysis

The main objectives of the LCA work is the analysis of the environmental performance of the new carbon fibres produced in CARBOPREC project in comparison to the traditional PAN based carbon fibres.

The first part of the work was dedicated to create the LCA reference study on PAN Carbon Fibres; after that every processing step required for the production of lignin and cellulose based carbon fibre has been analysed starting from the extraction of the lignin and cellulose from biomasses up to the carbonization and sizing treatment. This part of the work required a strong collaboration between all partners in order to share data and information useful for the elaboration of the LCA studies.

The development of the LCA studies required three iteration in which technological updated have been implemented in the LCA models. At each iteration specific feedback to improve the environmental performance have been supplied to the researchers working on technical development of the new fibres.

Finally, the results achieved for PAN carbon fibres and the results achieved for lignin and cellulose carbon fibres have been in terms of different environmental indicators in order to evaluate the environmental performance of the new CARBOPREC products in comparison to the current benchmark on the market.

Cellulose route

The assessment of the safe process to produce carbon fibers has been carried out, the potential human hazards risks and risk of the environmental safety, avoiding the possible accidents and reduction of the time to eliminate them; and besides the analysis of the possibility to utilize the waste generated while producing the carbon fibers and the composite materials based on them.

During the assessment of impact of the bio-precursors based carbon fibers production process on human health and environment, it was carried out the analysis of presence and level of the hazard substances harmfulness that are used as the raw materials and the secondary materials, process liquids and gases; and also of the possibility of generation of the hazard substances as while the normal production as while accidents occurrence. The possible accidents, their consequences and the methods to avoid and eliminate them had been studied.

Lignin route

As far as the production processes of the cellulose-based and lignin-based carbon fibers are almost similar, the data concerning influence on the human health and environment as result of production of the carbon fibers based on cellulose is applicable relatively to the process of lignin based carbon production process.

While assuming the utilization issues from the one hand it has been considered that the cost of the carbon materials is rather high, so their wages are considered today as the valuable products to be recycled.

On the other hand, considering the specific properties of these materials such as resistance to the atmospheric exposure, the utilization issue has first of all the environmental nature.

The main way to solve the issue of the wages utilization being in form of carbon fibers generated while the different stages of the process is usage of the wages as filler in composite materials. As result, it is obtained the additional quantity of the useful products for the different industries and the environment re-pollution does not occur.

The most difficult is utilization of the composite materials reinforced with the carbon fibers as for the high strength properties as for the problems with re-usage of the utilized wages.

The basic methods of the composite materials utilization are studied: physical, chemical, thermal ones. All the methods of the reinforced composite materials utilization are united with necessity to destruct the matrix (bonder) in order to separate the reinforcing filler (fiber). The method selection is determined by the technical and economic factors, and with the environmental safety aspects.

It has been carried out the technical and economic evaluation of the costs to produce the carbon fibers from lignin and hydrated cellulose based precursors modified with carbon nanotubes being obtained in the frame of CARBOPREC project. The economic analysis was executed with comparing to the conventional process of glass and carbon fiber based on PAN.

While the economic analysis of the carbon fiber cost, the calculations considered the expenses for the preliminary precursor preparation (twisting, weaving), the secondary materials (secondary materials, chemical agents, reagents and others), the expenses connected to obtaining of the carbon fiber with the different physical and mechanical properties (electrical energy, natural gas, NaOH, C, N, cooling water), and also the production capacity of the equipment for the carbon fiber manufacturing and its yield (relation of the finished product weight to the raw materials weight).

Description of the main S&T results/foregrounds

a) Technical specifications

The end-user specifications have been completely finalized. The composite must not jeopardize the expensive E-coat bath and for the composite. The whole E-coat process must not significantly damage the composite. The expansion characteristics must be close enough to steel. The gravelling impact must be taken into account. Some non-destructive testing after bending tests must be performed (maximum deflection, Infrared Thermography, ultrasonic mono-elements). A comparative evaluation between carbon fiber vs. glass fiber will be carried out.

The important characteristics of the semi-products are now well determined: density, linear density, strength, modulus, elongation sizing, electrical resistivity, and spool length and spool weight. All of these will help to determine the material weight, width and construction (weave type).

Three important tests have been defined in order to characterise the suitability of CARBOPREC fibres for the automotive industry: (climate) ageing, corrosion and cataphoresis (E-coat) resistance. For each test, we must check the properties before and after with the following tests: mechanical tests (flexural and/or traction), visual control, metrological control (weight and dimensions), non-destructive test (C-Scan, ultrasound).

b) Bio-based precursor development

Lignin route

Production of an optimized organosolv-lignin

At the beginning of the project, organosolv-lignin (OL) samples were provided in a standard quality for the development of the compounding and melt spinning processes. In order to ensure a reliable feedstock supply, the reproducibility of the most important lignin properties of different batches was investigated and confirmed. Furthermore, the high purity of the OL was confirmed with an ash content below 0.1 % (w/w) and carbohydrate content below 3 % (w/w) for all batches. In addition, 5 kg of Kraft-lignin were provided. The analytic results showed that Kraft-lignin contains significant concentrations of inorganic impurities being problematic during the carbonization of the precursor fibers, where extremely low ash values are usually required. Spinning of fibres from Kraft lignin was also not successful compared to organosolv lignin. Therefore, no further activities on the isolation of Kraft lignin were followed.

After the first compounding and spinning trials using OL it was concluded that 1. particle size, 2. glass transition and 3. the brittleness of the melt spun precursor fibre are the major issues to be addressed.

1. In order to increase the particle size, a new method ("evaporative lignin precipitation") for the precipitation of lignin from the organosolv black liquor was applied. It can be used to increase the particle size as confirmed by granulometry measurements and application tests. The lignin batch K030 with an average D [4:3] of 26 µm was identified as the preferred lignin quality in terms of particle dimensions.

2. As the glass transition (T_g) was identified as one of the most important factors for melt spinning, it was tried to systematically identify the relevant process parameters within a wider range of values for H-factor (combining temperature and time) and addition of sulphuric acid. From the obtained data, it could be postulated that an increase in sulphuric acid concentration results in an increase in T_g and that an increase in H-factor has the opposite effect. However, it was not possible to find a clear correlation because the T_g varied only within a very narrow range, not allowing to specifically address this issue. So these results could more be interpreted as a trend, which was less clear than expected.

3. To tackle the brittleness of fibres four different new lignin qualities were produced and characterized. As new feedstock's spruce wood and wheat straw were used successfully adopting the organosolv process to fractionate these materials. In addition, several kg of a very high molecular

weight beech organosolv lignin could be isolated and distributed as a by-product from the black liquor handling. As a 4th quality, a tar fraction resulting from based catalysed depolymerisation of lignin was analysed.

Based on results from compounding and spinning the optimized lignin was produced being a mixture of beech and spruce lignin.

Various lignin grades were produced during the project adapting the Organosolv process to various feedstock and parameters.

167 kg of optimised lignin (beech:spruce 1:1 (w/w)) was provided as optimized precursor.

Functionalisation and derivatisation of lignin

The goal is the derivatization of lignin to enhance a plasma induced stabilization procedure of the carbon fibres after melt spinning. During a literature survey, strategies for functionalization, e.g. acylation of lignin in terms of feasibility, technical relevance and freedom from patents were evaluated. Then work was started for the chemical modification of lignin with first laboratory trials for the acylation of lignin. Based on the positive results from plasma treatment using Argon plasma, a preferred synthesis route was selected.

Plasma-active functional groups were successfully introduced into the lignin precursor.

For production of several kilograms of acrylated lignin, a scale-up was carried out in 100-L scale. However, the acylation reaction during the first scale-up trial was not successful. Immediate action was taken to investigate possible side reactions. The following problems were identified, which are more apparent during handling in large scale:

1. The acylation agent (GMA) primarily reacted with sodium hydroxide in solution,
2. Saponification also occurs with lignin and GMA under used reaction conditions resulting in an undesired hydrolysis of the target product, the coupled acryl ester.

In order to overcome the difficulties, the reaction mechanism of lignin acylation had to be studied in more detail by using model substrates, which are part of the lignin's subunits as shown in Figure 2.1.1. The focus was on conversion rate, stoichiometric adding of the acylating agent Glycidylmethacrylat (GMA), temperature and reaction time. Additionally, the influence of NaOH concentration regarding to the product stability was studied.

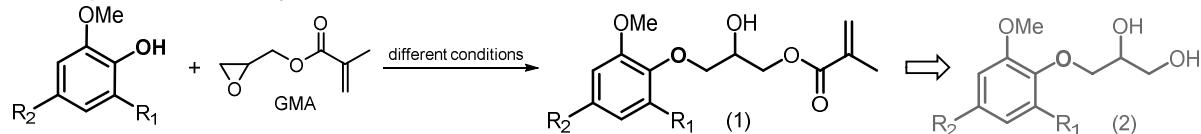


Figure 1: Acylation of monomeric substrates as a lignin model using glycidylmethacrylat (GMA); primary product (1) and secondary product (2).

It was possible to decrease the formation of undesired secondary products (2) down to an acceptable minimum of saponification of below 10% as well as aliphatic OH-acrylation of below 15%. The best conditions were selected to aim high conversion rates and desired selectivity. Consequently, the reactions conditions were adapted to favour the desired primary product (1). The second scale-up successfully delivered acrylated lignin.

The studies demonstrate a straightforward approach to easily produce acrylated lignin. An amount of 3.0 kg of acrylated lignin could be provided as additive in lignin formulations.

Analytical lignin characterisation

The analytical characterization of all lignin samples was performed. Furthermore, lignin blend formulations were characterized for a better understanding of the reactions that occur in the extruder.

Joint efforts of UHAM and FRAUNHOFER were made to prepare a report on the detailed analytical characterization of various lignins.

Cellulose route

Production of dissolving pulp from paper grade pulp

Dissolving pulp, as starting material for the “cellulose route”, can be produced by NaOH extraction of hemicelluloses from paper grade pulps. Four commercial paper pulps (Eucalyptus-Cacia, Eucalyptus-Fibria, Softwood-Stendal, Beech-Stockstadt) were provided, characterized and extracted. Additionally, KOH was investigated as a possible alkaline extracting agent. Furthermore, two more pilot scale extractions (5 kg) were performed. The produced pulp material was used to optimise the refining process after extraction and was supplied afterwards to the consortium for further dissolution and spinning tests. Regenerated cellulose samples were characterized by viscosity and carbohydrate composition to evaluate the effect of the different pulp qualities.

Based on the experience from the extraction and spinning tests as well as the quality of the regenerated cellulose and spun fibres, the Eucalyptus Kraft pulp was selected for the production of 120 kg purified cellulose by the UHAM in cooperation with FRAUNHOFER's pilot plant. A first large scale extraction test (25 kg scale) was carried out for testing the technical equipment. Based on the lab scale extractions in Hamburg the necessary processing steps (disintegration, extraction, washing, refining & drying) for the production of 120 kg of dissolving pulps from paper grade pulps were performed as depicted in Figure 2.

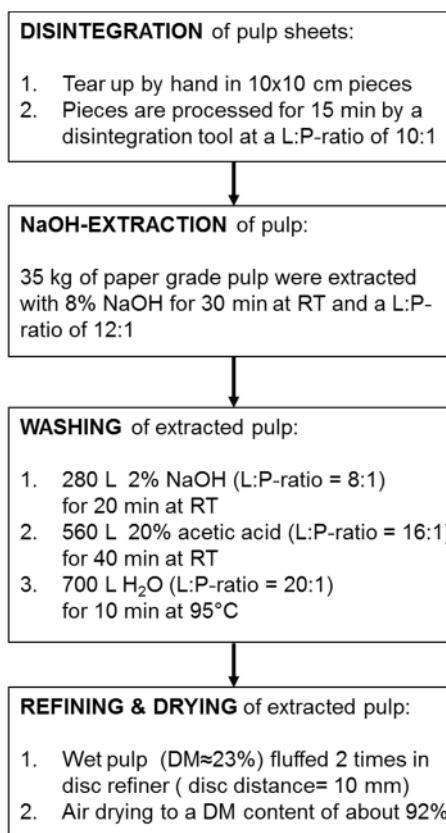


Figure 2: Process steps for 35 kg pilot scale extractions

The comparison of the carbohydrate composition of the pulps shows that the pulp extracted in Leuna has with 95.6% nearly the same purity level as the eucalyptus pulps produced in smaller scales in Hamburg. However, the yield after the large-scale extraction is about 20% lower due to different mesh sizes used for the filtration. In addition, the extracted pulp has with 440 ml/g an essential lower viscosity than the pulps produced by the smaller scales in Hamburg. This reduction of viscosity was attributed to an oxidative alkaline degradation induced by prolonged storage between the processing

steps of extraction, dewatering and washing of pulp. However, the dissolution of the pulp in H_3PO_4 worked well, also with the addition of 0.1% carbon nanotubes (CNT). Thus, the spinning step was also possible with a low starting viscosity of about 440 ml/g and with using FRAUNHOFER's technical equipment. For the final up-scaling of extraction several changes were implemented. To reduce the yield loss the screw press was equipped with a custom-built screen with a very low mesh size of 150 μm . To minimize oxygen degradation of cellulose after NaOH washing the pulp was stored over night at 8°C to minimize viscosity loss. With these changes, the pulp was obtained in good yield with high cellulose purity of 94 % and a viscosity of 700 ml/g.

The process for dissolving pulp production could be successfully scaled-up to pilot scale to provide 120 kg of purified cellulose.

In addition to the extracted paper grade pulps, an alternative dissolving pulp precursor was manufactured from wood chips by proven technologies for dissolving pulp production. This task was fulfilled by the treatment of beech wood chips with a prehydrolysis soda anthraquinone (AQ) cooking process and a subsequent elemental chlorine free (EFC) bleaching sequence. By this, 1.2 kg of the conventional beech dissolving pulp was analytically characterized and delivered for testing its dissolution and spinning properties in comparison to the produced Eucalyptus Cacia dissolving pulp. Both dissolving pulps rank among high-grade commercial dissolving pulps and show only minor deviations in their respective characteristics.

An alternative dissolving pulp precursor was produced and delivered.

Production and characterization of regenerated cellulose samples

For an optimal dissolution in H_3PO_4 it is necessary to treat the NaOH extracted pulps by refiners or mills to get a fluffy structure with a maximised surface area. To optimize the dissolution in H_3PO_4 the extracted pulps were treated by three different refiner treatments prior to dissolution. The results of the H_3PO_4 dissolution tests showed that two times fluffed pulps have good homogeneous dissolution properties.

Another aim of the H_3PO_4 dissolution and spinning tests was to investigate the effect of temperature and dwell time on the viscosity and the carbohydrate composition of the regenerated cellulose or spun fibre samples. One important result of the dissolution tests is that the purity level of hardwood regenerated cellulose is further increased to 98%, whereas the purity level of the softwood sample is only increased to 96%. Furthermore, the regenerated cellulose from the softwood pulp has a more inhomogeneous composition due to the occurrence of residual mannan as well as of residual xylan, possibly causing more problems in the further processing steps (spinning, carbonization).

Finally, two optimized hardwood pulps were compared in detail through the spinning process into the final fibre. This was done with the extracted eucalypt pulp produced in 120 kg scale and the alternative beech dissolving pulp. The differences regarding the chemical composition of fibres and the losses of hemicelluloses during spinning and regeneration were very small. Therefore this difference will hardly affect the impurities in the spinning bath and the recycling of H_3PO_4 . The fibres produced from beech wood pulp had small advantages in terms of finesse and Young modulus, but the tensile strength was identical for both fibers. The results confirm that the dissolution and spinning process is quite robust. Therefore, the dissolving pulp quality obtained by alkaline extraction of hardwood Kraft pulp is suitable for the CARBOPREC process chain for fibre production.

c) Dispersion

Different kinds of carbon nanotubes (MWCNT) were produced:

- t-MWCNT (lab scale): screening of several catalyst composition and determination of diameter of the different CNT prepared,
- o-MWCNT (lab scale): dry process to reduce numbers of post treatment, use of air between 400 and 600°C to oxidize CNT surface (muffle furnace), poor control of oxygen control – partial destruction of CNT structure,
- p-MWCNT (pilot scale),

- HT-MWCNT: high purity CNT.

From these CNT, ready-to-use masterbatch were produced:

- preparation of compound p-MWCNT/hydrosoluble polymer; dispersion trials of cellulose in H3PO4; preparation at lab scale of CW2-45 HP (CMC + C100 HP) and CW3-2.5 (C100HP + polycarboxylate) MB,
- preparation and evaluation of several formulations {lignin – binder – CNT}; compounding of lignin + NTC masterbatch.

Dispersion of standard CNT in cellulose and lignin were done and tested by spinning,

The choice of CNT type and the technology to introduce it in Cellulose and Lignin precursor have been developed. Several kg of all CNT and new master batch based on new MWCNT have been prepared.

The compatibility investigation of CNTs and Cellulose and Lignin confirmed the right choice of master batch matrix for CARBOPREC project: Carboxymethyl cellulose for cellulose precursor, and cyclic oligo-ester (CBT) for lignin formulation. Nevertheless, the precursor preparation techniques developed for both precursors, imposed the development completely new dispersion approaches designed for each formulation.

Therefore, the final solution for Cellulose precursor is purified CNT directly dispersed in liquid formulation compatible with phosphoric acid media. For the lignin formulation, the CBT based CNT master batch could be compounded in 2 steps with final lignin precursor formulation to be used in industrial scale production.

Cellulose precursor

Firstly, pilot scale batch of purified CNTs have been produced and a few kg were supplied for CARBOPREC needs. The choice of this kind of CNT is that the solvent spinning process is extremely sensitive to impurities, as confirmed in preliminary trials. ARKEMA purification process allows to eliminate catalyst particles. These CNTs are used in a specific designed technology (ball mill coupled with ultra-sound) of aqueous CNT dispersion with subsequent acidification and dilution in H3PO4 and use of these acidic dispersions to solubilize cellulose. Prepared liquid CNT master batch are stable in time and may be stored during few months period. The solution of cellulose in H3PO4 cannot be stored and should be prepared just before fibre spinning process.

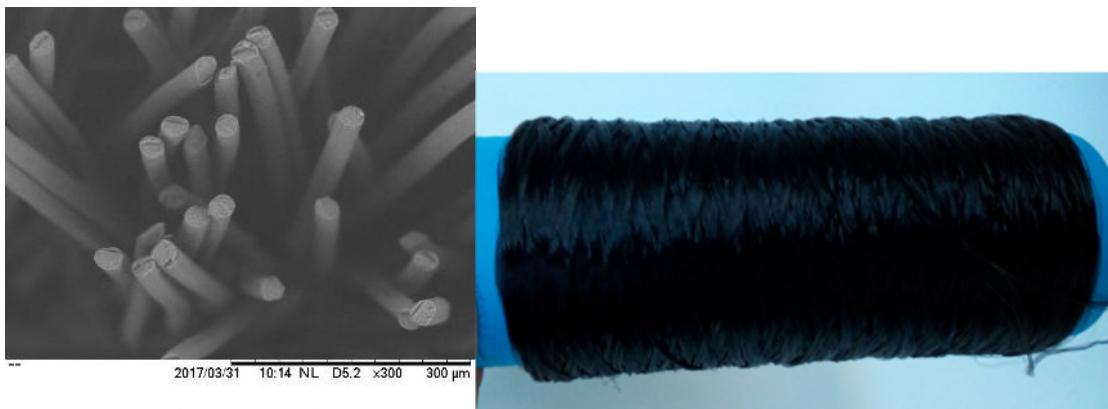
Lignin precursor

Comparability studies and preliminary lab scale trials confirmed that CM12-30 master batch is a right choice for lignin base formulations. The first difficulty to mix current CM12-30 (pellet form) with lignin in powder form had been solved. Cryo milling process allowed to obtain needed quantities of the master batch in powder form, granulometry distribution have been managed below 400 µm. These present good results in term of processing without modifying the dispersion state (T3.3).

Two steps formulation process have been developed for the lignin formulation plasticized with PEO, obtaining 10% CNT formulation in first step, and 1-2% ready to use master batch in the second step. Both steps processed in well-defined and controlled temperature conditions. The process of master batch preparation have been fitted to the Lignin formulation production. 150 kg trial have been successfully realised for the spinning process.

d) Spinning

For the spinning of cellulose, a new dissolution reactor and spinning pack for the multi-filaments wet spinning pilot plant was installed. It allows to process the cellulose spinning dope which exhibits high viscosity. During the project, we focused on the optimization of the formulation of the spinning dope, containing cellulose and carbon nanotubes in phosphoric acid (H₃PO₄). After finding the best spinning conditions, carbon nanotubes reinforced cellulose precursor fibers were obtained. Several kilograms were produced and sent for carbonization. The obtained precursor fibers are non-porous, cylindrical, individualized and with an average diameter of 20µm. More work need to be done on diameter reduction to increase the mechanical properties. It should be possible by stretching more the fiber during the spinning process and by injecting the spinning dope using an air-gap above the coagulation solution.



Static / discontinuous carbonization at lab scale were done to evaluate the potentiality of **cellulose** fiber as precursor for carbon fibers. The trials led to the optimization of both temperature profile and tensile load. The maximum carbonization temperature was 1100°C. The main challenge with using cellulose as precursor is to increase its very low carbonization yield: 10%. To achieve the targeted selling price starting with cellulose, this carbonization yield should be multiplied by 2 or 3. One way to do this is to impregnate the precursor fibers with additives such as flame retardant prior to carbonization.

For the **lignin route**, trials to spin fibers using only were done. It leads to very brittle fibers. Therefore, it was decided to blend the lignin with plasticizer to obtain spinnable formulations. Carbon nanotubes masterbatch were used and mixed with lignin and plasticizer. The total amount of lignin is between 75 and 95%. Lots of work was done on the spinnability of the formulations to reach the requirements of the multifilament melt spinning line. The main parameters that were optimized are the nature of the additives, their concentration, the viscosity of the blend and the extrusion temperature profiles. More than 100kg of ready-to-use lignin based pellets were produced and delivered for multifilament spinning. The spinning was done on a pilot line after definition of extrusion temperature profile, optimization of drawing process and some modification of the pilot line. Thanks to the process parameters optimization, around 40kg of homogeneous lignin fibers doped with CNT have been prototyped. These fibers need to be stabilized before carbonization.

The usual approach to obtain carbon fabrics is first to carbonized precursor fibers and then weave these carbon fibers. In CARBOPREC, another approach was tried: firstly weave precursor fibers (cellulose fibers in our case) and then, do the carbonization of the fabrics.



These carbonized fabric was used to manufacture some demonstrator parts.

e) **Bio-based carbon process**

The first topic was how plasma processes can support the stabilization of fibers obtained from lignin and hydrated cellulose. The objective was to develop a process to treat the precursor fibers in continuous plasma processes prior to carbonization at LLC-BCP. Due to delays caused by technical difficulties in fiber production, fiber was available at a late stage of the project. The focus was set to a general screening of different chemical formulations of Lignin, and commercial fiber to study the effect of plasma on the properties. The continuous treatment process was demonstrated on commercial Viscose fiber.

Secondly, the effect of plasma treatment on the properties of the hydrated cellulose modified fiber, on lignin fibers compared to the fibers obtained with the different production methods (PAN fiber, hydrated cellulose fiber TENCEL/ LENZING, CORDENKA® 700 Super 3), and also on the properties of the carbon fiber obtained based on the above mentioned precursors were assessed. The aim was to achieve the same physical and mechanical properties conforming to the precursors requirements, and besides they shall not be melted while carbonization, give the high carbon fiber yield; the obtained carbon fiber shall have the high physical and mechanical properties.

On the **lignin route**, experiments, in particular with acrylated lignin powder, showed clear trends to enhance cross-linking by plasma and UV-irradiation at 254 nm. This was seen in experiments with Lignin film samples by SEC. The optimization of the production is not finished as at the state of this report, fiber can be continuously produced by the partners, but the chemical composition/formulation of additives need to be further optimized. Currently, some additives necessary during fiber production lower the fiber stability upon temperature exposure.

The plasma treatment of the lignin based precursor samples before the high temperature treatment (carbonization) did not give any better results than untreated fiber. In any case, the fiber was destroyed during thermal treatment. This was caused by the lignin based samples being single-filament fibers with low physical and mechanical properties not corresponding to the requirements determined for the carbon fibers precursors. In spite of the several corrections of the process parameters, the high temperature treatment led always to their destruction; they were melted at the temperature of about 200°C and destructed inside the carbonization oven. It is impossible to carbonize the lignin fibers without the previous stabilization (oxidation), for which, despite of the method (thermal, plasma, UV, etc.) the chemical composition would need to be further optimized.

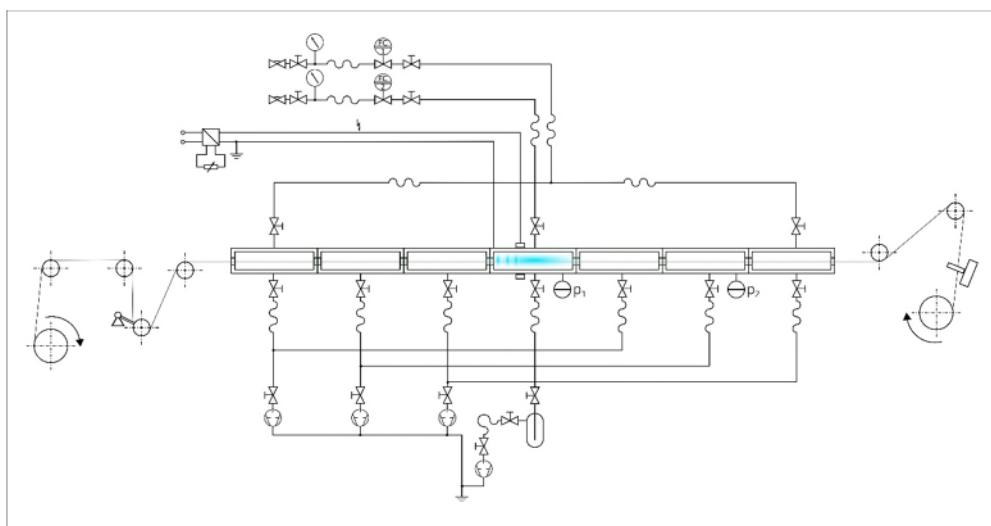


Figure 3 : Schematic setup for the continuous treatment of carbon precursor fiber.

For **hydrated cellulose**, homogenization of the fiber was observed as a major outcome during stabilization and carbonization experiments at LLC BCP. This resulted in lower variance of the mechanical fiber properties in the native state as well as after stabilization. The plasma treatment of the hydrated cellulose fiber (modified and not modified with CNT) during the stage of the precursor high temperature treatment preparation allowed to reduce variation of the physical and mechanical parameters and increase by 10% - 30% the strength characteristics as of precursor as of the carbon fibers after the structure modification and the fibers surface condition changing.

The statistical analysis of the obtained results had shown uniformity of the physical and mechanical parameters. It characterized the variation index that is calculated as relation of the mean deviation to the mean value. The variation index is the most common used parameter showing the level of the values variability. For the tested samples, the variation index does not exceed 30%, which means uniformity of the measured values relatively to the average one.

For viscose, roll-to-roll experiments were carried out. Some parameter sets allowed to increase Young's modulus and tensile strength according to testing at CANOE. The results indicate that the mechanical properties of Cellulose and Viscose can be changed by plasma treatment. To benefit from these modifications, the stabilization and carbonization processes should be varied in future to identify an optimum in time savings and energy consumption. It is planned to continue the research on basis of the final results.

Cellulose route

The evaluation of the possibility to obtain the carbon fiber (based on the continuous process of the carbon fiber production) based on the hydrated cellulose fibers modified and not modified with carbon nanotubes has been carried out, compared to the commercial hydrated cellulose fiber TENCEL, LENZING and hydrated cellulose yarn CORDENKA® 700 Super 3.

The physical, mechanical and microscopic testing of the cellulose and carbon fibers were carried out.

In spite of correction of the parameters for the process of carbon fibers production based on the modified precursor, the carbon fiber is very fragile and has the low strength. The precursor does not conform to the set requirements (namely: the high linear density of filament, high diameter of filament and low value of the unit breaking tenacity, high content of phosphates and the high fiber defectiveness).

In order to obtain the carbon fiber according to the continuous process with the high physical and mechanical properties it is necessary to continue the work with the hydrated cellulose fiber modified with the carbon nanotubes having the linear density of the filament not higher than 0,17 - 0,2 tex, and the unit breaking tenacity not lower than 350-500 mN/tex and the low fiber defectiveness.

The influence of the CNT being introduced in the structure of precursor while its preparation for carbonization process has been determined on the carbon fiber properties.

Based on the received results it was carried out the work as for obtaining the carbon fibers with the preset properties through the introduction of the CNT in the hydrated cellulose fiber structure (TENCEL/LENZING, CORDENKA), while the stage of the precursor preparation for the high temperature treatment. For this purpose, the CNT dispersion was used.

During the carbon fibers production, according to the continuous process and the corrected parameters of the carbonization and graphitization processes, an ultimate tensile strength of 350-417 MPa for the carbon fiber has been obtained.

The optimal concentration of CNT in the fire-retarding solution the correction of the parameters of fibers and the high temperature treatment permitted to increase the carbon fiber strength up to 420-582 MPa. It is reasonable to continue the research in this direction using the precursor modified, additionally while the fiber forming, to obtain the carbon fibers with the highest physical and mechanical properties.

It was mastered the process of carbonization and graphitization of the hydrated cellulose precursor in the form of the woven materials and yarns as being modified as not modified with CNT, compared to the commercial precursors.

The carbon fibers produced based on the hydrated cellulose fibers are worse as for the strength properties compared to the PAN based carbon fibers. Thereby, processing of the carbon hydrated cellulose fibers into the woven material using the textile machinery is rather difficult.

For production of the carbon hydrated cellulose fibers in the form of the continuous yarn it is required an additional stage: the preparation that consists of twisting and weaving.

Carbonization and graphitization are made for the finished textile structures (fabrics with the different weaving) or the technical ribbons (spaced out), where it is used the twisted filament yarn folded as warp, and as weft – the single filament yarn. After completion of the high temperature treatment, the carbon ribbon is separated in single carbon fibers.

To work through the parameters of the process to produce the carbon fibers based on the different textile structures the following materials were used:

1. hydrated cellulose fiber with the linear density of 184 tex, produced in India (commercial one),
2. the woven material in the form of the ribbon based on the commercial hydrated cellulose fiber produced (India) that had been produced at the facilities of SIGMATEX.

The physical and mechanical properties of the commercial hydrate cellulose fiber produced in India are conformed to the requirements set for the carbon fibers precursors.

As the result of the mastering of the carbonization and graphitization conditions, according to the continuous process of the carbon fiber production, the following was achieved:

1. It was produced the carbon yarn with the high strength characteristics. The ultimate tensile strength of filament was equal to 900-936 MPa,
2. The carbon content in the carbon yarn was equal to ~99,5 %,
3. To obtain the hydrated cellulose based carbon fibers with the high physical and mechanical properties, before the high temperature treatment of precursor it is required the additional process operation – producing of the woven material (ribbon, fabric with the different weaving) based on the hydrated cellulose fibers.

The carbon fibers samples were produced and sent to the partners in order to use them in composite materials for demonstrators.



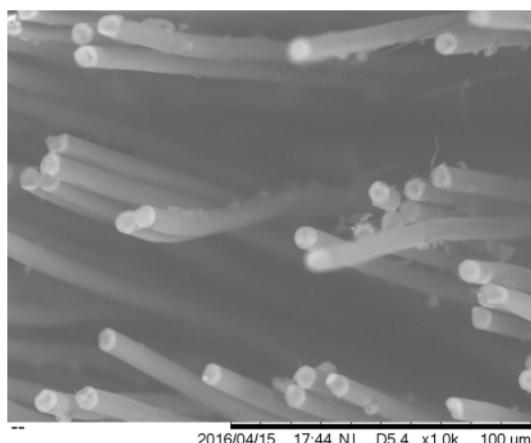
Figure 4: Carbon fiber and carbon ribbon

Lignin route

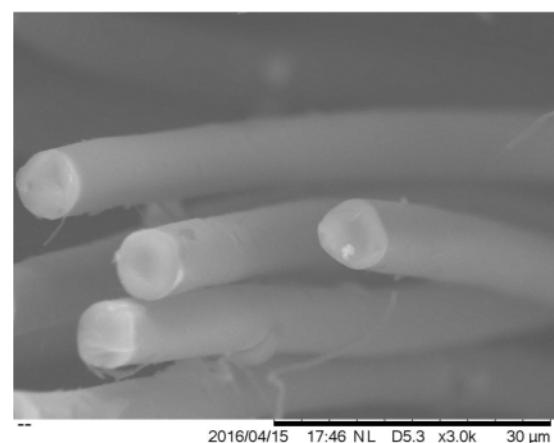
It was carried out the evaluation of the possibility to obtain the carbon fiber using as the precursor the commercial hydrated cellulose fiber TENCEL/LENZING and hydrated cellulose yarn CORDENKA with the previous application of organosolv lignin on their surface.

All the attempts to execute the high temperature treatment of the lignin based samples led to their thermal destruction; they were melted at the temperature of about 200°C and destructed inside the carbonization oven.

In connection to this, the idea appeared to use the commercial hydrated cellulose fiber TENCEL/LENZING and CORDENKA as the precursor with the preliminary application of organosolv lignin on its surface. As a result, we determined the conditions of the organosolv lignin application on the precursor surface and the parameters of the carbon fiber production process. The uniform distribution of lignin on the fiber surface thanking for the high adhesion of the doping solution to the fiber had allowed to obtain the smooth fiber surface.



Microscopic research



Filaments with lignin (circular cross-section)

Introduction of the additional doping of the commercial precursor with the organosolv lignin solution, and correction of the process parameters permitted to obtain the lignin based carbon fibers.



Figure 5: Samples of carbon fibers with lignin (tow and yarn)

Similar results are expected for the hydrated cellulose fiber obtained in the frame of the project if its physical and mechanical properties conform to the precursor requirements.

This work had not been programmed in the frame of the project. Still the obtained results demonstrate the potential possibility to carry out some researches in this direction.

It was mastered the process of carbonization and graphitization of the hydrated cellulose precursor in the form of the woven materials and yarns as being modified as not modified with CNT, compared to the commercial precursors.

The carbon fibers produced based on the hydrated cellulose fibers are worse as for the strength properties compared to the PAN based carbon fibers. Thereby, processing of the carbon hydrated cellulose fibers into the woven material using the textile machinery is rather difficult.

So for production of the carbon hydrated cellulose fibers in the form of the continuous yarn it is required the additional stage – the preparation that consists of twisting and weaving.

Carbonization and graphitization are made for the finished textile structures (fabrics with the different weaving) or the technical ribbons (spaced out), where it is used the twisted filament yarn folded as warp, and as weft – the single filament yarn. After completion of the high temperature treatment, the carbon ribbon is separated in single carbon fibers.

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The carbon fibers samples were produced and sent to the partners in order to use them in composite materials for demonstrators.

It was originally foreseen to develop processes for fiber functionalization on carbon fiber produced in the project. Due to delays caused by technical difficulties in fiber production, the fiber was only available at a late stage of the project. Therefore, the screening was carried out on different replacement materials. Several processes were made available. The processes differ in the precursors used for functionalization and the use of different processes. Two processes based on ammonia, resulting in amino functionalization, were used. The third process which is based on ring-opening plasmas was used for amino-, hydroxyl- and aldehyde- functionalization. Plasma has been shown to alter the properties of the material surfaces in the wanted direction. The processes were demonstrated on different materials, either carbon fiber or chemically similar material. For this proof, different surface analytical methods had to be applied such as XPS measurements and derivatization by stationing and fluorescent dyes. The results indicate that the surface modification can be carried out in the desired way. The final proof that fiber-matrix adhesion can be improved requires larger amount of project carbon fiber which was not yet available at the end of the project. It is planned to continue the research on basis of the final results.

Simulation on RTM process

CTAG carried out the simulation of the manufacturing process using Moldflow software. This virtual tool allows forecasting the resin flow and the final warpage of the part.

It was initially intended to simulate the RTM process. However, the first manufacturing trials were not complex and complete enough to reach a good characterization of the porosity, permeability and flow type, due to the limited amount of fabric.

It was decided to take profit of the high reliability and accuracy of Moldflow regarding the injection moulding process to characterize the CARBOPREC fibre behaviour using it as an insert to be over-moulded with a thermoplastic resin.

This change in the scope allows us to reach some interesting information about the CARBOPREC fibre performances compared to the benchmark.

Since no fabrics are included in the Moldflow database, the direct simulation of the composite manufacturing process based on over-moulding was not possible until now. To allow this modelling, a characterisation of the fabric as an orthotropic insert was made and a correlation was carried out to guarantee the validity of the method. The correlation was made not only with CARBOPREC fabric, but also with three different carbon fabrics available in the market.

The characterisation of the fabric as an orthotropic insert has proven to be an accurate methodology to simulate the warpage in the final part when a carbon fabric insert is over-moulded.

However, the final values of the orthotropic insert have to be readjusted according to the interface quality between the thermoplastic matrix and the fabric, which is difficult to determinate before the manufacturing process.

Assuming a good interface quality, the values exposed in the following table are considered correct and provides a good correlation between the modelling and the real part.

Taking into account that the CARBOPREC fabric have not sizing, the interface presents poor quality and therefore, both the mechanical properties and the warpage are lower than the ideal case. It is expected that the addition of a correct sizing will provide better interface, and therefore, a good correlation using the selected orthotropic insert values.

In any case, the characterisation could be easily modified according to the achieved results, as the methodology has proven to be correct.

f) Demonstrators of composite parts from bio-based carbon fibres

The actual cataphoresis resistance test require a lot of material. Therefore it was decided to simulate the cataphoresis resistance test by means of a simplified procedure. Some preliminary tests have been performed in order to compare measured values with values calculated by the simulation.

Another specific test for automotive industry is the gravelling impact resistance test: a first trial was also performed on a benchmark using glass fiber.

AVANA has designed and developed an aluminum tooling which will be used to provide some composite plates.

The lignin based precursor fibres are not weavable. The cellulose precursor fibers are not weavable as twill when carbonized but they are weavable before carbonization.

Concerning the final demonstrator with the CARBOPREC fibers, it was decided to abandon the demonstrator with TP resins and to focus on TS (poor results with benchmark resins and not enough CARBOPREC tissues to conduct all important tests with more promising resins, so we did not want to waste the little tissue we had).

For SMC, the results are very disappointing, with a tensile strength of 20MPa and a modulus of 10MPa (to be compared with respectively 140 and 35 MPa for the benchmark). The reason of such a poor result is possibly partly due to the fact that the processing with the CARBOPREC fiber was very difficult. It looks like the impregnation was not good enough. For some reasons (inappropriate sizing? Roughness?) It seems that the surface properties of the CARBOPREC fibre is not compatible with existing SMS technology.

The CARBOPREC project synthesized enough fibres to produce good quality composites with the selected thermoset systems. We could compare the characteristics obtained with the CARBOPREC fibres the commercial benches. The result was disappointing for the automotive demonstrator but promising for the wind blade one. The reasons of the difference of behaviour may be due a difference in compatibility between the surface of the CARBOPREC fibres and the resins used by both industries. More work will be necessary to cover the fibres with a sizing more suitable with the high temperature resins uses for the automotive demonstrators.

g) Fundamental understanding of interactions

The interfacial interactions between lignin (alternatively cellulose) polymers and CNT shall be unraveled and the impact of the molecular structure of the wood biopolymers on their miscibility and adhesion with CNT deciphered. We demonstrated that lignin and cellulose molecular attributes, as they might be tailored from the project production method, have a minor influence on their interaction potential with carbon nanotubes.

Lignin Route:

Based on solubility parameter studies, neat organosolv lignin was found to be miscible with neat carbon nanotubes. Lignin hydroxyl content and their acidity had little influence on their solubility parameter. The interactions were found to be mostly of dispersive nature from simulations and a clear correlation between carbon nanotube oxidation treatment and miscibility and theoretical energy of adhesion was determined.

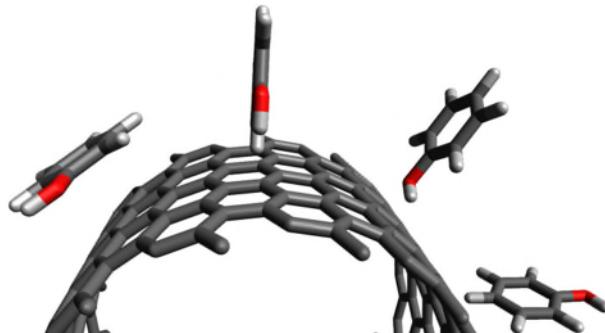


Figure 6: Schematic setup of DFT adsorption simulations. The simplified lignin model molecules interact non-covalently with the nanotube section. Surprisingly strong correlations between a special set of adsorptions and bulk-related solubility parameters were found (J. BADORREK, M. WALTER, M.-P. LABORIE, "Tuning intermolecular interaction between lignin and carbon nanotubes in fibre composites – a combined experimental and ab-initio modelling study", Renew. Mater. 2018, accepted.)

Furthermore, experimental determination of solubility parameter was found to be a good tool to assess compatibility between the various components of the precursor masterbatch.

Concerning the precursor lignin fiber masterbatch selected in the project, a clear effect of shear rate on the blend morphology could be established. Increases in shear rate led to a perfectioning of the spherulitic crystalline structures and crystallinity increase, which can be seen in the following figure revealing results obtained by DSC measurements.

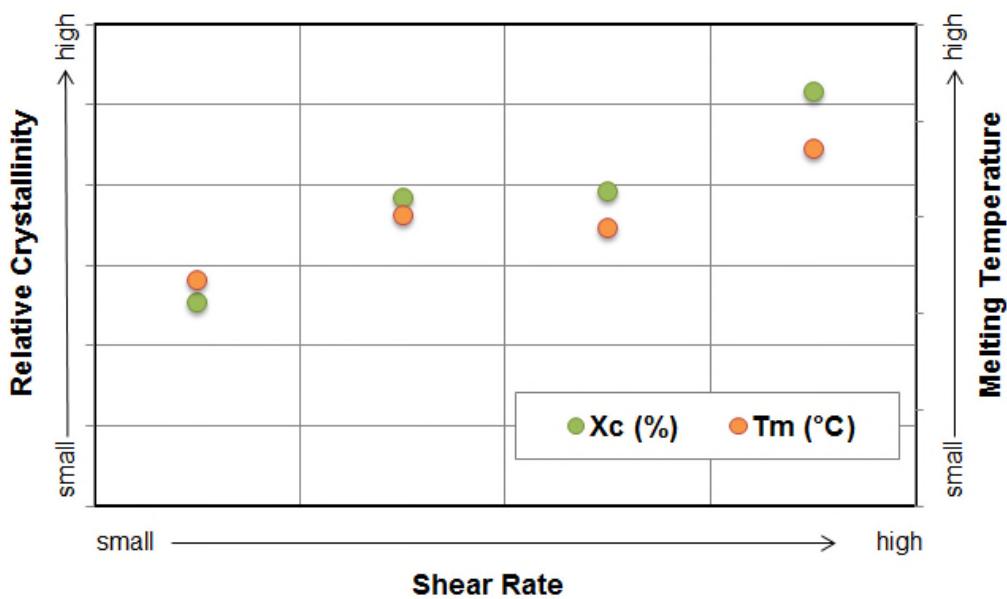


Figure 7: Effect of shear rate on relative crystallinity and melting temperature in precursor lignin fibers

This effect of perfectioning of spherulitic structure was especially observed in presence of carbon nanotubes. As visible in the figure below, which were taken with the help of polarized optical microscopy (POM), spherulitic structures become more perfect with increasing carbon nanotube content from 0.1 (a) to 1 (b) percent.

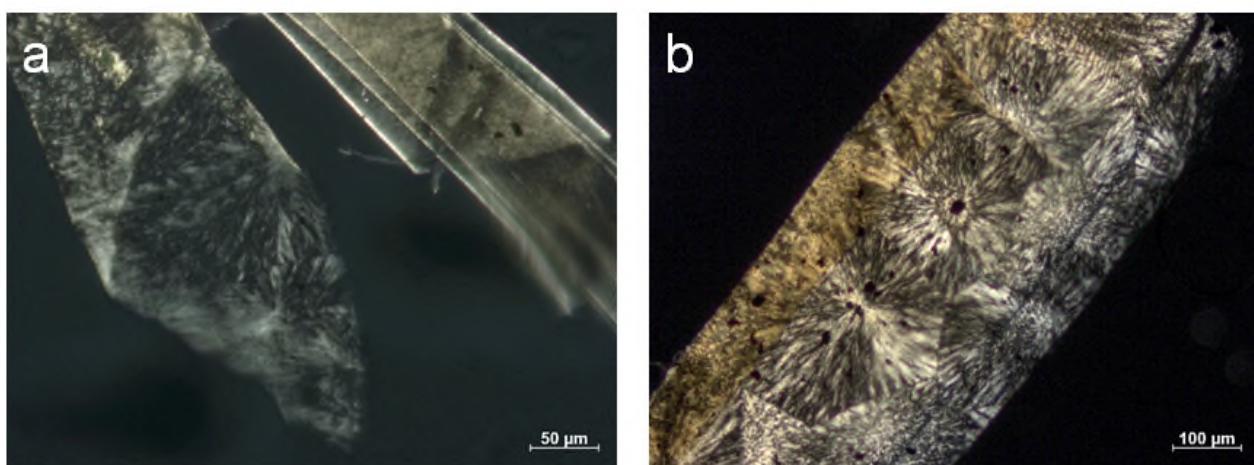


Figure 8: Comparison of Sample with a carbon nanotube concentration of 0.1 (a) and 1 (b) percent

These results hence confirm that carbon nanotubes and shear rate synergistically act to template the precursor masterbatch.

Cellulose Route:

Cellulose was shown to be incompatible with neat CNT. Carbon nanotubes and shear rate significantly altered the morphology of the masterbatch selected in the project (based on the previous outcomes). In presence of carbon nanotubes, cellulose crystallinity increased, however shear rate had little effect.

In the second goal, we particularly considered the surface properties of bio-based carbon fibers and their petroleum-based counterparts. Additionally, epoxy-carbon fiber composite demonstrators were mechanically tested to assess performance. The surface properties (surface energy (Table xy)) of the bio-based carbon fibers and their adhesion into an epoxy matrix were of the same order as those measured for commercial carbon fibers.

Table 1: Surface energy of the commercial CF and CARBOPREC CF

Surface energy	Commercial CF	CARBOPREC CF
γ^{Total} (mJ/m ²)	48.6	51.5

In demonstrators, the CARBOPREC composites exhibited bending properties alike those of commercial carbon fiber composites (Figure 9).

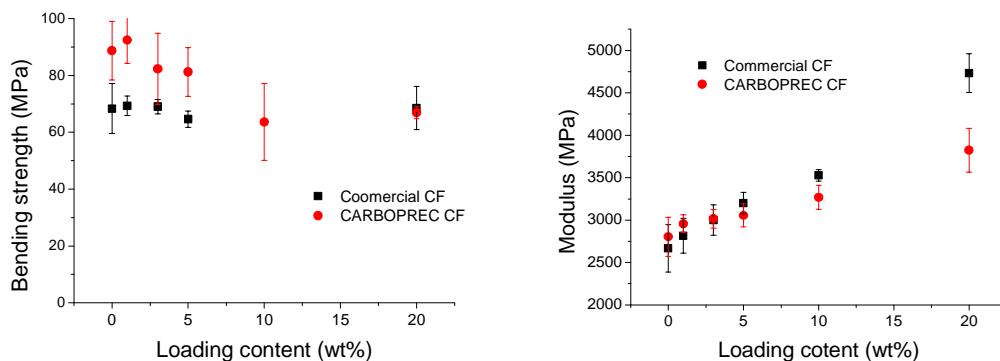


Figure 9: Results of the bending tests (bending strength and modulus)

In short, from the lab-scale evaluation, the CARBOPREC CF has satisfied interfacial interaction with epoxy resin, and it is a promising and competitive new-generation bio-based carbon fibers.

h) LCA, recycling, safety issues & economic analysis

LCA studies in CARBOPREC project have been performed by using SimaPro 8 software with Eco-invent 3 libraries.

The LCA studies are compliant with the indications contained in the respective ISO references; in particular the structure of the studies start with the objective definition, continue with the inventory and impact assessment steps and finish with the interpretation of the results.

LCA studies have been performed by using different impact assessment methods in particular one multi-indicators method has been used together with two mono-indicator methods and in particular these are: ReCiPe 2008 (multi-indicators method) IPCC 20yr (for the analysis of carbon footprint) and Berger 2014 (for the analysis of the water footprint).

During the development of LCA models for lignin and cellulose carbon fibres, different sensitive processing steps in terms of environmental performance of the products have been identified. In particular the use of acid in cellulose processing, the use of solvents in lignin extraction, the yield in cellulose precursor conversion and in general the energy spent on the whole process are very important issues, and thanks to the results of LCA studies the researchers have continuously worked to improve as much as possible the impact of these items.

Due to the complexity of the model it has been necessary to use also secondary data in the study, for this reason during the last period an analysis of the uncertainty of the results has been performed. In particular data coming from publications and software libraries have been used in the LCA study in this project. It is important to outline that the majority of the info used are in any case primary data from project partners.

Finally, as showed in the following figure 10 it is possible to assess that the new precursors allow to achieve carbon fibre with good environmental behaviour in comparison to traditional PAN based carbon fibres.

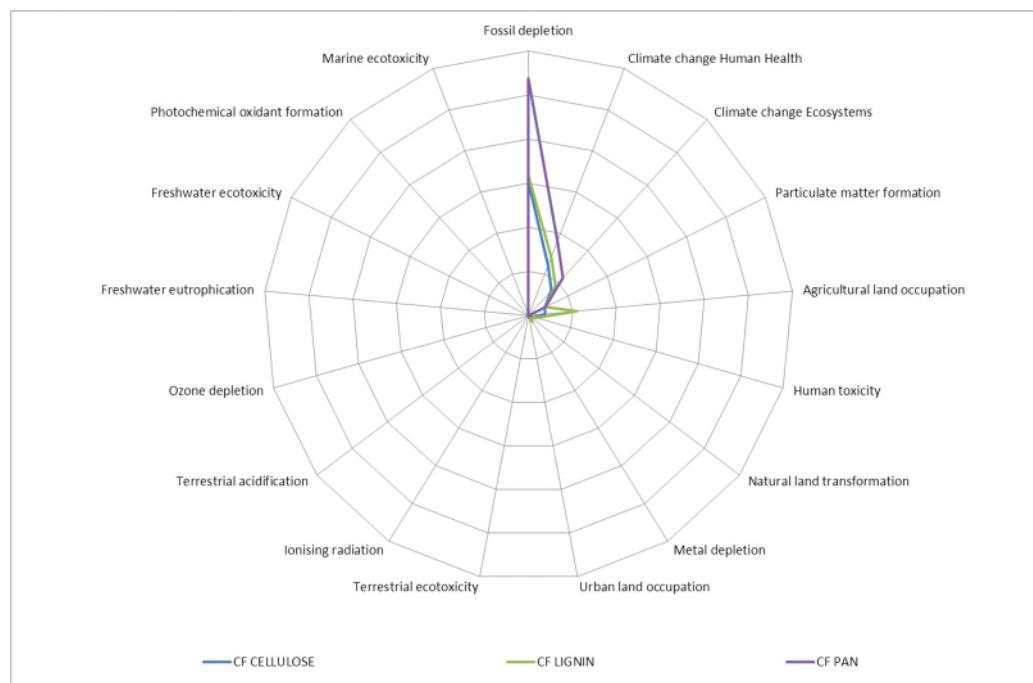


Figure 10: LCA results in terms of different indicators at mid-point of ReCiPe 2008 method of the different Carbon Fibres studied in CARBOPREC. It is clearly visible the advantage of new precursors in terms of fossil fuel depletion. Note the picture is not reporting the graduation of the scale in order to avoid any diffusion of sensitive information for the companies who supplied us the data for the LCA study

In particular both precursors show a slightly better overall score in ReCiPe 2008 impact assessment (Figure 11), and a significantly better Carbon footprint. Vice versa, the new precursors pay something in the water footprint in comparison to PAN due to the necessity of this resource for the growth of biomasses and the extraction processes (Figure 12).

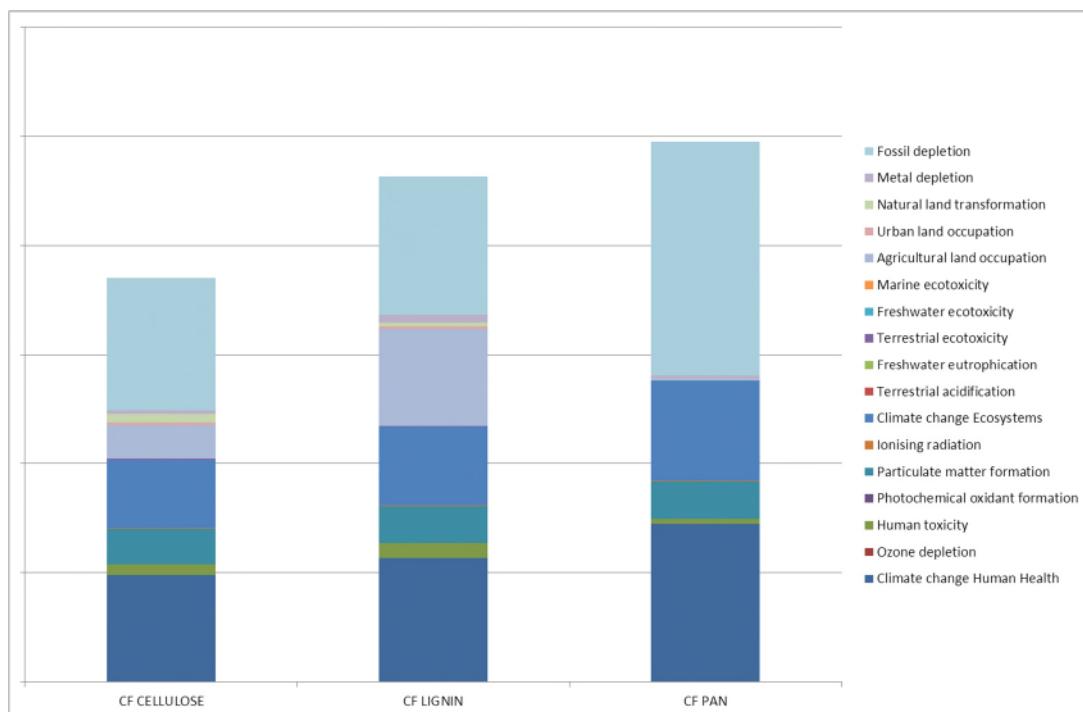


Figure 11: Overall score representation of impact assessment with ReCiPe 2008 method. Here it is possible to analyse the overall environmental behaviour of the carbon fibres analysed. Also in this case the values are not reported in order to avoid the diffusion of sensitive information

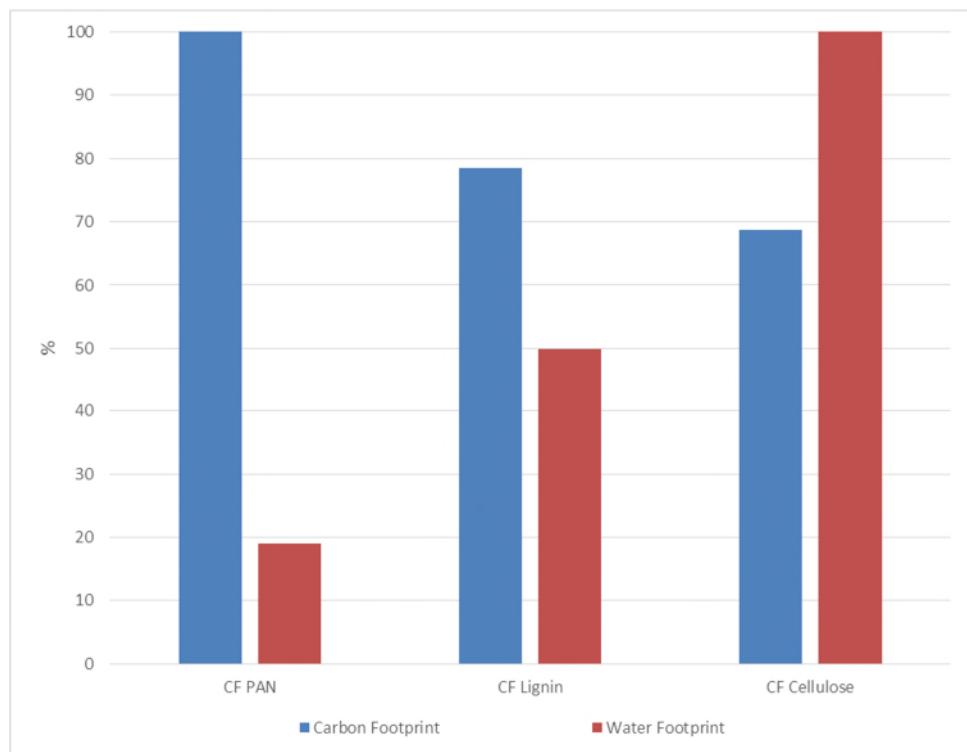


Figure 12: Carbon footprint calculated with IPCC 20 yr 2013 method and water footprint with Berger 2014 method. Also in this case the values are not reported in order to avoid the diffusion of sensitive information

In any case, it is possible to assert that the overall environmental performance of new CARBOPREC carbon fibres is slightly better to traditional PAN carbon fibres.

The main purpose of the safety assessment of the new carbon fibers production process is analysis (evaluation) of the potential human hazards risks and risk for the environmental safety, avoiding the possible accidents and reduction of the time to eliminate them.

Evaluation of impact of the cellulose based carbon fibers production process on environment has shown that this process does not affect significantly the human health and the environment safety.

Using of the natural renewable resources as the raw materials is also a very important aspect regarding the environment exposure. Actually, the renewable resources have the positive effect in the cycle of CO₂, as far as they absorb CO₂ from ambient while their life cycle. Additionally their impact on the resources depletion is very low as they are natural and renewable. From the other hand, the raw materials being commonly used in the process of the PAN based carbon fibers production, affect as the CO₂ cycle as the resources depletion, because it is not the renewable one and it doesn't absorb CO₂.

The issue of the energy consumption is also very important to assess and optimize the CO₂ emissions while the production process. The analysis demonstrates that duration of the stages of carbonization and graphitization processes for the bio-based carbon fibers production will reduce that ensures the CO₂ emission level reduction while production.

The new process is eco-friendlier compared to the process of the PAN-based carbon fibers production.

The main task of the recycling assessment is analysis of the possibility to utilize the wages generated while production of the carbon fibers and polymeric composite materials based on them.

The basic way to solve the issue of utilization of the wages in the form of the carbon fibers generated while the different process stages is usage of the wages as the filler in composite materials. As a result, we obtain the additional quantity of the useful products applicable for the different industries and it does not suggest the environmental pollution.

The main way to solve the utilization problem of the wastes in the form of the composites is recycling for reusing as the filler in composites.

Nowadays three disposal methods are conditionally considered: physical, chemical and thermal ones.

Physical methods of PCM processing

Mechanical method is a method of milling, grinding and re-pulping. The main product of this process is recycled (PCM disposal product) of the different milling degree.

The process execution of the mechanical processes can be made in the different forms beginning with the common shredders and breaking machines and finishing with the air breaking machines of «zigzag» type (figure 13).

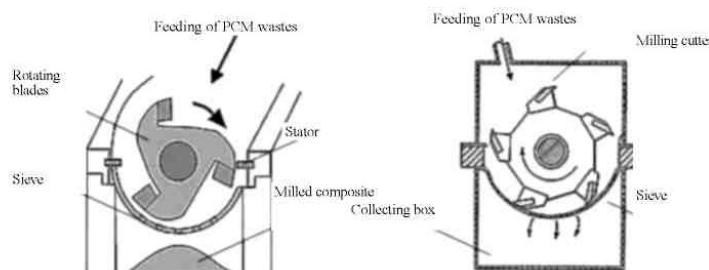


Figure 13. Design of the mechanical breaking machines for PCM

The advantage - rather easy process design for any PCM and polymers, the parallel recycling of fibers and polymeric binder and also lack of the hazardous emissions.

The disadvantages - the high energy consumption, difficult adjustment of the milled PCM size, reduction of the mechanical properties of the milled reinforced plastic materials, the limited secondary usage of the processed materials.

Chemical methods of PCM processing

The chemical method of PCM disposal is based on de-polymerization (chemical destruction) of the polymeric binder. Its product is fiber.

Thermo-catalysis is based on de-polymerization of the polymeric binder. The content of the initial reagents medium is selected properly for every binder to be disposed.

Solvysis – is the process of the matrix de-polymerization where the different liquids are used as the medium (supercritical water, alcohols) with accelerators in the form of alkali salts.

Advantages: the rather easy equipment design, energy efficiency of the process, application of the epoxy binder degradation products while the repeated synthesis of the epoxy resins. The output products are fibers and depolymerized epoxy binder.

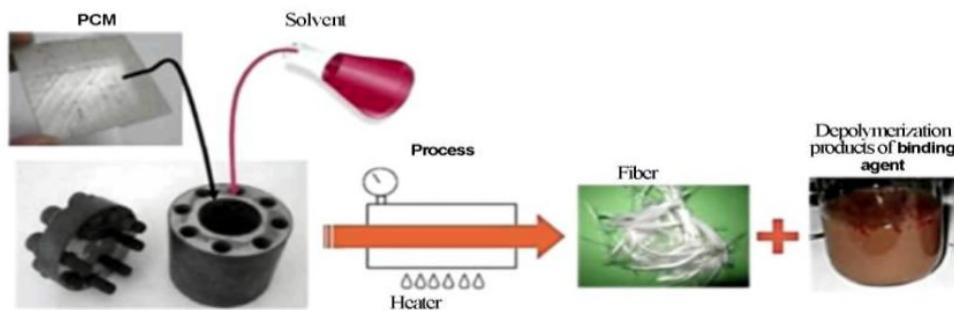


Figure 14: The relative diagram of PCM disposal with solvolysis method

Solvysis method disposal could be applied for the carbon fiber composites and some types of fiber glass materials as the main requirement is the chemical stability of the filler to reagents.

Oxidation in the pseudo-fluidized layer (fluidized bed process (FBP)). This process has been developed by the Nottingham University.

Oxidation in the pseudo-fluidized layer is consisted of the following: in the bath filled in with the solid particulate filler (for example with sand) it is introduced the reinforced PCM to be disposed, and then it is fed the hot gas (under the temperature of 450 - 550°C) enriched with oxygen (air). The heated gas passed through the sand layer which oxidizes the polymeric binder, and then the hot air flow takes away the fibers and the polymeric binder oxidation products from the reaction area. In the cyclonic collector the fibers are separated from the polymeric binder oxidation products. The under-oxidized compounds of the polymeric binder are completely oxidized in the burning chamber. Using this process, it is possible to remove the different PCM containments – any organic metals (polymers, paints, foams) are oxidized and the metals (metal wire, fasteners and inserts) remain in the pseudo-fluidized layer.

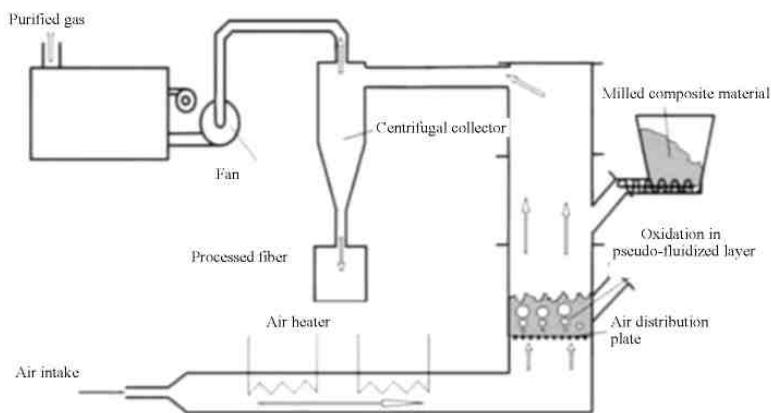


Figure 15. Diagram of the «oxidation in the pseud-fluidized layer» process with cyclonic collector

Thermal methods of PCM processing

Burning is a method based on PCM elimination under the oxygen content close to or above the stoichiometric value. This method is not reasonable as far as the only product that could be used in this process is heat. Besides it, burning leads to environmental contamination (of the air and water basins), so this disposal method is forbidden in many European Union countries.

Gasification is the process of PCM degradation (under lack of oxygen) including the synthesis gas applied for manufacturing of the heat and electric energy. The gasification disadvantage is destruction of the most valuable PCM elements and the high possibility of the hazardous gases emission in ambient.

Pyrolysis – is the mostly widely used disposal method for the reinforced plastic materials nowadays. This method is mostly used in German, Great Britain, USA, Belgium, and France and in the other West Europe countries.

The pyrolysis is divided in:

- low temperature one (300 - 500°C) whose products are fibers and also the oils and solids – degradation products of the polymeric binder,
- medium temperature one (500 - 800°C) whose products are fibers, oils and gas; in a less degree – solids,
- high temperature one (800 - 1500°C) whose products are fibers and pyrolysis gases; the solids and oils yield is not significant. The pyrolysis process is carried out under lack of oxygen and very often in the inert gas medium (nitrogen).

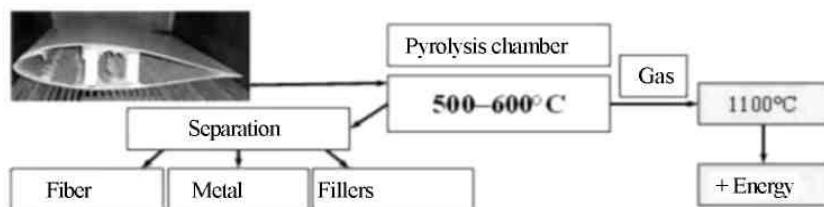


Figure 16: Diagram of the pyrolysis process of the reinforced plastic materials

The pyrolysis advantage is the high fibers yield with the optimized process, usage of the heat of the polymeric binder degradation, generality of the equipment, high adhesion of the epoxy binder to the processed fibers of the reinforced plastic materials and the ample opportunities of the commercial application.

The pyrolysis disadvantages are the non-uniform heating of the reactor working area and in consequence the binder degradation could be incomplete and also the necessity of detoxification of the pyrolysis gases containing the hazardous substances compounds.

The analysis of the foreign experience in PCM disposal has shown that for every type of the fillers it is reasonable to choose its own disposal method:

- for the carbon fibers composites: thermos-catalysis, solvolysis and pyrolysis,
- for the glass fibers materials: pyrolysis and in a less degree – thermos-catalysis,
- for the green plastics: low- and medium-temperature pyrolysis.

Economic analysis of CARBOPREC concept consists of the technical and economic evaluation of the costs to produce the carbon fibers from the lignin and cellulose precursors being modified with the carbon nanotubes. It was carried out in comparison to the conventional process of glass fibers and PAN based carbon fibers production. The processes routes and distribution of the basic costs as for the production stages are shown in the following figures.

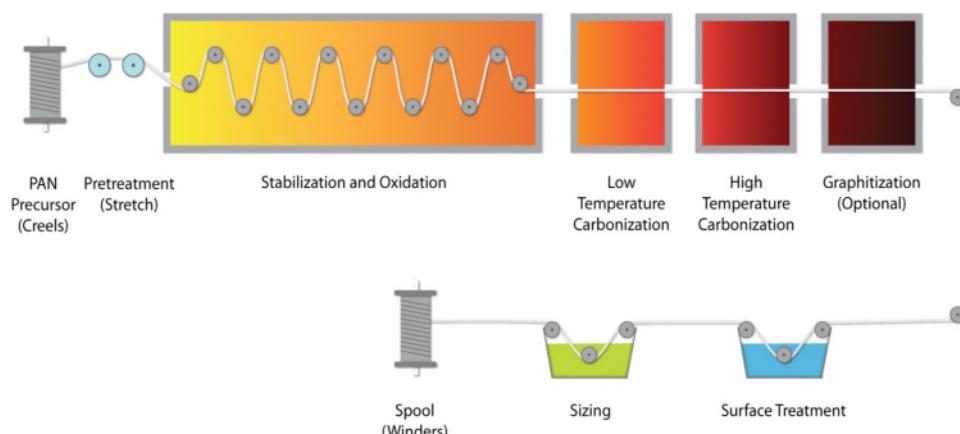


Figure 17: .Conventional production of the carbon fibers based on PAN precursor

Major Cost Elements

Precursor - 43%

Oxidative stabilization -18%

Carbonization - 13%

Graphitization - 15%

Other * - 11%

*sizing, final treatment, quality control

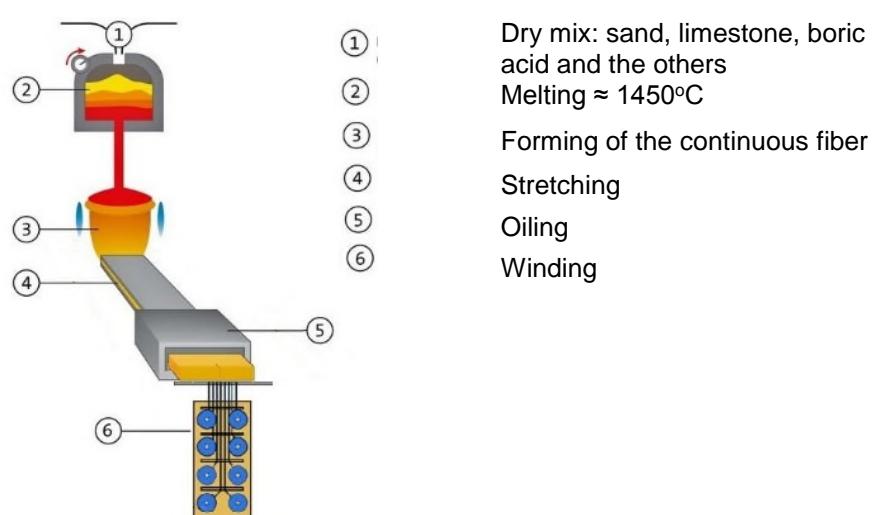


Figure 18: Conventional GLASS Processing

Major Cost Elements

Precursor - 15%

Melting - 31%

Molding - 28%

Other* - 26%

*sizing, final treatment, quality control

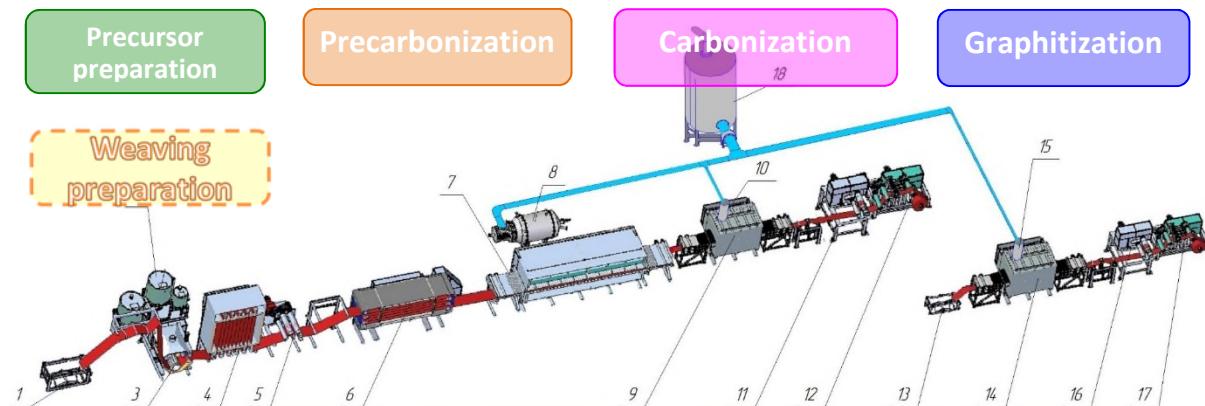


Figure 19. Production of the carbon fibers based on the hydrated cellulose precursor.

Major Cost Elements

Precursor - 47%

Pretreatment (weaving, doping, thermostabilization) - 7%

Pyrolysis, oxidation - 36%

Carbonization, graphitization – 9%

Other* - 1%

*sizing, final treatment, quality control

Plasma treatment and CNT modification should exclude the expensive stage and increase the carbon fiber yield

The executed evaluation has shown that the cost of carbon fibers obtained according to the new process is lower compared to the commercial carbon fiber based on PAN precursor.

The same calculations were done with the production of 12000t/year of cellulose based precursor fibers leading to 4000t/year of carbon fibers. In this case, the selling price of the carbon fibers decreases to 8.22€/kg, and the cost of the raw material represents 50% of this price.

In addition, this study leads to a selling price of lignin based carbon fibers of 8.5€/kg. It is below the target price of CARBOPREC objectives.

The results obtained in the frame of the project demonstrate that the further work with the plasma-treatment of the carbon fibers and precursor modifying (based on lignin and cellulose fibers) with the carbon nanotubes permits to reduce the costs for the most expensive stage of the carbon fibers production (pyrolysis (oxidation)), to increase the carbon fibers yield and also to reduce the cost and increase competitiveness of bio-based (cellulose and lignin based) carbon fibers.

The potential impact (including the socio-economic impact and the wider societal implications of the project so far)

On the lignin route, here is the list of potential impacts:

1. The production set up for various lignin grades in pilot scale was defined. This allows adapting the Organosolv process to various feedstock and parameters and, based on the in-depth analytical characterisation of the lignins, targeting of specific lignin characteristics. This will not only be relevant in the field of carbon fibres, but in all potential lignin applications. Progress beyond the state of the art concerns particularly the production of special lignin qualities in pilot-scale (e.g. high-molecular weight lignin and organosolv-lignin from spruce),
2. The parameters for producing organosolv lignin as optimised carbon fibre precursor were defined. This is an important step towards lignin-based carbon fibres,
3. Plasma-active functional groups were successfully introduced into the lignin precursor. This will be relevant not only for application in carbon fibres, but also in other applications where fast cross-linking of polymers may be of advantage,
4. A process was developed to produce acrylated lignin in pilot scale. Scaling of this derivatisation reaction has been a challenging task, but provides now the basis for transferring this process to higher TRL,
5. Various lignin grades were produced during the project adapting the Organosolv process to various feedstock and parameters,
6. An amount of 167 kg of optimised lignin (beech:spruce 1:1 (w/w)) was provided as optimized precursor,
7. Plasma-active functional groups were successfully introduced into the lignin precursor,
8. A process was developed to produce acrylated lignin in pilot scale. An amount of 3.0 kg of acrylated lignin could be provided as additive in lignin formulations,
9. A report on the detailed analytical characterization of various lignins was provided.

On the cellulose route, here is the list of potential impacts:

1. The process for dissolving pulp production could be successfully scaled-up to pilot scale to provide 120 kg of purified cellulose. In addition, an alternative dissolving pulp precursor was produced and delivered. This allowed the direct comparison of two feasible routes for the preparation of dissolving pulp with regard to dissolution properties and fibre spinning. These results are well transferable to future tasks involving cellulose spinning. In addition, insights were gained on important issues arising during scale-up of hemicellulose extraction. This know-how is applicable to future extraction tasks,
2. A report on the analytical characterization of cellulose-based precursor was provided. These results are the basis for a better understanding of the production of different cellulose precursors and how to target specific properties. Thus, this outcome is relevant and transferable to other cellulose-based applications,
3. A report concerning the correlation of dissolving pulp and fibre properties was provided. This is the basis for understanding the behaviour of the interaction of cellulose, H₃PO₄ and CNT. Especially on the latter, no data has been available so far and therewith it constitutes a starting point for new possibilities in carbon fibre manufacture. The report confirmed as well, that the spinning process based on H₃PO₄ is flexible and not very sensitive to small fluctuations of pulp quality,
4. The process for dissolving pulp production could be successfully scaled-up to pilot scale to provide 120 kg of purified cellulose,
5. A report on the analytical characterization of cellulose-based precursor was provided,
6. An alternative dissolving pulp precursor was produced and delivered,
7. A report concerning the correlation of dissolving pulp and fibre properties was provided.

The address of the project public website, if applicable as well as relevant contact details.

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Use and dissemination of foreground

Section A (public)

This section includes two templates

- Template A1: List of all scientific (peer reviewed) publications relating to the foreground of the project.
- Template A2: List of all dissemination activities (publications, conferences, workshops, web sites/applications, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters).

These tables are cumulative, which means that they should always show all publications and activities from the beginning until after the end of the project. Updates are possible at any time.

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES										
NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers ² (if available)	Is/Will open access ³ provided to this publication?
1	<i>No peer-reviewed publication</i>									

² A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

³ Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

Nº	Type of activities	Main leader	Title	Date	Place	Type of audience	Size of audience	Countries addressed
1	Posters	ALU-FR	Student's information day: "fundamental understanding of interactions between carbon nanotubes and lignocellulosic matrices - adsorption experiments under quiescent conditions"	16/06/2014	Freiburg, D	Scientific community (higher education, Research)		Germany
2	Oral presentation to a wider public	CANOE	International Carbon Composite Conference: "continuous spinning of composite fibers: towards new cost-effective precursors for low cost carbon fibers"	13/05/2014	Arcachon, F	Industry		international
3	Oral presentation to a wider public	CANOE	Conférence annuelle du Groupe Français d'Etude sur le Carbone: "low cost carbon fibers supply chain"	15/05/2014	Orléans, F	Industry		France
4	Oral presentation to a wider public	CANOE	Conference of the French Society for Metallurgy and Material: "procédés de fabrication de fibres de carbone bas coût à partir de bioressources"	14/06/2014	Bordeaux, F	Scientific community (higher education, Research) - Industry		France
5	Oral presentation to a wider public	CANOE	Les rendez-vous "chimie & matériaux": "manufacture of low cost carbon fibers from bio-based precursors"	28/01/2015	Bordeaux, F	Industry		France
6	Oral presentation to a wider public	CANOE	JEC (Journées Européennes des Composites) 2015	11/03/2015	Paris, F	Scientific community (higher education, Research) - Industry - Civil society		international

7	Oral presentation to a wider public	CANOE	Symposium on Green Chemistry	03/05/2015	La Rochelle, F	Scientific community (higher education, Research) - Industry		France
8	Oral presentation to a scientific event	FRAUNHOFER	Carbon 2015 : "renewable source nanostructured precursors for carbon fibers"	12/07/2015	Dresden, D	Scientific community (higher education, Research) - Industry		international
9	Oral presentation to a scientific event	UNIVERSITAET HAMBURG	Freiburg Materials FMF Colloquium "investigation of miscibility and properties of lignin/polycarboxylate polyether blends"	15/10/2015	Freiburg, D	Scientific community (higher education, Research) - Industry		international
10	Oral presentation to a scientific event	CANOE	Biopolymers International Conference 2015: "multiphase materials based on lignin, cellulose and carbon nanotubes: morphological and adhesion studies"	14/12/2015	Nantes, F	Scientific community (higher education, Research) - Industry		international
11	Oral presentation to a scientific event	CANOE	Biopolymers International Conference 2015: "spinning of composite fibers from renewable materials: towards new low cost carbon fibers"	14/12/2015	Nantes, F	Scientific community (higher education, Research) - Industry		international
12	Exhibitions	CANOE	JEC (Journées Européennes des Composites) 2016	08/03/2016	Paris, F	Scientific community (higher education, Research) - Industry	20000	international
13	Exhibitions	CTAG	European Conference Industrial Technology	22/06/2016	Amsterdam, NL	Industry	10000	international
14	Posters	FRAUNHOFER	EWLP 2016 European Workshop on Lignocellulosics and Pulp: "lignin and cellulose precursors for novel carbon fiber production"	28/06/2016	Autrans, F	Scientific community (higher education, Research)	1000	international
15	Posters	FRAUNHOFER	OrgChem 2016: "efficient acylation of organosolv lignin using their subunits 4-hydroxy-3-methoxy-benzylalcohol, syringol and guajacol as a	05/09/2016	Weimar, D	Scientific community (higher education, Research) - Industry	1000	international

			model to establish the conversion process"					
16	Posters	ALU-FR	Macromolecular Colloquium 2017 : "designing the interface in lignin-based carbon nanotube composites to enhance interaction"	15/02/2017	Freiburg, D	Scientific community (higher education, Research)	200	international
17	Oral presentation to a scientific event	ALU-FR	ICBMC (International Conference on Bio-based Materials and Composites) 2017 : "tuning intermolecular interaction between lignin and carbon nanotubes in fibre composites ? an ab-initio modelling study"	29/03/2017	Nantes, F	Scientific community (higher education, Research)	200	international



Section B (Confidential⁴ or public: confidential information to be marked clearly)

Part B1

The applications for patents, trademarks, registered designs, etc. shall be listed according to the template B1 provided hereafter.

The list should, specify at least one unique identifier e.g. European Patent application reference. For patent applications, only if applicable, contributions to standards should be specified. This table is cumulative, which means that it should always show all applications from the beginning until after the end of the project.

TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights ⁵ :	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
PATENT	YES	30/04/2018	PCT: PCT/FR2017/052952	PROCEDE DE FABRICATION DE FIBRES DE CARBONE A PARTIR DE PRECURSEURS BIOSOURCES ET FIBRES DE CARBONE OBTENUES	ARKEMA, BCP

Note: ARKEMA's patent claim could not be indicated on the Participant portal.

⁴ Note to be confused with the "EU CONFIDENTIAL" classification for some security research projects.

⁵ A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.

Part B2

Type of Exploitable Foreground	Description of exploitable foreground	Confidential	Foreseen embargo date	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved	Explain of the Exploitable Foreground
General advancement of knowledge	Methodology for testing composites (virtual and physical)	yes	01/01/2018	selling a new service	automotive	01/01/2019	not planned	CTAG	Methodology for testing composites (virtual and physical testing), especially ageing testing that currently are not standard in automotive sector.
General advancement of knowledge	In-depth analytical characterization of lignin valuable for a variety of applications	yes	01/01/2018	Data on lignin	multi	01/01/2019	not planned	FRAUNHOFER	Scientific publication in a peer-reviewed journal and development of partnership with University of Hamburg
General advancement of knowledge	Protocol for acrylation of lignin in pilot-scale	yes	01/01/2018	Lignin with plasma-active functional groups	multi, e.g. carbon fibres	01/01/2019	not planned	FRAUNHOFER	Scientific publication at conference, Follow-up research on various applications of plasma-active lignin
General advancement of knowledge	Insights on physical properties of lignin (miscibility)	yes	01/01/2018	Development of partnership with University of Freiburg, data on lignin miscibility	multi	01/01/2018	not planned	FRAUNHOFER, ALU-FR	sharing better knowledge on the physical properties of lignin for various applications
Commercial exploitation of R&D results	Insights on lignin film behaviour during plasma-treatment	yes	01/01/2019	new application?	multi	01/01/2020	patent	FRAUNHOFER	Patent on lignin acrylation and subsequent plasma-treatment in discussion, development of partnership with University of Hamburg for future project on fundamental studies of reactions during plasma-treatment
Commercial exploitation of R&D results	New methods to adjust the size of lignin particles during precipitation	yes	01/01/2018	commercialization of the organosolv technology	multi: pulp and lignin industry	01/01/2020	not planned	FRAUNHOFER	Use knowledge on lignin properties and specifications for thermoplastic processing of lignin for the commercialization of the organosolv technology
General advancement of knowledge	First time proof of technical feasibility of organosolv fractionation of softwood (spruce)	yes	01/01/2018	commercialization of the organosolv technology	multi: pulp and lignin industry	01/01/2020	not planned	FRAUNHOFER	Use knowledge to broaden the raw material base for a potential commercial plant

Commercial exploitation of R&D results	Different behaviours of lignin (depending on raw sources or linked to functionalization)	yes	01/01/2018	new process	composite, 3D printing	01/01/2018	not planned	CANOE, FRAUNHOFER	FRAUNHOFER provided different kind of lignin (different raw materials, different extraction process) leading to lignin with different properties (Tg, granulometry, chemistry ...). All these lignins were deeply characterized on analytical way and also behaviour during extrusion
General advancement of knowledge	Knowledge on lignin melt spinning processing conditions	yes	01/01/2020	improvement of current services	multi	01/01/2020	not planned	CETI	melt spinning process of lignin will be used as knowhow for further projects, improvement of knowledge on spinning process and modification of process, new knowledge on unusual polymer processability
General advancement of knowledge	Insight on carbon fibers and composite production	no	01/01/2020	improvement of current services	multi	01/01/2020	not planned	CETI	better knowledge on composites, better understanding for future BtoB projects on this matter.
Commercial exploitation of R&D results	Methodology to assess the value of composite for automotive	yes	01/01/2019	new methodology, sold as a service to customers	automotive	01/01/2018	not planned	RENAULT	better knowledge on composites, which is one of the key lever to achieve significant weight reduction in order to reduce CO2 emission
Commercial exploitation of R&D results	The basic requirements to the hydrated cellulose fibers used as precursor for carbon fibers production	yes	01/01/2018	Hydrated cellulose obtained based on the new process and being modified with the carbon nanotubes. It could be used as the precursor for the carbon fibers production	automotive, composites production, medicine	01/01/2018	not planned	LLC BCP	Hydrated cellulose modified with CNT significantly improves its physical and mechanical properties as the precursor that permits to obtain the carbon fibers with the improved characteristics from the renewable raw materials. Production of the new type of hydrated cellulose will lead to the growth of the carbon fibers precursors market.

Commercial exploitation of R&D results	Processes of the hydrated cellulose fibers preparation for thermal treatment using the different recipes of the impregnation solutions of catalysts (salt, organic silicone)	yes	01/01/2018	The new process of the cellulose preparation	automotive, composites production, medicine	01/01/2018	not planned	LLC BCP	Use of the precursor preparation for heat treatment (catalysts types). Application of the new types of impregnating solution including the ones with CNT, permits to correct the process of the carbon fibers production (decrease the energy consumption through excluding certain stages of the process, increase the finished product yield), increase the carbon fibers competitive capacity.
Commercial exploitation of R&D results	Process of the complete cycle of thermal treatment (thermal stabilization, pyrolysis-oxidation, carbonization, graphitization)	yes	01/01/2018	The new processes of the heat treatment for the hydrated cellulose in the form of filaments and woven materials; the new process of the carbon fibers obtained through lignin application on the surface of the hydrated cellulose precursor	automotive, composites production, medicine	01/01/2018	not planned	LLC BCP	The new processes of the heat treatment of filaments and woven materials allows to increase the range of the products and the carbon fibers application scope in different industries: automotive, carriages manufacturing, production of composites, medicine, energy accumulators, gas and water purification, electromagnetic hardening.
General advancement of knowledge	Detailed knowledge on Lignin characterisation and properties	yes	01/01/2018	Improved utilisation of lignin in various applications	Thermoplastics	01/01/2018	not planned	UHAM, FRAUNHOFER, CANOE	Scientific publications
Commercial exploitation of R&D results	LCA modelling for key process about extraction of cellulose and lignin, carbonization of PAN, cellulose and lignin, as well as the spinning of cellulose and lignin	yes	01/01/2018	improve future studies on LCA	multi	01/01/2018	not planned	MDP	Short term: the results will be directly on the market for other LCA studies on similar products. Medium to long term: new research activities in the field of Carbon/carbon composites with innovative precursors and the results achieved in CARBOPREC will be the starting point for the environmental evaluation.

Commercial exploitation of R&D results	development of thermoplastic tape	yes	01/06/2018	new product, will be used internally	multi	01/06/2018	not planned	AVANA	new product, will be used internally. Details not available yet.
General advancement of knowledge	New process of fabrication for specific carbon fabrics	yes	01/06/2018	Divide operations to use two different resins for structural and hood parts	Wind and energy	01/06/2018	not planned	PLASTINOV	Future projects, not clarified yet
Commercial exploitation of R&D results	Alternative fiber for bio-based application projects	no	01/01/2018	New proposition for customers concerned by the origin of materials. CARBOPREC fibre can be used in addition to flax fiber and bio based resins or thermoplastic and recyclable resins.	Building, energy, sports etc.	01/01/2018	not planned	PLASTINOV	To discuss with partners and customers. The main constraint is to supply a sufficient quantity of this fiber.
General advancement of knowledge	Elaboration of masterbatch for CNT dispersion in lignin matrix	yes	01/01/2018	commercialized master batches	compounding, thermoplastics	01/01/2018	patent	ARKEMA	Masterbatch to allow a good dispersion of carbon nanotubes in the precursor material
General advancement of knowledge	Knowledge in noncovalent interactions between bio-based matrices and carbon nanotubes	no	01/01/2018	Development of partnership between University of Freiburg and ARKEMA	bio-based materials, nanocomposite	01/01/2018	not planned	ARKEMA	Deep understanding of the interactions between CNT and cellulose or lignin at nanoscale. Needed to have good dispersion and compatibility between the CNT and the bio-based matrix.
General advancement of knowledge	Homogeneous and stable liquid dispersion of CNT for addition in cellulose dope	yes	01/01/2018	Spinning dope	energy storage, mechanical reinforcement, electrical conductivity	01/01/2018	not planned	CANOE, ARKEMA	Use of special surfactant for the aqueous dispersion of CNT. This dispersion remains stable in acid media.
Commercial exploitation of R&D results	Implementation of multifilament wet-spinning line for carbon nanotubes doped cellulose fibers	no	01/01/2018	production of CNT reinforced multifilament cellulose fibers at pilot scale	composite, sensors and actuators, textile industry, energy storage	01/01/2018	patent	CANOE	wet spinning process for the production of CNT reinforced multifilament cellulose fibers at pilot scale

General advancement of knowledge	Carbonization at lab scale with deep study of the influence of time, temperature and tension.	yes	01/01/2018	new process and new equipment. New collaborations with other members of CFPC cluster	Structural and smart composite materials, energy storage	01/01/2018	will be patented	CANOE	thanks to these developments, a carbonization pilot line (1t/year of carbon fibers) will be installed in Lacq (France) in 2018 for carbonization of different precursors up to 1200°C. New collaborative project for low cost carbon fiber for automotive and sport and leisure : FORCE
Commercial exploitation of R&D results	Increase of carbonization yields by additives	yes	01/06/2019	new processes	Structural and smart composite materials, energy storage	01/10/2018	Patent	ARKEMA, LLC BCP, CANOE	this patent (PROCEDE DE FABRICATION DE FIBRES DE CARBONE A PARTIR DE PRECURSEURS BIOSOURCES ET FIBRES DE CARBONE OBTENUES) describe a way to increase the carbonization yield of cellulose fibers.