INSTITUT CARNOT POLYNAT

ACTIVITY REPORT

2016
2017

INSTITUT CARNOT PolyNat

EDITORIAL

Selected for the second time as a Carnot Institute, PolyNat is expanding and broadening its scientific scope: it is now a network of eight partners working on developing **eco-friendly carbohydrate engineering to drive innovation and address industrial issues.**

Our objective focuses on the eco-design and eco-production of innovative and functional biosourced materials and devices. It revolves around the challenges of overcoming scientific and technical obstacles : from functionalizing biosourced building blocks, controlling their self-assembly and nano-organization, to miniaturizling devices and developing pilot-scale proofs of concept.

Within the region's academic fabric, PolyNat ties in seamlessly with the Grenoble "COMUE" (Grenoble Alpes University), and the goals of the IDEX project ("Initiative of Excellence"), which notably involves PolyNat partners contributing to the Cross Disciplinary Program project "Glyco@Alps".

Within this context, we are also striving to enhance our exchanges with the COMUE technology transfer departments and the Linksium Technology Transfer Accelerator in Grenoble, in order to maximise the value of our scientific projects for industrial applications.

Since 2015, PolyNat has been raising its profile on the international front, organizing annually an Industries Forum, which has given the opportunity to develop international projects involving industrial partners.

To conclude, this activity report will give you a glimpse into the commitment of researchers, and the synergies generated and harnessed on our main themes - the (bio)materials of tomorrow and their applications - by working hand-in-hand with our industrial partners.

I wish you all an excellent 2018, and every success with your projects.

Redouane Borsali,
Director of PolyNat
January 2018

CONTENTS

1. PolyNat Presentation

After five years of remarkable scientific collaborations and industrial partnerships, PolyNat has been awarded the Carnot label of excellence for the second time.

Our institute includes now three new partners. They strengthen the range of expertise we are able to offer to companies willing to innovate in order to produce clean and sustainable products and processes.

PolyNat's ambition is to work for and with companies to design new biosourced materials and devices with hitherto unrivalled properties, produced using sustainable and renewable resources.

GOVERNANCE

To ensure a strong and balanced governance framework, PolyNat is managed by three committees :

EXECUTIVE COMMITTEE

Chaired by Redouane Borsali

The **Executive Committee** is composed of a representative from each partner organisation of PolyNat, and meets on a quarterly basis.
The main tasks of this committee are to oversee the institute, coordinate the partnership-based research, validate the R&D projects and define the communication strategy.

STRATEGIC ORIENTATION COMMITTEE

Chaired by Gilles Lenon

This committee draws up strategies to exploit the results obtained during R&D projects funded by the Carnot institute. Drawing on business intelligence tools, it constantly monitors developments on the market in order to identify companies that could collaborate with PolyNat teams.

SCIENTIFIC COORDINATION COMMITTEE

Chaired by Serge Cosnier

This committee comprises the Director of the institute and two scientific representatives from each PolyNat partner. It meets twice a year, in autumn during examination of the projects submitted, and in spring during the 'PolyNat Days' to review the projects funded.

COORDINATION, MANAGEMENT, COMMUNICATION

Charlène Efligenir
Project manager

EXPERTISE

The Institut Carnot PolyNat brings together the expertise of eight partners in the Grenoble area, covering an extremely wide range of fields:

TARGET MARKETS

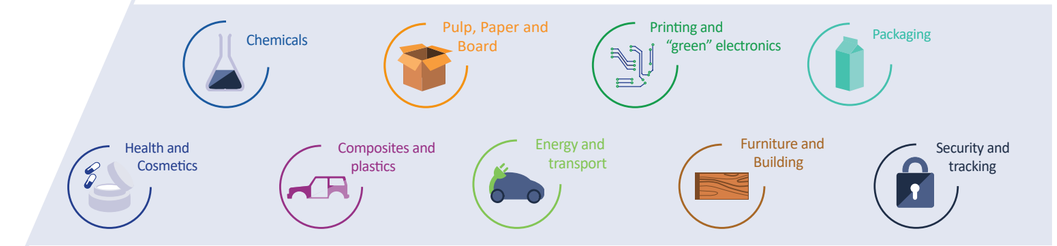
PolyNat's mission is to create groundbreaking biosourced functional materials.

The properties that all our teams strive to achieve are of interest for a wide range of industrial markets, offering methods and materials that respond to the new social and economic challenges of the present and the future.

The short-term targeted sectors are those in which PolyNat's members have acquired solid expertise, such as **chemicals**, the **pulp, paper and board** industry, **packaging, printing and cosmetics.**

The integration of three new partners enables PolyNat to reach out to a number of promising new markets:

- **Electronics** associated with green processes such as printed electronics, plastronics and biosensors;
- **Energy** generated from biomass or **electrochemical biocells;**
- **Pharmacochemistry** including topics such as the extraction of molecules from Alpine flowers, diagnosis, drug delivery, and active molecule chemistry;
- **Wood products,** from species improvement through to finished timber products for furniture and construction.



OBJECTIVES

What are PolyNat's objectives?

PolyNat's ambition is to make progress in all fields - business development, collaborative research and the exploitation of promising results .

Bulding up a partnership-based research to drive industrial innovation

The PolyNat International Industries Forum
Since its creation in 2015, this event has become an unmissable annual highlight for our institute as it invites its socio-economic partners to come and present their R&D prospects and discuss the biosourced materials of the future with our researchers.

Funding of international assignments
Backing our researchers' contributions to international projects is essential, which is why PolyNat undertakes to finance several prospecting assignments each year. In 2016 and 2017, PolyNat funded six prospecting assignments in Japan, South Africa and Sweden involving meetings with companies in the papermaking and green electronics sectors.

Business meetings
Each year PolyNat attends the MICM (Innovative Materials and Material Chemistry) business meetings in Bordeaux and, naturally, the "Rendez-Vous Carnot" (Carnot Meetings), a major event aiming to drive innovation in companies.

Building links with local bodies
PolyNat is building closer links with local bodies such as competitiveness clusters and the Linksium Technology Transfer Accelerator in Grenoble in order to step up its prospecting efforts and consolidate the development and maturation processes, .

Implementing a best practice approach:

Developing communication initiatives to raise the institute's profile within the scientific community.

Organizing a "Visiting Committee": each year PolyNat invites its key institutional and socio-economic partners to a Visiting Committee session with a view to defining the institute's areas of strategic focus.

Implementing a quality approach to guide researchers' actions in their partnership relations, from initial contact through to project completion.

KEY FIGURES

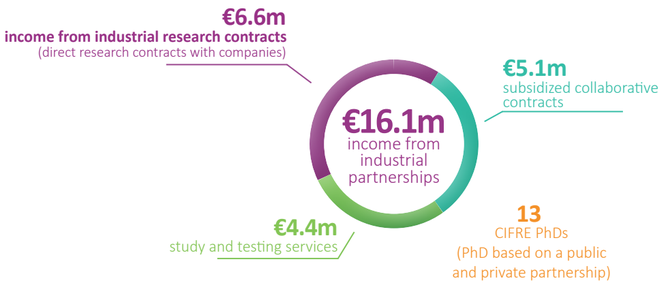
Scientific figures (2016)

316 patents held in our portfolio

250 A-ranking publications

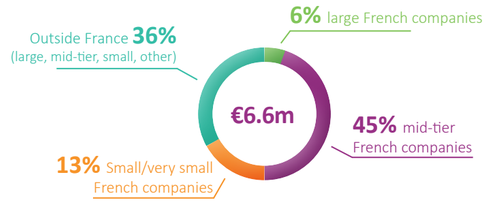
400 research employees of whom **100** PhD students

Contractual figures (2016)

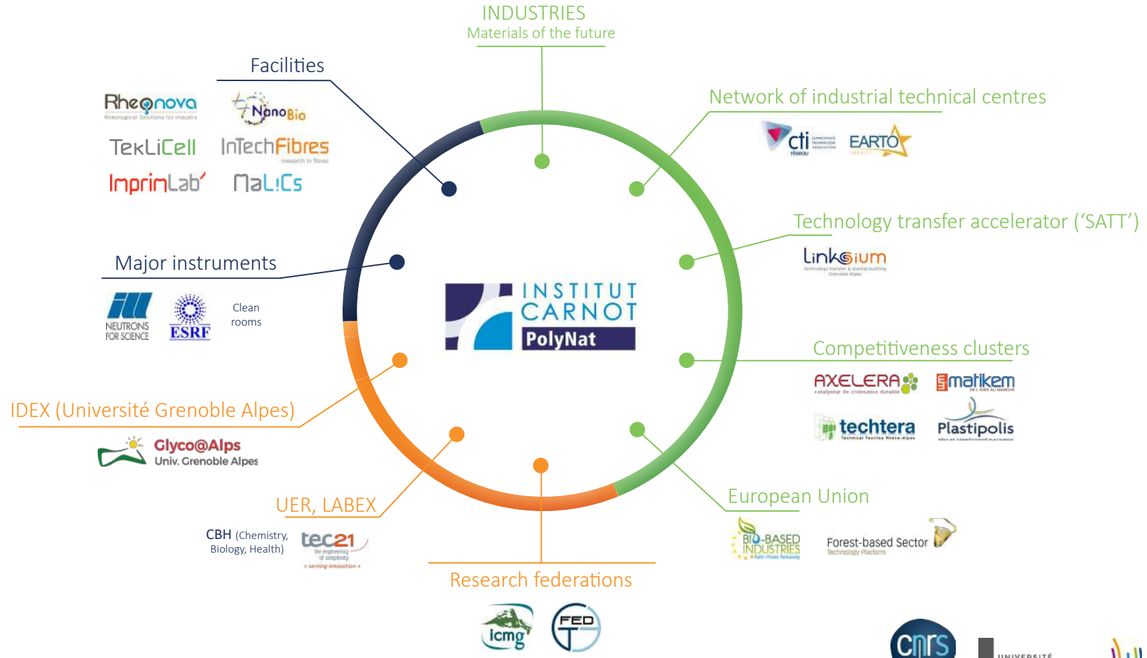


Value of industrial research contracts since 2010 (m€)

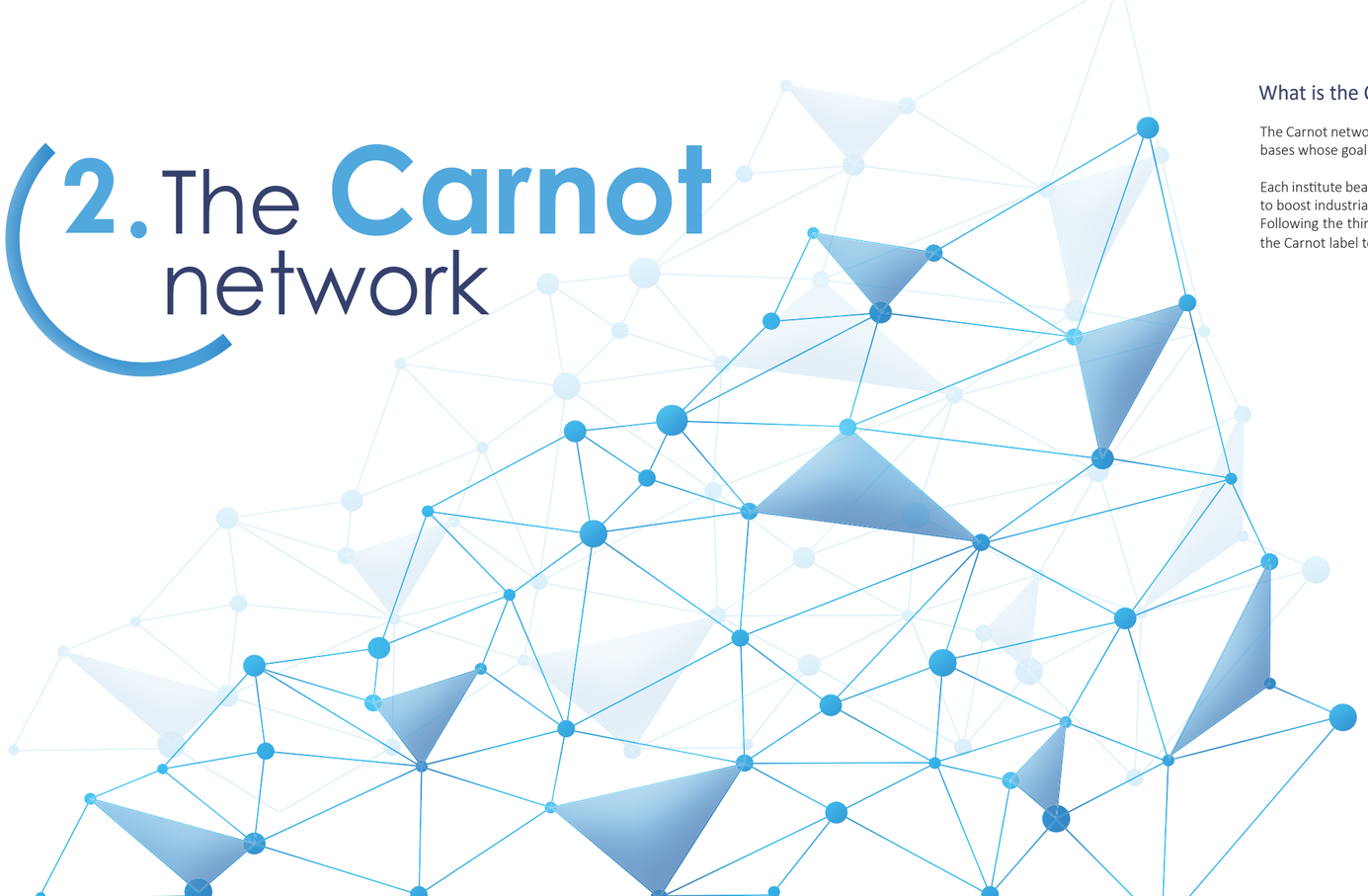
Breakdown of industrial research contracts by type of company



POLYNAT AND ITS ENVIRONMENT



2. The Carnot network



What is the Carnot network?

The Carnot network is **a network of multi-disciplinary research institutes** with strong local bases whose goal is to transfer technologies and drive business innovation.

Each institute bearing the Carnot label undertakes to conduct and develop its R&D activities to boost industrial innovation.
Following the third call for applications in 2016, the French ministry for research awarded the Carnot label to 38 bodies.

Carnot network: key figures

29 Carnot institutes

9 associated Carnot, representing

50% of the R&D funded by companies in French public research

i.e. **11,000** research contracts per year

What are the benefits of collaborating with a Carnot institute?

The scientific excellence and professionalism that come from a partnership-based relationship;

Compliance with the requirements of the Carnot Charter to guarantee satisfaction for partners, in particular:
- A professional approach to confidentiality management;
- A transparent and balanced intellectual property and licence transfer policy;
- Simplified access to scientific and technological expertise;

Responses geared to their needs and constraints throughout the project life cycle;

An understanding of their expectations, to anticipate market developments;

Mobilization of the technological expertise and facilities required to meet their needs, addressing in particular the specific features of SMEs and mid-tier firms in various industrial sectors.

Association INSTITUTS CARNOT

To find out more about the network: www.instituts-carnot.eu

3. RESEARCH

SCIENTIFIC CHALLENGES

To back up its strategy of developing partnership-based activities, each year PolyNat finances R&D projects with industrial potential sponsored by teams from at least two of its member laboratories.

Each project must aim to generate new knowledge or validate new concepts in order to develop our scientific and technological offer, in accordance with industrial companies' expectations and their commitment to promote the bioeconomy via collaborative programs or direct partnerships. These actions correspond to one or more of the four scientific challenges that PolyNat has identified:

Four scientific challenges

CHALLENGE 1 — Biosourced building blocks : extraction and characterization

- Oligosaccharides, glycopolymers, biopolymers, nanocellulose, cellulose fibres;
- Extraction, purification and separation processes;
- Use of "green" solvents and low-energy processes

CHALLENGE 2 — Building blocks and materials functionalization for targeted innovative properties

- Chemical and/or enzymatic modifications or physical treatments of biosourced (macro)molecules;
- Design of biosourced devices with innovative properties: hydrophobic, anti-microbial, bionano-electronic, etc.

CHALLENGE 3 — Controlled self-assembly and nano-organization

- Directed self-assembly of biosourced building blocks;
- Innovative processes to obtain nano-structured materials: nanoprecipitation, spin- or dip-coating;
- Development of smart surfaces, three-dimensional materials, and functionalized and multi-compartmentalized glyco-nanoparticles

CHALLENGE 4 — Production and development processes of biosourced materials

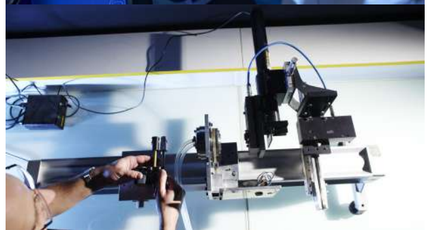
- Adapting or developing techniques that foster industrial transfer
- Understanding interactions at interfaces for an advanced design of biosourced devices

Proof of concept : from the laboratory to pilot plant

PolyNat aims to produce biomaterials at pilot scale
Each development step takes into account the regulatory and environmental requirements

Modelling, simulation and characterization resources

For each of these challenges, the research performed is based on the development or adaptation of approaches combining experimental characterization, modelling and simulation.



FACILITIES AND INSTRUMENTS

NanoBio icmg

Technological resources dedicated to **nano-sciences**

Rheonova
Rheological Solutions for Industry

Facilities for monitoring and developing **fluid materials** and their **industrial processes**

TekLiCell

A partnership on two themes:
"smart paper and printing of the future" and **"biomaterials, bioenergy, bioprocesses"**

InTechFibres

Facilities for producing **functionalised lignocellulosic fibres** and **particles** and shaping **process panelboards**

MaLiCs

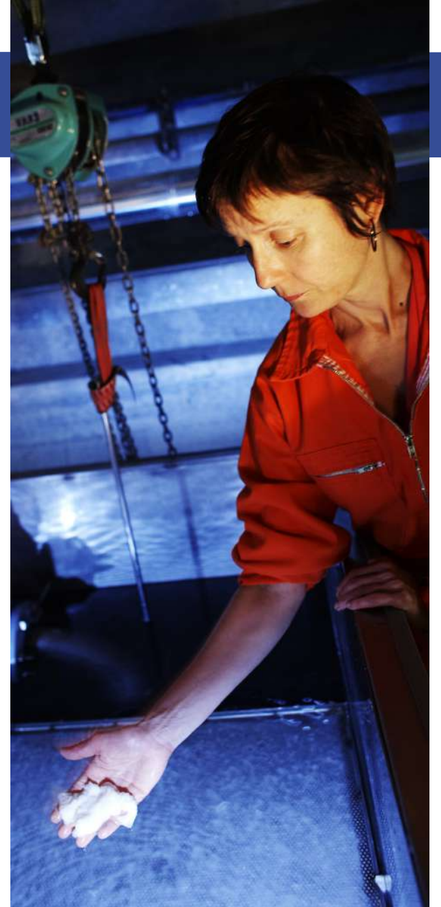
Developing leading-edge solutions for the **packaging of tomorrow**

ImprinLab

An innovation cluster specialising in **printed electronics** for **printing and converting firms**

ESRF NEUTRONS FOR SCIENCE

PolyNat is a stakeholder in various scientific facilities in the Grenoble area, and has special access to major instruments used for imaging and modelling down to the nano scale.



PROJECTS FUNDED

RESOURCE BUDGET

9 projects funded
1 Inter-Carnot project
Total budget
2016 **€908,892**

13 projects funded
Total budget
2017 **€756,000**

2016 PROJECTS

AME3D

Development of **paper 3D structures** for **sandwich-structured composites**

Sandwich-structured composite materials are used in many industrial sectors. The high bending and torsional strength under flatwise compression, impact strength and thermal or soundproofing properties of sandwich panels are to a large extent induced by the three-dimensional structure of the core.

The cores most widely used in the paper-making sector are the corrugated and honeycomb types. However, the range of physical and mechanical properties offered by these configurations is limited.

The aim of the Ame3D project is to develop new light, high-performance three-dimensional core geometries in order to improve these properties and open up new applications for sandwich-structured composites based on cellulose fibres.

Two strategies for developing new core architectures were studied:

1. "Re-entrant"-type cellular geometries were developed using cutting, folding and gluing techniques. These give sandwich panels auxetic properties and substantially improve their bending strength *(see illustration)*.

2. Random 3D structures were created by crumpling high-density papers. These form panels with highly interesting mechanical properties, in between flexible polymer foams and rigid foams. These have potential for use in a large number of fields.

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Jérémie Viguié, research engineer, CTP

"Ame3D was a fascinating project because it adopted a highly original approach: forming materials with new properties using perfectly ordinary, commercially-available papers."

PARTNERS

CTP: David Guérin, Laurence Leroy
LGP2: Isabelle Desloges
3SR: Jean-Francis Bloch, Laurent Orgéas

BIO3D

Biomaterials processing through **3D** printing

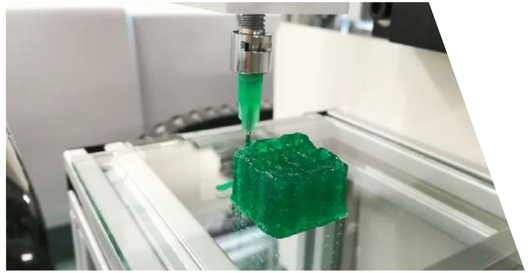


Image: stable complex 3D structure obtained through the 3D printing of cross-linked alginate using a new in situ process

The objective of BIO3D is to optimise biosourced gel 3D printing processes.
The materials studied are microfibrillated cellulose (MFC) hydrogels, stimulable biopolymers such as alginate, pH-sensitive gels and their composites.

Special attention was paid to the rheology of the gels, the physical and physico-chemical gelling processes during printing, and the spatial and temporal stability of the printed structures.

The first phase consisted in building multi-functional 3D printers suited to the biosourced gels to be simulated and to pasty gels such as MFCs.

A study of the relationship between the rheology and printability of shear-thinning gels was performed on associative polymer gels and on modified MFC composites.

The spatial and temporal stability of the printed structures in relation to their yield point and their relaxation or recovery time following destructuring was studied. Yield point was shown to be a vital parameter governing printed structure stability.

In another study a new process was developed to print alginate efficiently in 3D with in-situ cross-linking by calcium ions to improve the spatial and temporal stability of the structures.

CHALLENGE 3

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Yahya Rharbi, CNRS and LRP researcher

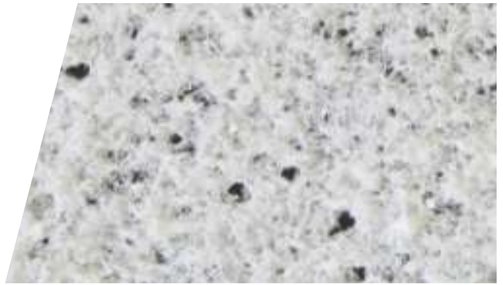
"3D printing seems to be offering infinite possibilities for the industry of the future, and pushing its boundaries to print biosourced materials makes an enthralling challenge and a fascinating project."

PARTNERS

LRP: Nadia El Kissi, Didier Blésès, Ahlem Romdhane, Ako Komla,
CTP: Elisa Zeno
LGP2: Davide Beneventi

CELLUFOAM

Cellulose foams



The Cellufoam project aims to develop biosourced foams with similar properties to the oil-sourced foams (expanded polystyrene, polyurethane) conventionally used in packaging to improve impact resistance, compressive strength and thermal insulation.

This project, which ties in with and follows on the Microfoam project (funded by IC PolyNat in 2015), also enabled the development of a study methodology for choising the surface-active agents and of a fully-instrumented pilot foam generator.

This pilot and a commercially-available rotor-stator type generator were successfully used to produce continously stable foams, notably using a commercially-available biobased surface-active agent.

All that remains today is to determine more precisely the role played by cellulose materials and the drying technology, in order to propose a process that can be scaled up for the industrial production of biosourced foams capable of competing with their oil-sourced equivalents.

CHALLENGE 1 CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Elisa Zeno, project manager, CTP

"The Cellufoam project enabled us both to consolidate our expertise in the foams field and to confirm the positive synergy that has developed in this area between the CTP, LGP2 and LRP. Thanks to this close collaboration, in which our post-doctoral researcher Julie Chapelain played a very active role, we now have a substantial array of tools at our disposal and are coming ever closer to transferring the process of producing cellulose-based biosourced foam to industry. These results have also attracted interest from some of our clients."

PARTNERS

CTP: Bruno Carré
CERMAV: Redouane Borsali, Issei Otsuka, Sami Halila
LGP2: Davide Beneventi
LRP: Yahya Rharbi, Emeline Talansier

QUALIN

Development of **qua**litative tools for industrial **lign**ins specifically for their use and modification

Approximately 80 million tonnes of lignins are potentially available each year in pulp and paper mills. Currently only 1.5 million tonnes are recovered, mainly lignosulphonates to be used as dispersants, emulsifiers and surface-active agents.

Kraft lignins constitute 95% of the available lignin resources and are burnt in boilers and contribute to the energy self-sufficiency of the mills. Lignin is a cross-linked irregular aromatic polymer with a modest molecular size. It is slightly soluble in the usual solvents and insoluble in water, and possesses functional groups that make it chemically reactive and thermal-sensitive. The major obstacle for a better valorization of Kraft lignin is the complexity of the molecule, making its behaviour often difficult to control.

A precise chemical characterisation of Kraft lignin is costly and complex, involving either spectroscopy methods such proton, carbon and phosphorus NMR or chemical dosages that are long and tedious, and only controlled by a handful of laboratories.

The aim of this project was to develop fast and reliable analytical methods for the characterisation of industrial lignins, making it possible to evaluate the key indicators for differentiating lignins according to the target properties:

i) the sulphonic groups ($L\text{-}SO_3^-$) qualifying the solubility of lignosulphonates and sulphonated Kraft lignins
ii) the aromatic hydroxyl functions (Ar-OH/Ar-O^-) involved in the chemical modification of lignins and reflecting their reactivity, and
iii) the distribution of molecular weights revealing the macro-structure and heterogeneity of the lignins by means of GPC.

Applied to several industrial and commercial lignins of various origins, these tools made it possible to define quality criteria for Kraft/soda lignins compared with the lignosulphonates that are already on the market.

CHALLENGE 1 CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Frédérique Bertaud, project engineer, CTP

This project involved complementary collaboration between the CTP and the LGP2, focusing on lignin research in order to develop biorefining for application in pulp mills. The CTP wished to offer to its industrial partners an exhaustive and 'application'-oriented characterisation of lignins. The LGP2 wished to validate its latest analytical developments and deepen its understanding of lignin macro-structures. Hélène Lichère (intern) and Luis Serrano (post-doctoral researcher) succeeded in setting up titrimetric analyses for evaluating the reactivity of industrial lignins. These are now routinely used at the CTP, and have undergone inter-laboratory testing at an international level. The GPC method for measuring molecular weights is now being applied on a large scale in the thesis being prepared by Suddha Esakkimuthu at the LGP2. ***These results are being exploited 100%!***

PARTNERS

LGP2: Gérard Mortha, Nathalie Marlin

ROCOCO

Roll spin, **Co**agulation and **Co**re shell electrospinning of dissolved cellulose

Gelling of a cellulose solution dissolved in LiCl/DMAc by adding increasing volumes of water

The ROCOCO project endeavoured to replace petroleum based yarns / nanowires with yarn/wires made from dissolved and regenerated cellulose, for textile (yarn) applications as well as the production of structured nanowires by electrospinning.

For textile yarn applications, the work focused mainly on the possibilities of dissolving celluloses pulps of high molecular weights (DP > 400) in cold-concentrated sodium hydroxide as an alternative to viscose and Lyocel processes.

The results showed that significant dissolution (> 80%) could be obtained, but at excessively low concentrations (1%) around -10 to 0°C and, especially, for DP < 400.

Several pre-treatments were also applied to the cellulose with a view to facilitating dissolution, but these did not bring about any variations in the characteristic % dissolution/ DP curve identified.

A complex methodology using DLA and DSC was also developed in order to monitor the kinetics of the gelling process and the properties of the regenerated cellulose gel.

Lastly, dissolved and regenerated cellulose and the electrospinning technique were successfully used to produce structured nanowires, which were then formed into either coaxial wires or filtering membranes.

CHALLENGE 1 **CHALLENGE 2** CHALLENGE 3 CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Bruno Carré, head of the "materials structuring" team, CTP

"I am very pleased with this PolyNat project, which is the first I have been involved in. It enabled me to set up some interesting collaborations and bring together a lot of people with a vast range of highly enriching experience. We progressed on the scientific front, publishing six articles and identifying a number of new leads to pursue."

PARTNERS

CTP: Auphélia Burnet, Saurabh Kumar
CERMAV: Issei Otsuka, Yoshiraru Nashiyama, Laurent Heux, Redouane Borsali,
LGP2: Dominique Lachenal, Nathalie Marlin, Gérard Mortha,
LRP: Denis Roux, Frédéric Bossard, François Caton
3SR: Lucie Bailly, Laurent Orgéas

BIOGRAFT

Generalisation of chromatogeny to various substrates and reagents obtained from plant biomass

The objective of the Biograft project was to gain a greater understanding of the mechanisms involved during the heterogeneous-phase grafting of fatty acid chlorides on modelled hydroxyl substrates.

The project consisted in performing these treatments on cellulosic substrates obtained through evaporative drying (paper pulp sheets, papers, microfibrillated cellulose films) in an initial phase, and on freeze-dried microfibrillated cellulose aerogels with controlled specific surfaces varying between a few m^2/g and nearly $300 m^2/g$ in a subsequent phase.

The study demonstrated:

(i) a good correspondence between two types of grafting density analyses based on either NMR or a hydrolysis/GC-FID combination;

(ii) the possibility of varying the specific surface area of the aerogels by selecting the solvent before freeze-drying and the nature of the microfibrillated cellulose;

(iii) a linear relationship between specific surface area and grafting density with a bifunctional fatty acid chloride, and

(iv) the dense nature of the molecular cover.

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

David Guérin, project manager, CTP

"This project, conducted by Emilie Ressouche in the framework of her post-doctoral research, provides a scientific response to an industrial issue.
It also led to the production of innovative materials and shook up certain assumptions… while providing leads for future developments."

PARTNERS

CTP: Mathieu Schelcher
CERMAV: Laurent Heux, Sonia Molina-Boisseau

CERISE

Cellulose pretreatment for in situ fibrillation by twin screw extrusion

This project concerns the development of innovative MFC production processes using twin-screw extrusion.

The first stage was to select four chemical pre-treatments to facilitate MFC release: phosphorylation, ozonation, cationisation and enzymatic treatment.

The second stage focused on optimising the extrusion process in order to enable nanofibrillation at a high concentration in an energy-efficient continuous system. The study showed that minimising energy consumption required the lowest possible dryness, the highest possible flow rate and the lowest possible speed; and that maximising quality required the lowest possible dryness, the highest possible flow rate and the highest possible speed. A compromise will hence have to be found depending on the desired quality and energy to be supplied.

Lastly, we studied the nanofibrillation process during extrusion. Various screw profiles were tested, and the study demonstrated that it was important to have a high-shear screw profile with several small shear zones: when the screws are composed only of conveying components, no MFC are produced.

The rheological profiles were analysed in relation to different zones of the extruder in order to understand the "black box" constituted by the extruder and hence limit the number of passes through it. The first pass remains essential and has the greatest effect on the fibre. At least four passes are required to obtain good-quality MFC. Creep tests were performed, and showed that the parameter with the greatest impact is concentration.

CHALLENGE 2 CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Julien Bras, lecturer, LGP2

"This project is an excellent example of the collaborative aspect of PolyNat's work and the high-calibre expertise of Grenoble's nanocellulose production research hub. Following a preliminary project at LabEx Tec21, PolyNat decided to back and co-finance this ambitious project aiming to develop a new low-energy and high-concentration microfibrillated cellulose production technique. The project partners are collaborating in highly enriching, open and complementary ways."

PARTNERS

LGP2: Naceur Belgacem, Alain Dufresne
CTP: Valérie Meyer, Michel Petit-Conil
LRP: Nadia El-Kissi

OCTOPUS

Oxidation of Cellulose using TempO in the Presence of UltraSound: the OCTOPUS Pilot

The objective of the OCTOPUS pilot project is to develop an adapted ultrasound device to acheive chemical modifications to wood pulp nanocellulose under ultrasonic irradiation.

The key project task consisted in designing, setting up and then characterising an ultrasonic process at laboratory pilot scale in order to couple the physical and chemical effects of the ultrasound waves. Special attention was paid to managing viscosity and temperature.

In a second stage, TEMPO oxidation tests were performed on microfibrillated cellulose and paper pulp suspensions.

Comparisons were made between four operating cases: silent conditions, high-frequency ultrasound alone, low-frequency ultrasound alone, and both high-frequency and low-frequency ultrasound.

The following key outcomes were obtained:
- Shorter reaction times in the presence of ultrasound (reduced by 63%).
- A larger proportion of small and fine objects, which are the products of interest of the oxidation process called into play (corroborated by material balances and TEM examinations).
- Steady or increased degrees of fine object oxidation (corroborated by two analytical methods).

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Stéphane Baup, lecturer, LRP

"This project is at the interface between the fields of cellulose chemistry and ultrasonic process engineering, so it calls on a wide variety of skills. It has brought about genuine collaboration between CERMAV and the LRP: Sonia Boisseau and myself are now actively involved in the thesis being prepared by Ayoub Barchouchi (LRP 2016-2019), who had been hired for the OCTOPUS project in the framework of his master's degree internship."

PARTNERS

CERMAV: Sonia Molina-Boisseau, Jean-Luc Putaux, Laurent Heux
LRP: Nicolas Gondrexon

COSMONDA

Chemical modification of natural resources using a microwave-assisted process

INTER-CARNOT PROJECT

INSTITUT CARNOT PolyNat

INSTITUT CARNOT Chimie Balard Cirimat

The cosmetology sector is increasingly using compounds obtained from natural resources, particularly plants (polyphenols, oils, polysaccharides, etc). Incorporating these natural molecules into cosmetic formulations often poses problems relating to blending, compatibility and long-term stability.

To solve these problems, chemists often try to modify some of these molecules. However, this "conventional" chemical approach, with long reaction times, can alter the chemical structure of natural molecules (with consequences for their properties), and often requires the use of reagents and catalysts that can be toxic for the target final application.

This project, performed in partnership with Institut Charles Gerhardt in Montpellier, is based on using the microwave activation process to modify natural compounds in less harsh conditions.

The study focused on modifying heat-sensitive water-soluble natural antioxidants (phenols and polyphenols) in order to incorporate them in the oily phase of cosmetic emulsions and, more precisely, on studying gallates.

Before the antioxidants could be incorporated into the oily formulations, they had to be modified by hydrophobic chains including a cleavable link. To do so, microwave (MW)-assisted esterification was considered.

The work demonstrated the benefits of this method, since it brought about a clear improvement in both reaction yield (MW yield > 70% compared with 50% by conventional thermal heating) and reaction kinetics (4 hours with MW heating compared with 18 hours by thermal heating). The oil-in-water emulsion formulations are still being developed, and their physico-chemical characterisation (shape and size) in solution remain to be finalised.

A WORD FROM THE PROJECT LEAD

Jean-Jacques Robin, project manager, ICGM

"The project carried out by Céline Schmitt, a post-doctoral researcher, demonstrated the feasibility of these reactions for modifying sensitive natural compounds using equipment that is easily accessible at an industrial level. The specific organisation of modified polyphenols in emulsions is likely to lead on to new developments for the economic sector concerned."

PARTNERS

Redouane Borsali, head of research, CERMAV, "self-assembly and physico-chemical aspects of glycopolymers" team

3D RAPID-PRO

Rapid prototyping of complex moulded cellulose objects

Image: moulding manufacturing process:
a) Setting up the mould on the filtering bench,
b) Moulding by immersion and aspiration of the fibrous suspension,
c) Final fibrous mattress, before
d) and after compression.

For several decades, moulded cellulose has offered an alternative to oil-sourced materials in the field of packaging manufacture. However, the complexity and cost of the forming moulds and the low quality of the fibres used mean that the use of moulded cellulose has been restricted to the mass production of low value-added products (packaging materials, food trays, plates, etc.).

The objective of the 3D-RapidPro project is to use new prototyping techniques (in particular 3D printing) and cellulose fibres/nanofibres to produce small series of objects with controlled geometries and physical properties.

The results obtained in the first phase of the project showed that the additive manufacturing process with fused deposition modelling® coupled with the use of specialist polymers techniques enables filtering moulds to be produced with filtering efficiencies similar to those of conventional metal-mesh filters and capable of withstanding the cellulose drying conditions (~100-130°C, ~1-2 bars).

Dripping and moulding techniques based on vacuum aspiration or pressurisation were tested successfully, and the drying phase and mould design optimisation are the steps that remain to be completed in order to achieve the project objectives.

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Davide Beneventi, researcher, LGP2

"This project, which aims to study a complete manufacturing process, gave us initial insight into the undeniable benefits that the new rapid prototyping techniques can bring and a glimpse of the very active role a "mature" industrial sector such as the paper sector will be able to play in the industry of the future."

PARTNERS

LGP2: Evelyne Mauret, Julien Bras, Didier Chaussy, Maxime Terrien
CTP: Thierry Delagoutte
3SR: Sabine Rolland du Roscoat, Laurent Orgéas

3W

Wood Without Water Innovative treatments to limit interactions between solid wood and water

Solid wood is highly hygroscopic. It interacts with water due to its chemical composition. Unfortunately, this can have undesirable consequences such as dimensional variations, biodegradation with development of wood-degrading fungi, and colour changes when the wood is exposed to the outdoor environment.

The 3W project, set to last a year aims to reduce wood's affinity for water. It has been launched as a partnership between the CTP, LGP2, DPM and FCBA (French institute of technology for forest based and furniture sectors). Three environmentally-friendly solutions using non-toxic components are considered, they are currently being applied or targeted for applications other than wood.

Chromatography modifies the hydroxyl groups. It has been successfully optimised for paper-making applications, and its transfer to wood is now being studied. Acid chlorides with long carbon chains react with hydroxyl-type functions available on the matrix surface and generate hydrophobic properties. Migration of the water through the wood matrix is hence impeded.

Lignin, obtained from biomass, is being tested following application to the wood surface in a similar manner to a finishing product. The commercial lignin is modified in order to obtain a hydrophobic liquid solution. This method has been tested taking a variety of treatment conditions into account: reaction conditions, methods for applying the lignin solution, and in-situ modifications following application to the wood.

Chemical modification of the phenolic functions on the wood has also been considered, by means of a catalysed reaction drawn from organic chemistry. The results obtained revealed significant changes during the immersion tests, related to functionalisation of the groups responsible for making the wood hygroscopic.

The most effective treatments identified in the laboratory will be applied to larger samples. They will be subjected to accelerated ageing and the consequences for wood properties will be evaluated. It will hence be possible to assess the potential of the experimental 3W solutions in comparison with common commercially-available treatments with known performance levels.

CHALLENGE 2
CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Michael Lecourt, project manager, FCBA

"The project partners come from a variety of application sectors, some having very little to do with wood. They enrich the project with their experience and knowledge, helping us to formulate original solutions and areas for further development."

PARTNERS

CTP: Philippe Martinez
LGP2: Gérard Mortha, Nathalie Marlin
DPM: Yung-Sing Wong

BIOGLUE

New developments for wood-based panels

Wooden panels are produced by compressing particles of varying sizes, making it possible to transform an abundant and inexpensive resource into materials with a small carbon footprint that can be recovered at the end of their lifecycle. However, their properties depend intrinsically on the quality and the even distribution of the binder (or glue) holding the particles together.

Most of the glues used to manufacture wooden panels are oil-sourced and based on formaldehyde. This compound, ~~which is~~ classified as CMR (carcinogenic, mutagenic, or toxic for reproduction), is the main criterion considered in classifying panel VOC emissions, i.e. the release into the atmosphere of toxic and polluting compounds that potentially contribute to the greenhouse effect, significantly undermining the environmental qualities of the material.

One solution for reducing these emissions involves optimising adhesive use and/or replacing the compounds known to release VOCs with a functionalised biosourced polymer. This could hence become the raw material for an environmentally-friendly "green glue".

This project thus aims to develop a resin formulation for wooden panels with a low environmental impact and low VOC emissions, taking advantage of an abundant, renewable resource with no competition for food use.

To meet this scientific, technological and environmental challenge, two academic laboratories specialising respectively in cellulose (CERMAV) and structural characterisation (3SR) have joined forces with a technical centre, the French institute of technology for forest based and furniture sectors (FCBA), ~~which is~~ familiar with the product and the industrial fabric.

The goal is to develop eco-friendly chemicals (providing the functionality) and detailed characterisation methods using X-ray tomography combined with an optical microscope (to identify the glue interfaces) in a material that seems simple but is highly demanding in terms of formulation and process.
A multi-disciplinary team comprising chemists, structural experts and process specialists has hence been formed for this project, with the goal of proposing innovative solutions for eco-friendly wood panel formulations.

CHALLENGE 2 CHALLENGE 4

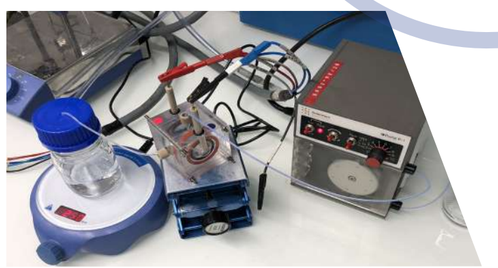
A WORD FROM THE PROJECT LEAD

Laurent Heux, research director, CERMAV

"Bioglue is typical of the collaboration that can emerge within IC PolyNat. The FCBA, a new partner, was looking to develop biosourced glues for wood panels, but was facing difficulties characterising the glue interfaces. So researchers from CERMAV and 3SR joined forces to propose an applied, multi-disciplinary project.
Its implementation was placed in the hands of Quentin Charlier, a young doctor who had done his thesis in the field of materials science in a context that already involved both academic and industrial laboratories. Blending scientific expertise, technological obstacles, innovation and team work is the key to progressing in designing materials for the future that (we hope!) are cleaner, greener and more environmentally friendly."

PARTNERS

FCBA: Michael Lecourt, Sandra Tapin-Lingua
3SR: Sabine Rolland du Roscoat, Robert Peyroux



BIOGLYCO

Regenerable **bio**fuel cells based on enzymatic and redox **gly**conanoparticles

The BioGlyco project is currently focusing on the use of glyconanoparticles to solubilise redox species for the mediated electron transfer of molecular oxygen reduction using bilirubin oxydase (BOx).

Various synthesis approaches have been evaluated, without any real variation of final nanoparticle (NP) size. The average diameter of the spherical particles is 50 nm. A first scientific paper on the formulation and electrochemical characterisation of this biocathode (with or without the biological catalyst) has been submitted to the *Journal of the American Chemical Society.*

We have also undertaken research on the development of glyconanoparticles whose redox mediator will be used to oxidise glucose. Drawing on our research on carbon-based paper, we have decided to use certain quinones for the mediation of FAD-dependent glucose dehydrogenase (the enzyme responsible for glucose oxidation). These quinones have a number of benefits over the bis-pyrene-ABTS approach required at the cathode side.

These redox molecules interact directly with cyclodextrins to form host-guest complexes. The modified redox mediator synthesis phase can hence be avoided. Moreover, in the absence of pyrene units (particularly bis-pyrene), the nanoparticles can no aggregate due to pyrene spacers. This enabled us to obtain a quasi-monodisperse suspension of nanoparticles (20 nm).

Electrochemical characterisation of the NPs and the enzyme was performed in the absence and presence of 50 mmol L-1 glucose. An oxidative electrocatalytic wave can be clearly distinguished in the presence of the substrate. The results are highly promising, because the currents obtained are already greater than those obtained with the cathode (35 µA cm-2).

The logical next step of the project will focus on creating carbon paper electrodes to increase the active surface area of the electrodes with the objective to increase the catalytic currents.

CHALLENGE 3 CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Serge Cosnier, research director, DCM

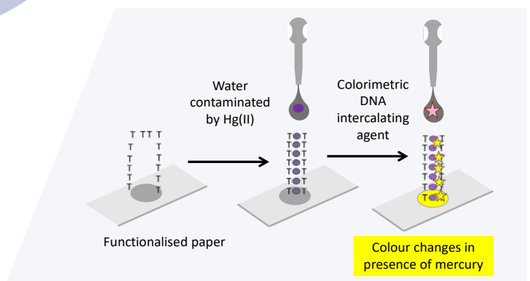
"The project perfectly illustrates the synergy that you would expect from combining two topics specific to CERMAV and the DCM, i.e. the production of functionalisable nanomaterials and the bioconversion of energy for healthcare- or energy-related applications with a leading-edge type of biocell. Post-doctoral researcher Jules Hammond is closely involved in this collaboration and contributing significantly to its success."

PARTNERS

CERMAV: Christophe Travelet, Redouane Borsali

CAPTDIAG

For **C**ellulose **Apt**amer
Diagnostics or
CApture **Diag**nostics



Rapid diagnostic tests as paper-based devices provide an alternative technology for simple, low-cost, portable, and disposable or recyclable diagnostic tools for many applications (including clinical diagnosis, food quality control, and environmental monitoring...).

This project proposes to combine the partners' skills in various fields in order to develop an original label-free paper-based test strip using functionalized oligonucleotides or aptamers as recognition elements with color detection and no prior marking (see diagram). The proof of concept will be established for mercury detection, which has already been tested in a homogenous medium at the DPM with a fluorescent DNA-intercalating dye, SYBRgreen.

Two approaches to paper functionalisation using the functional oligonucleotide (FO) have been considered: the first consists in employing tempo oxidized nanocellulose (NCC) which is grafted and then printed on the paper in the form of a coat; the second aims to deposit the FO directly on the appropriate basepaper through simple adsorption or covalent immobilization.

Functionalization of the NCC by the FO was successfully performed via a covalent amide link.

Unfortunately, the techniques used did not permit to quantify the amount of grafted FO. It was only possible to perform a single mercury detection test using the FO grafted on to the NCC. The result appears to be positive, but, must be reproduced in order to be confirmed.

Printing tests on NCC polymer films on which a fluorescent dye had been adsorbed produced interesting results. The behaviour of the NCC during printing in the presence of the FO remains to be tested.

In regard to the second approach, FO adsorption and fluorescence detection tests have been performed on various papers. The results obtained showed that many papers have a natural fluorescence and, hence, that this detection technique is not recommended at the fluorescence wavelengths of SYBRgreen. Moreover, the FO adsorption test results were not conclusive, so covalent grafting of the FO onto the paper will be preferred for the future experiments.

To develop the solution-based color detection system, ten or so DNA-intercalating dyes are currently undergoing UV-visible spectrophotometry screening.

A WORD FROM THE PROJECT LEAD

Corinne Ravelet, lecturer, DPM

"This project is a highly rewarding experience addressing a cross-disciplinary issue at the intersection between some very different "worlds" . It took us a little while to understand each other and start speaking a common language. We have obtained a number of results which will hopefully be completed on in the future."

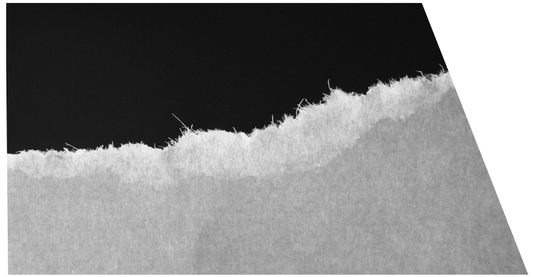
PARTNERS

DPM: Eric Peyrin
LGP2: Naceur Belgacem, Julien Bras
3SR: Jean-Francis Bloch
CTP: David Guérin, Elisa Zeno

CHALLENGE 2
CHALLENGE 4

FLOCS

Fibre **L**ocal **O**rganisation
Characterised at various **S**cales



The presence of flocs (clumps of fibres) during the papermaking process indicates a local variation in grammage, which governs the mechanical and optical properties of papers.

Current floc characterisation techniques, based on visible light transmission, X-ray or particle imaging, provide an overall analysis. However, they indicate neither the location of the flocs within the sheet of paper - particularly within its thickness - nor the organisation of their constituent fibres.

The objective of this project is to characterise flocs using X-ray microtomography and image analysis in order to obtain this information.

In this first part of the project, we proposed:
- A protocol for producing materials called "models" in which the presence of flocs was verified. These materials, composed of rigid fibres, were characterised from a structural viewpoint in accordance with current standards.
- Tools for characterising flocs and inter-floc regions based on X-ray tomography with a 10 µm resolution. The focus was placed on comparing the inner layers of the paper with the surface zones.

The second part of the project will consist in quantifying the microstructural parameters inside a floc or an inter-floc region at fibre scale using X-ray microtomography.

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Sabine Rolland du Roscoat, lecturer, 3SR

"In this project the CTP, a paper specialist, and 3SR, a microstructure characterisation specialist, have joined forces to gain a greater understanding of how a floc is organised within a sheet of paper. This project has instigated cooperation between two Carnot institute partners on a new topic, harnessing synergy in order to progress.
As project lead, I'm finding the experience extremely rewarding!"

PARTNERS

3SR: Jean-Francis Bloch
CTP: Bruno Carré, Patrick Huber

MANNABREAK

Research into new enzymes: Towards the preparation of building blocks obtained from wood galactoglucomannans

Galactoglucomannans are hemicelluloses extracted mainly from softwood (15-20% w/w). In spite of their low calorific value, hemicelluloses are burnt in the same manner as lignin during papermaking processes.

In this context, we propose to recover these hemicelluloses at the initial stages of the papermaking process and to produce oligosaccharide series with controlled structures and sizes for nutraceutical, cosmetic and/or elicitor applications.

The strategy envisonned was based on the detection of new hemicellulose degrading enzymes (e.g. glycoside hydrolases) and modifying enzymes (e.g. esterases).

We used bioinformatics approaches to select 72 potential enzyme genes, which were then cloned in Escherichia coli for heterologous expression essays.

At the end of the project, we have identified and produced all the enzymes involved in the degradation of acetylated galactoglucommannans including mannases, galactosidases, glucosidases and esterases.

CHALLENGE 1

A WORD FROM THE PROJECT LEAD

William Helbert, research director, CERMAV

"The goal of the Mannabreak project is to apply the tools used in white biotechnology to the recovery of waste in the papermaking industry. Beyond the technological challenges, this multi-disciplinary project is stimulating because it brings together rare complementary scientific skills and expertise relating to wood chemistry and all aspects of processing and chemically treating wood and its specific polysaccharide components on the one hand, and to hemicellulose enzymology on the other hand, with a view to obtaining specific oligosaccharides that can be recovered in various fields."

PARTNERS

Christine Chirat (LGP2)

MICRO-DES

Combination of deep eutectic solvents (**DES**) and ultrasound to produce MFCs from wood

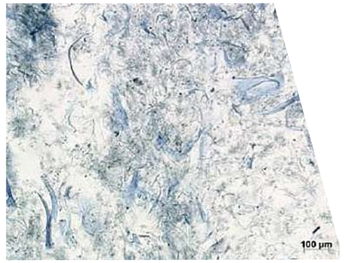


Image: MFCs obtained after extruding and homogenising pulps obtained from DES cooking

This project aims to propose a new process for preparing microfibrillated cellulose (MFC) that consumes less energy than the conventional processes while protecting the environment.

In this context, a recognised green deep eutectic solvent (DES) formed from choline chloride coupled with lactic acid was used to separate fibres from poplar wood and weaken their internal bonding strength. Use of the DES in combination with ultrasound was also considered as a means of improving DES transfer and reactivity.

The cooking parameters were optimised with a view to maximising delignification and reducing fibre length. The results showed that the wood must be treated with the DES at a temperature of 120°C for five hours for the fibres to be separated effectively.

The best cooking conditions produced fibres with half the length of those obtained with a conventional kraft process (approximately 500 µm) and high levels of polysaccharides (lignin content between 2.8 and 4.9%). Fibre weakening is enhanced when ultrasound waves are applied for one hour at a power of 500W.

The pulps obtained through DES cooking were extruded and then homogenised to produce MFC suspensions of very high quality. Their nanocellulose content and mechanical strength are even higher than those of conventional MFCs obtained from kraft pulp. The use of a deep eutectic solvent on wood chips prior to MFC production hence appears to be highly efficient and offer significant potential.

CHALLENGE 1

A WORD FROM THE PROJECT LEAD

Valérie Meyer, "InTechFibres" research engineer, CTP

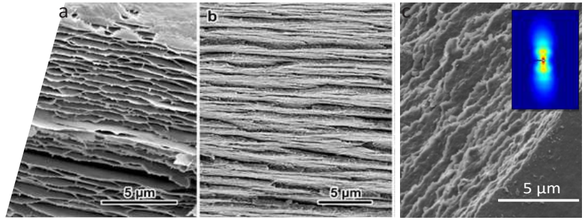
"This is an innovative project which, thanks to the remarkable efforts of the interns and the commitment from all the partners, has already produced a lot of results that can be taken forward."

PARTNERS

CTP: Mohammed Krouit, Michel Petit-Conil (InTechFibres)
CERMAV: Sonia Boisseau, Jean-Luc Putaux
LGP2: Julien Bras, Naceur Belgacem
LRP: Stéphane Baup

NANO COMP-UV

Development of anisotropic and nanostructured cellulosic nanocomposites by membrane separation process and UV curing



The aim of this project is to use a membrane separation process combined with photopolymerization to develop new controlled anisotropic and nanostructured cellulosic nanocomposites. Membrane separation processes have the advantage of starting the process from a low initial volume fraction for which the shear flow and pressure forces are sufficiently high to overcome the internal colloidal interactions between the nanoparticles. This allows a regular deposition, concentration and alignment of the colloids near the membrane surface.

After ultrafiltration, a UV curable polymer (UVCP) will be impregnated into the structured deposit and irradiated in-situ under pressure in order to freeze the structural organization. The systems studied are based on a UVCP/cellulose matrix composed of cellulose nanocrystals (CNC) or cellulose nanofibrils (CNF) combined with two types of colloidal systems of interest: reinforced and conducting systems in combination with graphite and carbon nanotubes, and reinforced and barrier systems in combination with clay platelets, imogolite nanotubes and α-lactalbumin nanofibres.

This project brings together researchers from four Carnot institute laboratories (LRP, CERMAV, LGP2, DCM), and benefits from the expertise of external collaborators, in particular Vincent Forge from LCBM and Professor Johan Foster from Virginia Tech University.

The project players will pool their knowledge in order to comprehend the various facets of this research (control of the interactions and surface chemistry of the various constituents, ex-situ and in-situ structural characterization of the nanocomposites and of their functional properties). The first ex-situ structural characterizations produced through filtration and then air-drying, have shown the formation of layered structures with alignment of the long length-scale of the nanoparticles, along the flow direction.

The long existing collaboration established with Theyencheri Narayanan, in charge of ID02 Beamline at the ESRF, on filtration processes combined with small-angle X-ray, has allowed to explore the structural and photopolymerization mechanisms involved during the production of these nanocomposites, from the nanometer scale of the particles to theirs micron scale organizations.

Illustration: SEM images of films prepared:
i) through filtration and air-drying:
a) Nontronite clay (cross-section)
b) NCC (cross-section)
ii) through filtration and photopolymerisation:
c) NFC – beidellite clay - UVCP (cross-section) and 2D-SAXS pattern of the in-situ organization during filtration.

CHALLENGE 1

A WORD FROM THE PROJECT LEAD

Frédéric Pignon, research director, LRP

"The results obtained and the collaborative work undertaken during Enrico Semeraro's post-doc research, which is financed by this project, demonstrated that cross-flow ultrafiltration process can be used to obtain homogeneously layered cellulosic nanocomposites with a suitable degree of orientation conserved after UV curable polymer impregnation and subsequent photopolymerization."

PARTNERS

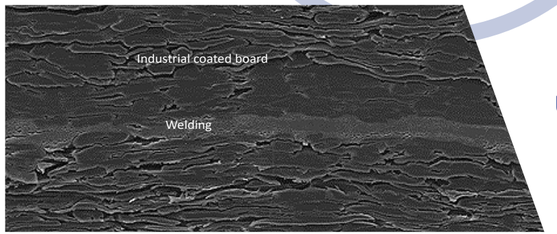
Bruno Jean, Jean-Luc Putaux, (CERMAV)
Didier Chaussy, Davide Beneventi, Julien Bras (LGP2),
Michael Holzinger (DCM)

EXTERNAL COLLABORATIONS

Vincent Forge (LCBM), Johan Foster (Virginia Tech)

NANO-SONO

Ultrasonic welding of papers and nanocelluloses



SEM image of a cross-section of a welded board assembly.

Packaging materials are generally assembled and glued using glues based on oil-sourced polymer formulations.

Gluing is a problematic issue in packaging on account of the risk of mineral oil contamination in the case of food applications, and it also complicates the paper and board recycling process. The hot-melt coatings used to seal flexible packaging or cellulose-based hygiene articles are also affected by this same issue.

The Nanosono project showed that ultrasonic welding is a means of achieving very high Peel strengths on certain papers and boards:

- 300 g/m² folding boxboards with a 15 g/m² pigmented coat to guarantee printability (composed of 85-90% mineral pigments and 10-15% butadiene styrene-type latex) demonstrate very high Peel strengths of up to 250 N/m, which is higher than those required by heat-sealability standards (160 N/m).
- Depositing non-functionalised cellulose nanofibrils (CNF) on the surface of a board with a pigmented coat obtains even higher Peel strengths, in the order of 350 N/m.
- Depositing non-functionalised nanocrystalline cellulose (NCC) on the surface of unweldable papers achieves a significant Peel strength. A patent has been filed for this result.

CHALLENGE 4

A WORD FROM THE PROJECT LEAD

Jérémie Viguié, research engineer, CTP

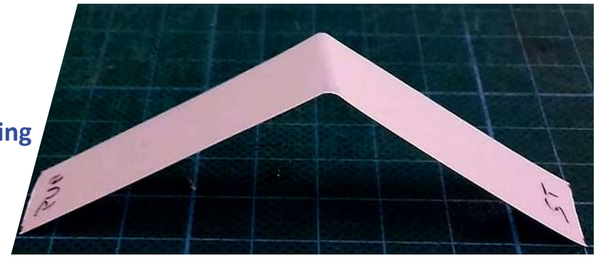
"Nanosono is a very exciting project, with both a very concrete technological objective and definite scientific interest.
It is also fortunate to benefit from the highly complementary expert skills contributed by the various partners."

PARTNERS

CTP: Laura Crowther-Alwyn, David Guérin
LGP2: Julien Bras, Martine Rueff
3SR: Barthélémy Harthong, Didier Imbault, Robert Peyroux

PRINT&FOLD

2D printing of papers for **self-folding** 3D shapes



Formation of a fold without mechanical action by depositing a line of water on a special paper.

Digital manufacturing technologies are booming. They are fostering the design and development of new architectured materials with programmable physical or mechanical functions.

In 2012, a fascinating and highly original technique called Hydro-fold was developed by a Swiss designer, showing that it was possible to print custom self-folding patterns on a sheet of paper using an ink-jet process. To date, little is known about the phenomena called into play when the creases are formed using this innovative process.

The first objective of the Print&Fold project is to reproduce this phenomenon, gain a deeper understanding of it and optimise the underlying forming mechanisms.

The ultimate objective is to obtain developable or non-developable 3D structures by printing origami-inspired patterns in 2D with a view to (i) using them as sandwich-structured composite material cores or as 3D packaging with complex shapes and, in the longer term, (ii) creating programmable paper structures that can be draped as required or evolve in line with external conditions.

The initial work focused on obtaining a fold from a very simple printed pattern. Several ink formulations were tested in order to experiment with the quantity of carrier (water) and the type of polymer. The hydro-mechanical couplings associated with fold formation were studied by combining 3D imaging and finite-element numerical simulation.
Flat or three-dimensional structures inspired by origami "tessellations" will eventually be created.

A WORD FROM THE PROJECT LEAD

Jérémie Viguié, research engineer, CTP

"Print&Fold is a highly stimulating project, because it enables us to apply our knowledge of the complex hygro-mechanical behaviour of papers and ink/paper interactions to the development of a groundbreaking process."

CHALLENGE 4

PARTNERS

CTP: David Guérin, Laurence Leroy
LGP2: Anne Blayo, Isabelle Desloges
3SR: Jean-Francis Bloch, Laurent Orgéas

EXTERNAL COLLABORATIONS

Pierre Dumont, Florian Martoïa (LaMCoS)

View of the experimental apparatus for the micro-scale tests

SIMUBONDS

Multi-scale modelling and characterisation of lignocellulosic fibrous material strength: From interfibre bond creation to material interlaminar strength

The objective of the project is to attempt to understand the mechanical strength of paper by obtaining an in-depth understanding of the interfibre bonds.

Lignocellulosic fibres with various flexibilities were used to form low-grammage papers. An experimental protocol was drawn up to characterise the internal bonding strength of the bonds. Tests were performed, mainly at macro-scale, on softwood fibres (flexible/rigid) and hardwood fibres.

3D microtomography will have to be performed in the second part of the project in order to analyse breaking during in-situ interlaminar strength (internal bonding) tests and measure the associated forces. These measurements, taken at micron scale, will be compared with the macroscopic mechanical values (force, deformation, energy) obtained experimentally and through finite element numerical modelling.

Various courses of action were studied:
(i) producing sheet formers with various grammages from pulp refined to varying degrees;
(ii) characterising these sheet formers;
(iii) building the experimental apparatus at micro-scale and performing preliminary tests (see image);
(iv) performing mechanical internal bonding strength tests in accordance with the experimental protocol drawn up during this first part of the study.

The subsequent stages of the project will involve:
(i) using microtomography to visualise and characterise a single fibre bond to serve as a basis for numerical modelling;
(ii) viewing the changes to the fibre structure during an in-situ interlaminar strength test of the materials at millimetre scale using 3D microtomography;
(iii) validating the numerical models through macro tests at a centimetric scale. Whenever possible, we would like to study the influence of moisture on the aforementioned results.

Fibre bond characterisation is still a vital element in assessing the usage qualities - both optical and mechanical - of lignocellulosic materials, and offers perspectives for reducing the costs of transporting finished products while minimising the quantity of raw materials used.

A WORD FROM THE PROJECT LEAD

Jean-Francis Bloch, lecturer, 3SR

"The initial results obtained on this project are the outcome of close collaboration between three laboratories (LGP2, CTP and 3SR) with complementary skills and expertise. The contributions from overseas interns have also been invaluable.
We have been able to have fruitful discussions, produce new materials and draw up experimental protocols at various scales (micrometric and millimetric) which will enable us to finalise our project. The work must now carry on, maintaining the same multi-disciplinary approach."

CHALLENGE 4

PARTNERS

LGP2: Barthélémy Harthong, Raphaël Passas
CTP: Patrick Huber, Bruno Carré

SÉCHAGE-FILM

Drying kinetics of PVOH/nanocellulose composite coats and MFC films

The “Séchage-Film” (“film drying”) project aimed to gain a deeper understanding of the drying kinetics of polyvinyl alcohol (PVOH)/nanocellulose composite coating and MFC (microfibrillated cellulose) films.

A short-wave infrared drying bench was used to perform the experimental work. The project required a number of experimental conditions to be fine-tuned: choice of substrate for the coatings, spreading of these coatings, and definition of the drying conditions (range of acceptable power densities). An experimental phenomenological study also had to be performed.

For the drying kinetics study, the main parameters (incident and transmitted radiative fluxes, temperature of the sample or its substrate and weight of the sample) were monitored and analysed. The kinetics can be broken down into three conventional periods: one during which the evaporation rate increases (heating period), a second during which the drying rate remains constant and a third during which this rate decreases.

From the quantity standpoint, the study showed that using microfibrillated or nanocrystalline celluloses as an additive in a polyvinyl alcohol solutions improves the drying kinetics and shifts the transition time between the second and third period. From the quality standpoint, these nanocelluloses delay or even limit the appearance of defects, which start to occur in the second period with PVOH alone.

In the case of MFC films, dried on the same substrates as the PVOH suspensions, the drying rate during the constant evaporation rate phase is approximately the same as in the case of the PVOH solution. On the other hand, the transitions between periods take place at different times with these films. They occur at higher moisture levels, probably on account of the higher initial moisture level in the films (approximately 10%) compared with the PVOH suspensions (18%). The phenomenon is accentuated in the case of films formed with highly fibrillated celluloses, which initially contain larger quantities of water.

In both cases (PVOH and MFC) a moisture gradient must develop within the material, with creation of a skin effect.

A WORD FROM THE PROJECT LEAD

David Guérin, project manager, CTP

The starting point for the “Séchage-Film” project was an observation made during pilot coating trials, where MFCs added to a polyvinyl alcohol solution were seen to be improve the drying kinetics and reduce the appearance of defects. This project perfectly illustrates the ability of different PolyNat players to join forces in order to develop the tools required to understand phenomena observed at an industrial scale. The project also made it possible to validate the use of nanocellulose as a drying additive for water-based barrier coatings, and to compare the relative performances of various types of nanocelluloses.”

CHALLENGE 4

PARTNER

Martine Rueff (LGP2)

ANNUAL 4. EVENTS

HIGHLIGHTS

2016 / 2017

"Technological Innovation" prize in the "Stars et Métiers" competition awarded to LGP2 and TCT

The "Fil Rouge" (red thread) project, a partnership between the LGP2 and Textilose Curtas Technologie, aimed to develop a 100% biodegradable and compostable paper twine for plant staking in the agriculture sector, electrical wiring or decorative uses.

MARCH 22nd 2016

MARCH 30th 2016

Launch of the MINT industrial research chair, shared by Schneider Electric and the Grenoble INP partner foundation.

This research chair has come into thanks to a common desire to drive plastronics research and technologies shared by Schneider Electric and the Grenoble INP, LGP2 and IMEP-LaHC science and engineering schools.

Plastronics aims to integrate electronic functions into three-dimensional moulded plastic shapes to create new smart objects and components.

Pulp&Paper Week, Stockholm

The InTechFibres CTP-FCBA plant chemistry team manned a stand at this major international exhibition for the forestry, wood, pulp and paper industry, and showcased their expertise in the field of lignocellulosic materials.

MAY 24-26th 2016

JUNE 2-3rd 2016

2nd edition of the PolyNat International Industries Forum

JUNE 13-16th 2016

TAPPI Nano 2016, World Trade Center, Grenoble

International conference on new technologies using nanocelluloses. PolyNat had an opportunity to showcase its skills in the field during the "lab tour" organised on June 13. CERMAV, LGP2, CTP, FCBA and 3SR welcomed a delegation of 70 people from all over the world (24 nationalities).

14th European Workshop on Lignocellulosics and Pulp (EWLP 2016), Autrans

One of the most important events in the field of lignocellulosic chemistry, characterization and use, organized by the CTP, CERMAV, LGP2 and FCBA and backed by Institut Carnot PolyNat.

JUNE 28-30th 2016

10th edition of the Carnot Meetings

OCTOBER 5-6th

NOVEMBER 16th 2016

Inauguration of the Lab3P joint lab operated by the CTP and Malengé Packaging

Named Lab3P for *Laboratory of Printable Protective Packaging*, the joint lab operated by the CTP and Malengé Packaging, a small business, was inaugurated in the presence of representatives of the French National Research Agency (ANR) and the Matikem competitive cluster.
The aim of this new lab is to develop new barrier materials from biosourced substrates and products in the very near future, to make 100% recyclable packaging.

5-6 JULY

PolyNat Days

Launch of the Glyco@Alps project

The Glyco@Alps project was officially launched in the presence of more than 150 people in the CTP's amphitheatre. Glyco@Alps brings together nearly 100 scientists from the Grenoble area and will foster new interactions between teams involved in exploring the biological diversity of Alpine resources, analysing the economy and innovations and developing production processes in glycosciences.

MARCH 10th 2017

MARCH 15TH 2017

Conference on *"Wood-based products of the future"* at the Académie de l'Agriculture de France

Julien Bras, Gilles Lenon and Redouane Borsali participated in this conference. They gave talks on the following topics: *The fine promises of nanocelluloses (J. Bras), Innovating for a sustainable future in paper and board materials* (G. Lenon), and *Auto-assembly of biomolecules for the biomaterials of tomorrow (R. Borsali).*

PolyNat Days

JUNE 29-30th

JUNE 14th

PolyNat Visiting Committee

JUNE 15-16th

3rd edition of the PolyNat International Industries Forum

MAY 10-11th 2017

MICM exhibition, Bordeaux

PolyNat attended the Innovative Materials and Chemistry of Materials exhibition under the aegis of a joint 'Carnot' stand.

24th International Symposium on Bioelectrochemistry and Bioenergetics of the Bioelectrochemical Society, Lyon

International congress on the various aspects of bioelectrochemistry, organised by Serge Cosnier (director of the Department of Molecular Chemistry at Grenoble university). The event attracted 280 participants from 36 countries, with 250 contributions spread over 7 symposia.

JULY 03-07th 2017

11th edition of the Carnot Meetings 'Rendez-vous Carnot'

OCTOBER 18-19th

NOVEMBER 21-22nd

Innovation Showroom, ATIP conference, Alpexpo Grenoble

Given the success of the first event, the 2017 congress of the ATIP (French paper industry technical association) organised a second "Product Innovation Showroom" featuring some thirty products developed by the main players in the sector.
This initiative was led by the CTP and Grenoble INP-Pagora LGP2, but also some key industrial players from the paper sector such as Papeteries Emin Leydier, the LeafLab, Clairefontaine, Munskjo, Antalis, Vicat-Vizile and the French public printing office, who came to showcase the skills and the fine prospects of the sector!

Julien Bras receives the *Espoir IMT-Académie des sciences* prize

Julien Bras, Deputy Director of LGP2, has been awarded this prize, created by the Mines-Télécom Institute (IMT) and the French Academy of Science, in the field of cellulosic biomaterials.

NOVEMBER 22nd 2017

DECEMBER 04th 2017

Redouane Borsali wins the "Etoiles de l'Europe" prize

The director of PolyNat received the *"Etoiles de l'Europe"* prize in the Innovation category for coordinating the H2020 GreenNanoFilms project, bringing together nine European partners.

RENDEZ-VOUS CARNOT'

The "Rendez-Vous Carnot" (Carnot Meetings) are unmissable opportunities to meet businesses from all sectors that are looking to initiate partnership-based research projects.

2016 and 2017 Carnot Meetings took place in Lyon and Paris respectively. The purpose of this business convention is to foster networking between scientific players developing industrial solutions and leading-edge companies.

The strong participation from companies proposing innovative projects and the high number of individual meetings held make the Carnot Meetings the biggest forum in France where research institutes meet industrial players. It is building a strong reputation as a place to "do business".

KEY FIGURES

2016
- **2600** participants
- **9500** individual meetings

2017
- **2800** participants
- **11,000** individual meetings

THE VISITING COMMITTEE

Each year PolyNat invites its institutional and industrial partners to give their opinions on its areas of strategic focus in the context of the "Visiting Committee".

This event, arranged by the Strategic Coordination Committee, brings together industrial players of all sizes, competitiveness clusters, representatives from the Linksium technology transfer accelerator in Grenoble, and delegates from the association of Carnot institutes. PolyNat presents the various actions and projects funded in the framework of its call for projects, and the committee shares its opinions and recommendations as regards the strategic positioning of the institute. It is an excellent opportunity to discuss the most promising industrial development leads.

In 2017, **bioeconomy** was the focus for the discussions. PolyNat placed its developments into perspective, tying them in with various French and European strategic areas of focus.

Since 2011, PolyNat has been highly committed to this annual event on account of its importance for defining and discussing the strategic directions of its research projects and keeping abreast of industrial prospects in the field of biosourced materials.

THE POLYNAT DAYS

PolyNat's 2016 and 2017 "science days" brought its teams together for two days dedicated to team-building, giving researchers, engineers, postdocs, PhD students and interns a chance to escape Grenoble for the countryside.

Each year in June, PolyNat organizes this event which aims at reviewing the projects funded and identifying areas of synergy that could be harnessed for future PolyNat projects.

The project leads present their scientific progress to the full PolyNat Scientific Committee, in order to carry out a mid-term review of ongoing projects and to assess completed projects.

Following the lakeside setting of Aix-les-Bains in 2016, the PolyNat teams met in the Vercors mountains on 29 and 30 June 2017: a place highly conducive to discussing the institute's scientific projects and building even stronger links between the people implementing them!

THE INTERNATIONAL INDUSTRIES FORUM

Following the success of the first **PolyNat International Industries Forum** in 2015, PolyNat held again this international meeting in 2016 and 2017.

The aim of the Forum is to foster constructive dialogue between PolyNat's research units and the companies in attendance, giving them the opportunity to share their perspectives and R&D challenges. The biosourced materials of the future form the common thread running through the discussions between the attendees from the various industrial sectors and the scientists from PolyNat.

In 2017, for the third year running, the PolyNat teams hence joined forces to attract very young businesses as well as larger national and international companies from all sectors, with a shared commitment to bringing the bioeconomy to fruition.

The highly fruitful exchanges with companies of all sizes (from SMEs to global leaders) illustrated the huge breadth of PolyNat's partnerships and the opportunities for collaboration offered by its teams of researchers and engineers.

In addition to demonstrating the scientific synergies between the PolyNat laboratories, this event helped to strengthen the links between researchers and industrial firms working together on the materials of tomorrow!

PolyNat is proud of the success of these forums, and intends to draw on this momentum for the years to come.

THE FORUM IN FIGURES

4 days of events
38 talks in English
23 companies
13 international speakers
210 participants

2016
2017

Thank you to all those who attended the PolyNat International Industries Forum in 2016 and 2017:
Ahlstrom Munskjö, Arjowiggins, Borregaard, CGL Pack, CEPI, CSEM, Ecoat, Elicytil, Gerflor, Glyco@Alps, Hitachi, Ionisos, INL, ITRI, Kangwon National University, Mecasonic, Medtronic, NANPAO, NewGenPak, Obducat, Poly-Ink, Rexor, Seppic, Solvay, Taekyung Polymer Co, Toshiba, Western Digital

La recherche CARNOT pour l'innovation des entreprises

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Published by: Institut Carnot PolyNat, CERMAV-CNRS CS40700, 38041 Grenoble Cedex 9
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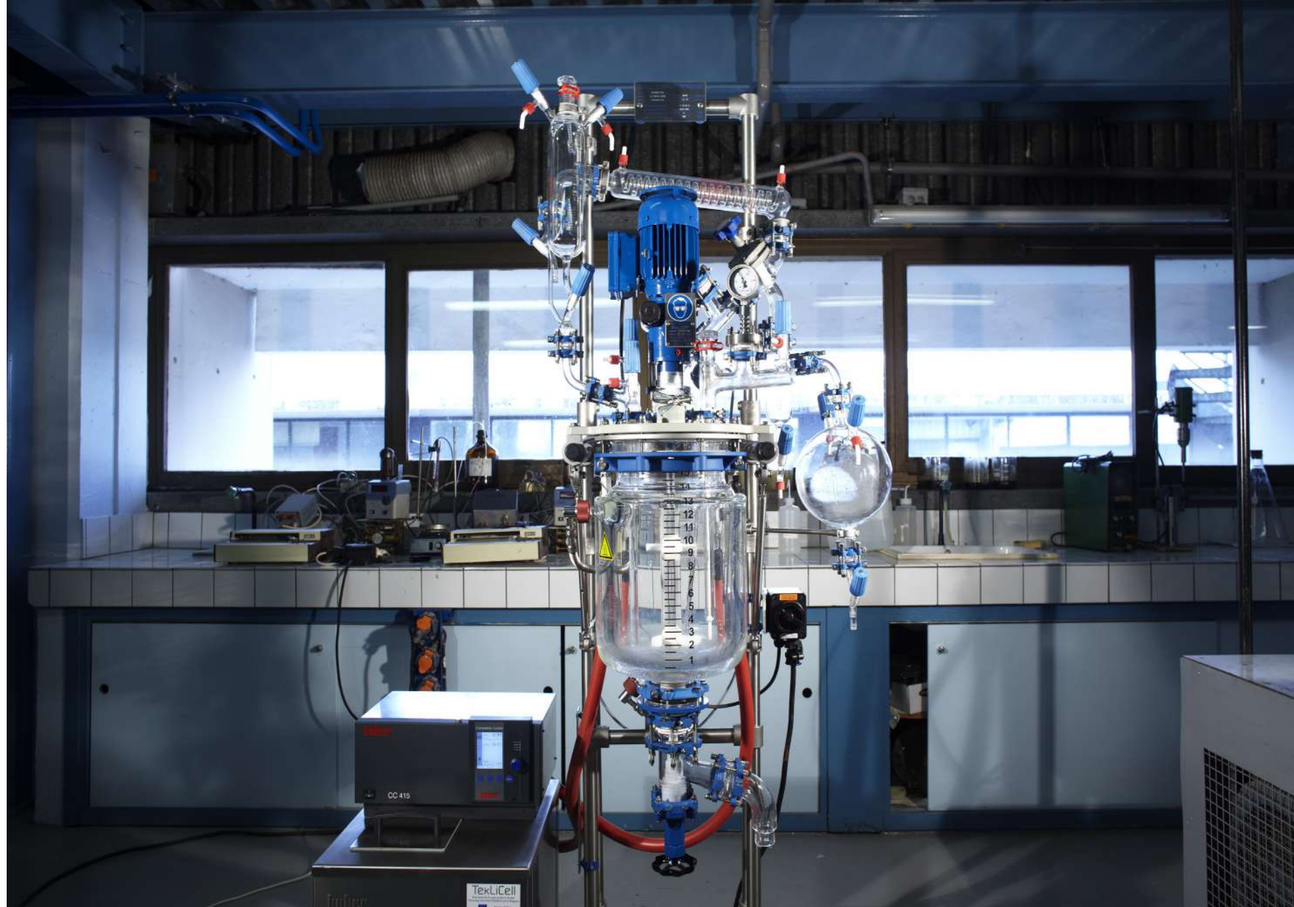
AGENCE NATIONALE DE LA RECHERCHE ANR

INVESTISSEMENTS D'AVENIR



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