Bio-based products *and materials*

AGROPOLIS INTERNATIONAL
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Physical, physicochemical and biotechnological means of processing agro-molecules, agro-polymers or complex matrices

The goal of the ***"Agro-polymer Engineering and Emerging Technologies"*** **UMR** (**UMR IATE, CIRAD/INRA/Montpellier SupAgro/UM2**) is to help increase knowledge of the functionalities of plant products and their constituents, to improve their performance in food and non-food uses.

It conducts research on physical, physicochemical and biotechnological means of processing agro-molecules, agro-polymers and complex matrices, in an effort to understand the impact of these changes, at different scales, on structures and target functionalities.

Its research activities are organized into five complementary multidisciplinary and multi-scale areas:

❶ Fractioning of agroresources
❷ Structuring of agro-polymers under stress and powder reactivity
❸ Matter transfers and reactions in food/packaging systems
❹ Microbial biotechnology and lipid and agro-polymer
❺ Knowledge representation and reasoning to improve food quality and safety

These research foci are concerned with green technologies in terms of a way of acquiring knowledge to design, develop and manage eco-efficient procedures for biomass deconstruction to produce polymers, useful molecules and synthons from which to regenerate biomaterials. The research is based on two platforms and several technical support centres:

▪ The plant fractioning platform* (low to intermediate moisture) focuses mainly on primary processing of cereals and lignocellulosic biomass and on forming materials from agro-polymers. It operates in two stages: first, mechanical separation and sorting of raw plant materials (mills, grinders…), then forming of materials by reconstruction and assembly under pressure (kneading, rolling…).

▪ The LipPol-Green** platform (an international partnership) offers scientific support and very high-level instruments for studies at the interface between plant science and environmental chemistry, in the fields of lipid biotechnology, physical chemistry of polymers and the exploration and use of plants' molecular diversity, to produce molecules, materials and fuels from biomass.

UMR IATE is a participant in the 3BCAR Carnot Institute (Bioenergy, Biomaterials and Biomolecules from Renewable Carbon) and LabEx Agro and is also involved in many partnerships, both academic and industrial (Alland & Robert, Panzani, BASF, Michelin…), in particular with partners from the countries of the South:

▪ The European project *"ECOefficient BIOdegradable Composite Advanced Packaging"* (2011-2015) seeks to supply the food industries with flexible, biodegradable packaging (funded by the 7th Framework Programme for Technological Research and Development [FPTRD].

▪ Since 2008, research activities on natural rubber in Southeast Asia have been carried on under the aegis of the platform *"Hevea Research Programme in Partnership"*.

▪ The METAGLYC 2 project (German fund to finance renewable resources, 2012-2015) is developing new ways of obtaining glycerol derivatives by chemical catalysis and biocatalysis.

The main team
IAM team Engineering and Macromolecular Architectures ICGM - Institut Charles Gerhardt, Montpellier UMR CNRS 5253 (ENSCM/CNRS/UM2/UM1) *60 scientists*
UMR IATE Agro-polymer Engineering and Emerging Technologies (CIRAD/INRA/Montpellier SupAgro/UM2) *49 scientists*
UPR CMGD Materials Research Centre (EMA) *40 scientists*

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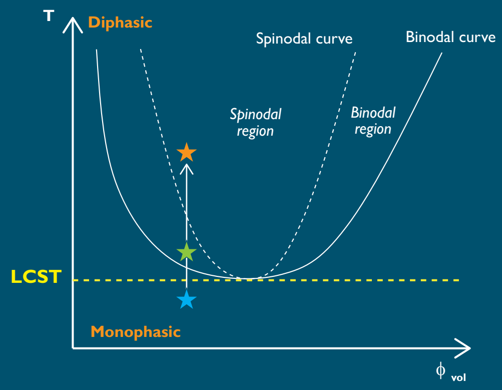
POMEWISO project
solvent-free membrane preparation from biopolymers

Porous polymeric membranes for use in water treatment are developed on an industrial scale from synthetic polymers dissolved in an organic solvent (acetone, DMF, NMP...). Porosity is generated by a phase inversion process, usually induced by immersion of the homogeneous polymer solution in a bath of non-solvent (water). Apart from the fact that the raw material is derived from a non-renewable land resource, large amounts of organic solvents are used, with the risk of generating environmental pollution and health problems.

The goal of the POMEWISO project (an IEM/IRSTEA collaboration) is to develop a new porous membrane production process that relies on clean, green chemistry, (i) using polymers from natural rather than synthetic resources and (ii) substituting water (the solvent for water-soluble polymers) for traditional organic solvents. Hence, the scientific problem is to fine-tune the process of developing membranes from different water-soluble polymers (polyvinyl alcohol [PVA], cellulose ethers, chitosan) with a low critical solution temperature (LCST), thereby controlling their morphological and functional properties. Once the phase inversion is induced by increasing the temperature (TIPS-LCST procedure), crosslinking of the polymer chains will be necessary to strengthen the film thus formed. This crosslinking will preferably be done by irradiation or heat treatment to avoid the use of chemical crosslinkers.



▲ *Influence of temperature rise during the TIPS-LCST process.*

A multi-scale analysis will be conducted to better understand the phenomena of phase separation, structure growth, and the final morphology of the membranes as well as their filtration properties. The experimentation will be done using light scattering methods, optical microscopy, near-infrared and confocal Raman spectroscopy, and dead-end filtration. It should be possible, using a modelling approach and solving the modified Cahn-Hilliard equation, to predict the evolution of structures over time until the final morphology is obtained.

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- The STOCKACTIF project of the French National Research Agency (ANR) (biomaterials & energy programme, 2011-2014) is looking at active storage of biomass to facilitate industrial processing.
- The SPECTRE project (international France-Mexico Programme Blanc [non-thematic programme], 2011-2014) focuses on the evaluation and control of industrial biotechnology procedures.
- The 3BCAR PEACE project (with the Environmental Biotechnology Laboratory [LBE], 2011-2013) is studying the effect of cell wall composition and thermomechanical pre-treatment techniques on the efficiency of the conversion of model biomass into energy products.
- The project on "Epoxidation of Polyphenols by a Chemo-enzymatic Approach" is aimed at obtaining bio-based epoxy resins (with UMR "Science For Oenology", [INRA, Montpellier SupAgro, UM1], 2010–2012 .
- Various projects supported by the LipPol-Green and Plant Product Processing platforms.

* www.3bcar.fr/~abcar/images/stories/pdf_3bcar/fiche_iate_plateforme_fractionnement_des_vegetaux_v3.pdf
** www.supagro.fr/plantlippol-green

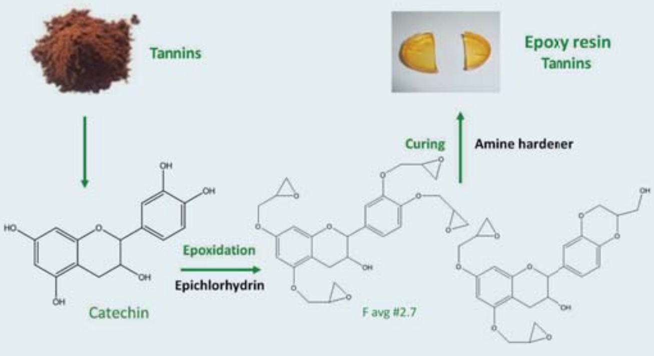
Monomers to polymers: integrated solutions for synthetic materials

The *"Engineering and Macromolecular Architectures"* **(IAM) team of the Institut Charles Gerhardt of Montpellier (ICGM), UMR CNRS 5253 (ENSCM/CNRS/UM2/UM1)** has since its inception been developing a chemistry based on the synthesis of controlled-architecture polymers, macromonomers, telechelic oligomers, graft or block copolymers, and telomers. In particular, the team has been studying particular applications of such telomers as reactive oligomers in photocrosslinkable compounds or as additives for coatings, surfactants or composite matrices, etc., all applications where low viscosities and controlled reactivities are sought.

The IAM team, whose core endeavour is the application of organic chemistry to polymers, is recognized for its expertise in developing integrated technological solutions for materials synthesis, from monomers to polymers, in order to offer solutions for high-performance applications. For many years, too, it has been developing a chemistry based on simple and clean processes (emulsion polymerization, supercritical fluids…) and on sustainable development (biodegradable polymers, polymer recycling, optimum use of agricultural resources…). The team is also recognized for its expertise in macromolecular chemistry involving the heteroatoms Si, P and F.

The "bio-based polymers" theme was begun more recently, based on laboratory skills in polycondensation, thiol-ene chemistry and chain polymerization. One of the objectives of the current work is to replace dangerous molecules with bio-based ones in the development of polyurethanes, phenol-formaldehyde resins, epoxy resins and unsaturated polyesters. The scientific issues involved relate to the use of renewable resources through the development of a reduction chemistry process that will enable the use of oxygenated raw materials and the development of depolymerization techniques (natural polymers such as chitosan, lignin, etc., often have very high •••

GreenResins project
new bio-based epoxy resins free of bisphenol A



▲ *Diagram of the production of bio-based epoxy resins from tannin-derived catechin.*

Because of their versatility and ease of use, epoxy resins are very widely used. They include a great variety of materials with a wide range of physical properties. However, they are mostly derived from bisphenol A (BPA), a compound classified as CMR (carcinogenic, mutagenic and reprotoxic).

The GreenResins project involves the use of natural, non-toxic aromatic and polyaromatic compounds derived from renewable resources as reagents for use in developing thermosetting epoxy resins as a BPA substitute.

The source of these natural phenolic compounds is tannins from forestry or viticulture by-products, so there is no competition with food crops. Among the phenolic compounds being studied by the IAM (ICGM) team, in collaboration with the UMR "Science for Oenology" (INRA, Montpellier SupAgro et UM1), is catechin, a molecule with four phenolic groups. Catechin is epoxidized with epichlorohydrin. The phenols in catechin's two aromatic rings display different levels of reactivity, leading to two products: one molecule with four epoxy groups and a cyclized by-product with two epoxy groups. The average functionality is 2.7 epoxy groups per molecule. The mixture is used unpurified to prepare epoxy resins with amine hardeners since both products obtained are functionalized and contribute to network development. Resins derived from functionalized natural compounds possess thermal and mechanical properties comparable to those of conventional fossil-fuel-derived resins such as the diglycidyl ether of BPA.

The possibility of obtaining bio-based aromatic resins that are more rigid and perform better than aliphatic resins is what distinguishes this work, which won the 2010 *Pollutec Award* for innovative environmental techniques.

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▼ *Comparative thermal and mechanical properties of resins prepared from the diglycidyl ether of BPA and from tannins.*

Sample	T_g (°C)	T_{d5} (°C)	T_{d30} (°C)	$Char_{800}$ (%)	Swelling (%)	Soluble (%)	Storage Modulus (Gpa)	
							Glassy region	Rubbery region
DGEBA	74	209	355	10	17	1	2.8	0.019
75 DGEBA 25 GEC tannins	75	221	337	14	4	1	2.5	0.016
50 DGEBA 50 GEC tannins	73	202	323	18	1	1	2.4	0.014

molar masses, making it impossible to use them directly), a return to polycondensation rather than free radical polymerization to make the best use of biomass reactive functions (acid, alcohol…) and the development of reliable access paths to compensate for changes in biomass composition. Thus, new ways of accessing bio-based epoxy resins based on tannins from forestry or viticulture by-products have been developed.

In addition, the IAM team has developed new reactive functional synthons from vegetable oils and fatty acids bearing amine, alcohol or acid functions that give access to new bio-based polymers (polyurethanes, polyesters…).

Many industrial collaborations are underway, with national and international companies. In 2010, the team was awarded the Pollutec award "Innovative Techniques for the Environment" *(cf. project GreenResins).*

Other teams working in this area
UMR IEM **European Membrane Institute** (ENSCM/CNRS/UM2) *50 scientists*
UR LBE **Laboratory of Environmental Biotechnology** (INRA) *16 scientists*

Life cycle assessment of polymers and composites: integration of materials from recycling and renewable resource channels into the development of innovative materials

The *Materials Research Centre* **(Internal Research Unit [UPR], CMGD)** is one of three internal laboratories of the *École des Mines d'Alès* (EMA), which is a national public administration (EPA) reporting to the Ministry of Industry. Because it places great emphasis on relations with the economic sector, CMGD is part of the M.IN.E.S. Carnot Institute (Innovative Methods for Business and Society), which brings together all French *Écoles des Mines* and their research association, ARMINES. The Centre is involved in various competitiveness clusters and maintains academic and industrial collaborations at the national and international level through European projects, projects funded by the Environment and Energy Management Agency (ADEME), ANR and FUI.

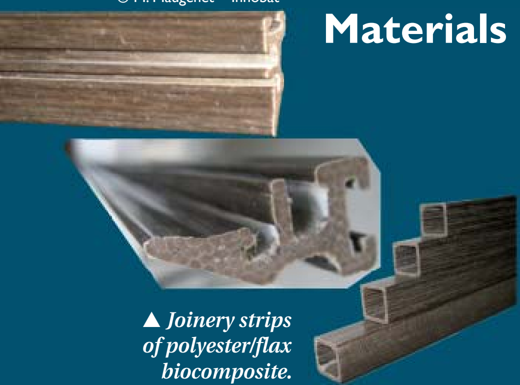
CMGD is structured into two research departments, namely "Advanced Polymer Materials" (MPA) and "Civil Engineering Materials and Structures" (MSGC). Materials life cycle assessment is central to the concerns of both departments, for with the implementation of European directives to promote end-of-life product recycling, advances are being made in the development of ever more efficient identification and sorting technologies, which may soon enable online identification of both plastics and their additives.

Thus, CMGD researchers are supporting the development of, on the one hand, prototype sorting equipment, and on the other hand high-performance plastic alloys that can be made from high-purity materials reclaimed from sorting.

Moreover, the growing global demand for energy, the need to find an alternative to fossil energy resources that are being depleted, and society's determination to reduce the environmental impacts of human activity and its carbon footprint are driving the partial or full integration of renewable resources (concept of bio-basing) into materials development. The compostability of materials is an added benefit now being worked on and which, provided collection channels are available, should allow for better end-of-life waste management. Thus, CMGD researchers are trying to remove many scientific and technological obstacles in order to turn these products to account in various application areas, such as packaging, agriculture, transport and building.

CMGD covers many disciplines, including chemistry, physical chemistry, mechanics and process engineering. In addition to a platform for the processing of polymers and concrete materials, it has a platform for materials characterization (mechanical, thermal and thermomechanical tests under standard conditions, fire resistance tests, aging tests, scanning electron microscope observations in environmental mode, X-ray diffraction, chemical and physicochemical analysis…). ■

Materials and eco-construction



▲ *Joinery strips of polyester/flax biocomposite.*

In the building sector, needs arise at two levels: first, to meet market expectations for "greener" products by paying attention to sustainable development objectives, and second, to comply with the *Grenelle de l'Environnement* by making use of more energy-efficient materials to reduce buildings' energy consumption, using renewable resources, recycling waste and reducing non-recyclable waste.

Thus, CMGD has since 2010 been working with the IAM (ICGM) team on a project funded by ADEME and supported by the Montpellier-area INNOBAT company, which won a *JEC Innovation Award in 2011*. This project is designed to develop a new material for joinery profiles, inasmuch as none of the traditional materials now used (wood, polyvinyl chloride [PVC], aluminium and polyester/glass composite) can meet the upcoming 2012 and 2020 thermal regulations while achieving the required level of mechanical performance level and meeting the architectural criteria, all with a lower environmental impact.

The new material is a pultruded composite with a thermosetting matrix derived in whole or in part from plant waste from the timber and wine industries and from continuous plant fibres. The project addresses many R&D issues:

- synthesis and formulation of thermosetting resins (epoxy and/or unsaturated polyester) derived in whole or in part from plant waste;
- preparation of flax plant fibres together with batch analysis and homogenization and possibly surface treatment of fibres;
- adaptation of formulas (resin reactivity, fibre tensile strength) to the pultrusion procedure;
- benchmarking of mechanical and thermal performance, fire retardancy and in-service ageing (humidity, temperature, UV exposure).

Prototypes are currently available and marketing is planned soon.

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Controlled lifetime biocomposites

The first generations of bio-based plastics were mainly targeted for short-lived applications such as packaging. Today, the demand has changed. What industry needs now are bio-based plastics with functionality at least equivalent to those of the current petrochemical-based plastics as regards barrier effect and mechanical, chemical and thermal resistance over the material's life cycle. There is a broad consensus to that effect in the scientific community. Thus, CMGD has been at the forefront of these developments. Beginning with foamed starch packaging for undemanding usage conditions, it went on to develop films and solid or foamed materials based on polylactic acid (PLA), a polymer obtained by fermentation of corn starch, less sensitive to moisture than starch and with better mechanical properties.

The COLIBIO project (COntrolled LIfetime BIOcomposites), funded by ANR and accredited by the Trimatec competitiveness cluster, aims to develop a biocomposite with very good mechanical and thermal properties, whose useful life can be controlled, to meet the requirements of the automobile industry. The idea was to reinforce a PLA-based matrix with glass fibres that would break down under normal composting conditions (temperature, pH, humidity); the scientific and technological obstacles were the ability to keep the biocomposite functioning with a high level of mechanical performance throughout its service life and to ensure end-of-life degradation.

Suitable biodegradable glass-fibre formulations were thus developed and the durability of the PLA/glass biocomposites under biomimetic conditions during use and at end of life was studied. It emerged that there is a strong interdependence between the alkalinity of the glasses and their mechanical behaviour under conditions simulating accelerated service use (immersion in water at 65°C) and the rate of their mineralization in soil, which may be accompanied by soil acidification.

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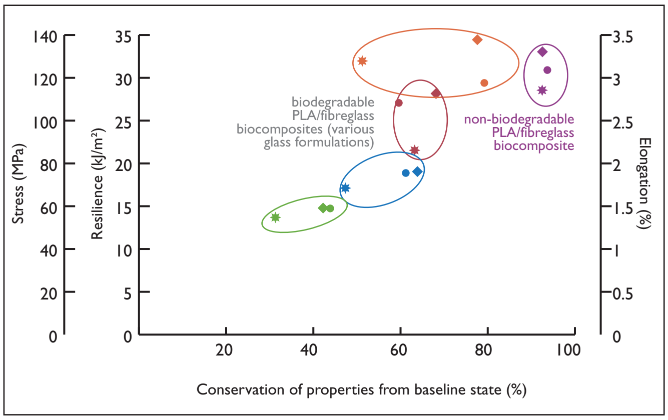
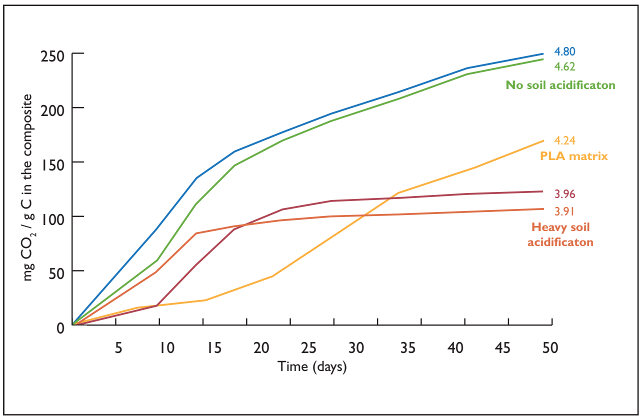
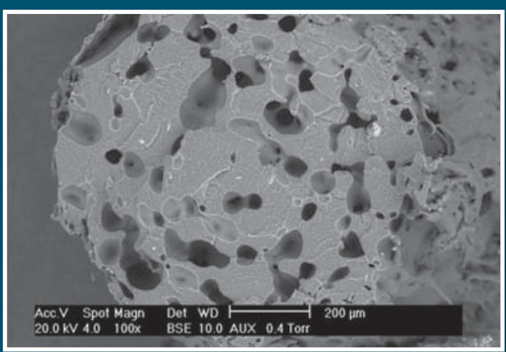


▲ *Degree of conservation of mechanical performance (● stress, ♦ elongation, ✱ resilience) of biodegradable and non-biodegradable PLA/fibreglass biocomposites after ageing under conditions simulating accelerated service use (24 hours' immersion in water at 65°C).*



▲ *Mineralization rates in soil simulating end of life of biodegradable PLA/fibreglass biocomposites under different levels of soil acidification.*

Bioplastics-based nanostructured materials



▲ *Scanning electron microscope view of a PHBV/clay bionanocomposite foam made by extrusion assisted by supercritical CO_2.*

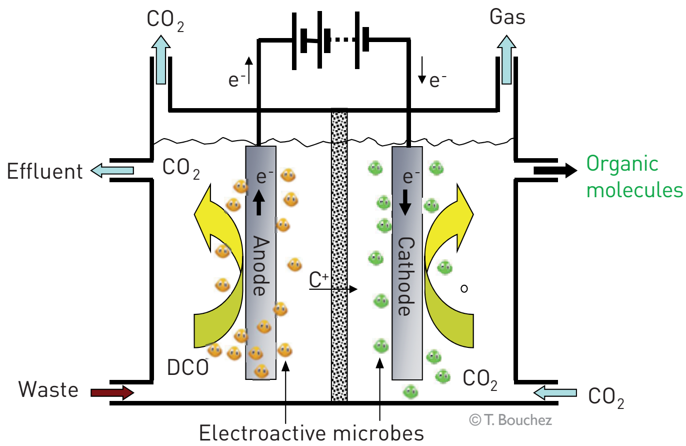
In 2006, in order to be more responsive to calls for proposals and enhance its ability to perform contract research in partnership with industry, the M.IN.E.S. Carnot Institute established a "NanoMines" group, with some fifty researchers from the various French *Écoles des Mines* working on the "nanostructures" topic. The aim is to bring out synergies between research teams by combining multidisciplinary skills in such areas as the development of nanomaterials, their characterization, modelling and application testing.

In this context, in 2011, CMGD and the RAPSODEE Centre of the *École des Mines d'Albi* undertook a project to develop bionanocomposites made up of nanoparticles in a bioplastic matrix, to control and improve the matrix's properties. Production of these bionanocomposites by supercritical fluid extrusion (CO_2) enables nanoparticles to disperse throughout the matrix, forming a foam without the use of chemical agents, while at the same time making the material lighter and more insulating.

The BIORARE project

Winner of the "Investments for the Future" national call for "Biotechnologies and Bioresources"

The BIORARE project (bioelectrosynthesis to refine residual waste, IRSTEA/Chemical Engineering Laboratory–French National Centre for Scientific Research/LBE-INRA/Suez-Environnement) focuses on how to use the concept of microbial electrosynthesis to biologically refine waste and effluents. This recent discovery could eventually enable the production of high-added-value molecules from the organic matter and energy in waste.



▲ *Principle of the microbial bioelectrosynthesis system used in the BIORARE project.*

Bioelectrochemical systems technology would be used to channel the metabolic reactions of the bioprocess into the production of building-block molecules with high added value for use in green chemistry. The organic material is oxidized in a first compartment by complex biomass, which transfers electrons to an anode. The electrons then go to the cathode, where they are used in a biological reduction reaction. By regulating the potential at the cathode to a value derived from a theoretical calculation (Nernst Law), one can artificially create thermodynamic conditions that will allow only certain reactions to occur.

These microbial bioelectrosynthesis systems maintain a physical separation between a "dirty" compartment containing the organic material to be processed and a "clean" compartment where the desired molecules are synthesized, metabolic fluxes are channelled, and oxidation reactions at the cathode are selected by regulating the potential.

Development of a detailed specification for the application of microbial electrosynthesis to the biorefining of organic waste requires the key components to be determined, together with the relevant specifications for a projected industrial development strategy. The scientific and technical basis of microbial electrosynthesis will be firmed up, then the relationship between the operating conditions and the molecules actually synthesized will be validated experimentally. Multidisciplinary approaches will be combined to better understand and identify the technological potential of these systems. Environmental assessment of strategies linking these systems to existing industrial installations will be carried out based on reference scenarios that will identify the environmentally sensitive components and provide guidance for technical and industrial choices. An analysis of economic, societal and regulatory factors will bring future industrial development strategies into better focus. A detailed specification for the implementation of microbial electrosynthesis systems for organic waste biorefining will be developed and related measures for the protection of intellectual property will be taken as necessary.

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The bioplastic matrix used in this project is a biodegradable polymer derived from microorganisms that belongs to the polyhydroxyalkanoate (PHA) family, specifically poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV). The matrix was reinforced with montmorillonite clay nanoparticles at a low uptake rate (less than 3% by mass). Incorporation of the clay significantly improved the matrix's mechanical and thermal properties and its fire resistance and helped control its biodegradation. The foams obtained have a porosity of up to 50%; the cell size homogeneity has yet to be improved through a study of the operating parameters of the process.

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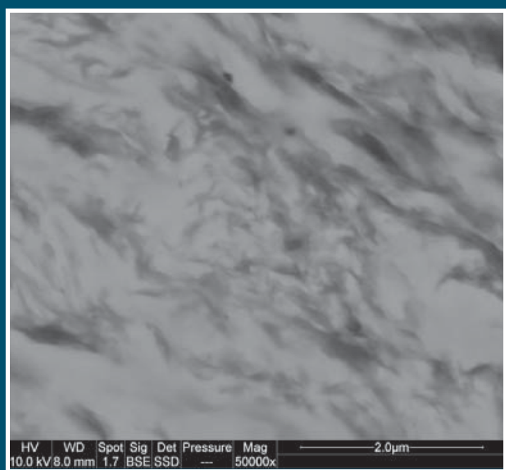

▲ *Transmission electron microscope view of clay dispersal in a PHBV/clay bionanocomposite foam.*

GreenCoat project
new bio-based polyurethanes from vegetable oils

Polyurethanes are among the best-selling polymers in the world, ranking 6th; world production is over 14 Mt. They are useful in many areas of everyday life, including thermal insulation and coatings. They are traditionally produced by reacting an isocyanate with a polyol oligomer. While the isocyanate is almost exclusively derived from petrochemical feedstocks, the polyol can be derived from renewable resources. However, most isocyanate compounds are highly toxic or even CMR (carcinogenic, mutagenic and reprotoxic) and are on the SIN list (*Substitute It Now!*—REACH, Annex XVII). The initial aim of the GreenCoat project is to develop new bio-based polyols, derived from vegetable oil, with new properties. A subsequent goal is to develop isocyanate-free bio-based polyurethanes from glycerol.

Bio-based polyols are synthesized from vegetable oil or from fatty acids or esters through thiol-ene coupling on the double bonds of the fatty chains. The thiol used has one or more alcohol functions. The addition reaction is carried out with neither solvent nor initiator, under UV; the yield is quantitative. This technology produces bio-based polyols with widely varying structure and functionality.

The development of isocyanate-free bio-based polyurethanes relies on the cyclocarbonate ring-opening reaction mediated by primary amines. Thus, the IAM (ICGM) team has produced oligomers bearing dicyclocarbonate functions from glycerol carbonate. Reacting these oligomers with diamines produces isocyanate-free bio-based polyurethanes.

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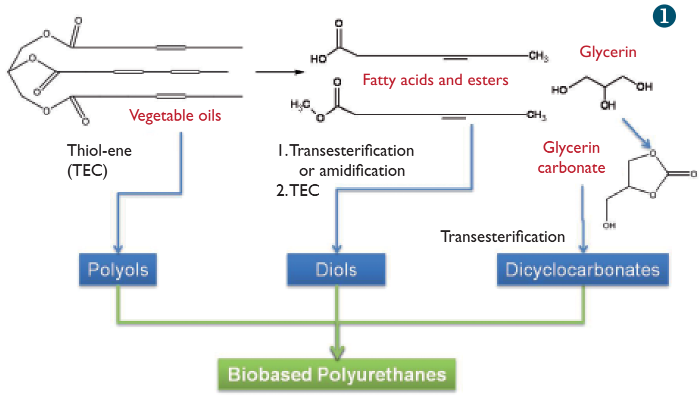

In both cases, the bio-based polyurethanes obtained have properties similar to those of fossil-fuel-derived polyurethanes and can be used in coatings, binders, paints, etc. This project has received funding from ANR Matepro and is being conducted in collaboration with the Organic Polymers Chemistry Laboratory (Bordeaux) and the Résipoly and SEG companies.

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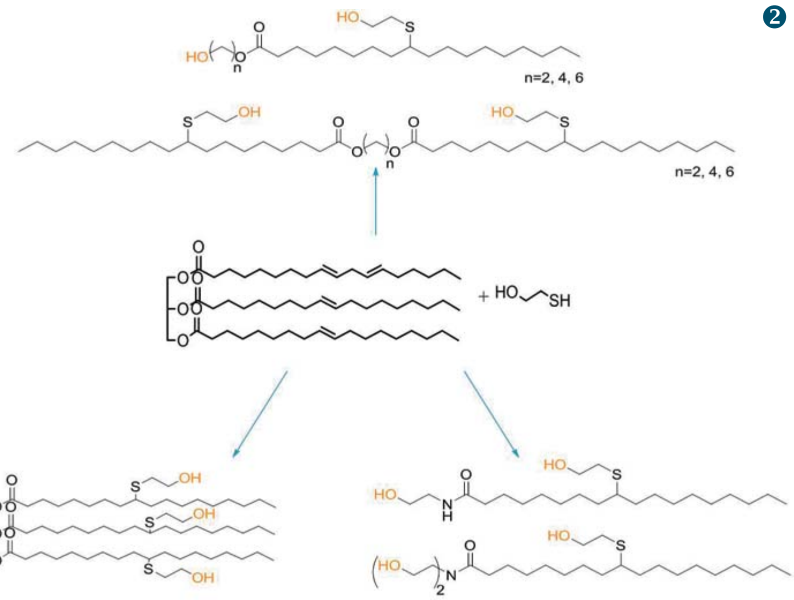

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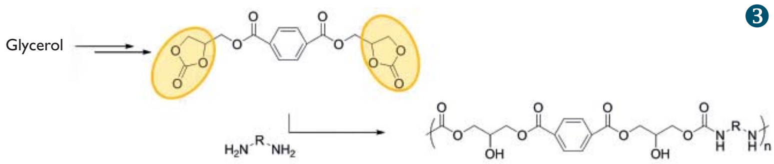

❶ Diagram of bio-based polyurethane production from vegetable oil and derivatives.

❷ Synthesis by thiol-ene coupling of new bio-based polyols from vegetable oils.

❸ Isocyanate-free bio-based polyurethane production.

▲▶ *Biodegradable packaging developed under the project.*

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EcoBioCAP project
Eco-efficient Biodegradable Composite Advanced Packaging

Over the past ten years, many types of biodegradable food packaging have been developed, the main goal being to imitate petrochemical plastics; however, no real evaluation has been done of their environmental benefits, economic viability or potential impact on the quality and safety of packaged foods. These packaging systems quickly bogged down, especially in the food industry, as a result of a number of major controversies (diversion of food resources, overly complicated recycling/recovery routes, for example). A more holistic, systemic approach is needed in developing such biodegradable packaging in order to restore the trust and consumers and users and to pique their interest.

The European EcoBioCAP project aims to supply European Union food industries with modular biodegradable packaging tailored to the requirements of perishable foodstuffs, with direct benefits for the environment and for European consumers in terms of food quality and safety. This new generation of packaging will be based on the multi-scale development of composite structures all of whose constituent parts will be from food industry by-products.

Production techniques and all the properties of the materials developed in the course of the project will be optimized through demonstration activities with industrial partners before industrial use is begun. The EcoBioCAP technology will be made available to all industry players through development of a decision support tool. Finally, outreach activities will be undertaken, not just to inform the scientific community of the project results, but also to make sure consumers and end-users know the benefits of such biodegradable packaging and how to use it.

The EcoBioCAP project has a budget of €4.2 million, financed by Europe (to the tune of €3 million over four years under the seventh Framework Programme for Research and Development. It brings together 16 partners from eight different countries, including six private companies.

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