



ref. 299219

SPECIFIC AGREEMENT OF INTERNATIONAL COOPERATION
Specific agreement of academic, scientific, technical and cultural cooperation

Between

The Federal University of São Carlos (Brazil), with registered offices on São Carlos campus, at Rodovia Washington Luís, km 235, in São Carlos, in the state of São Paulo, Brazil, represented by its Rector, Prof. Ana Beatriz DE OLIVEIRA, Ph.D., hereinafter referred to as “UFSCar”, on behalf of its Department of Materials Engineering,

and

The Centre National de la Recherche Scientifique, a public scientific and technological institution, headquartered at 3 rue Michel-Ange 75794 Paris cedex 16, France, represented by its Chairman and CEO, Antoine PETIT, who has delegated signing authority for this agreement to the Regional Delegate of the Alpes Delegation, Christophe J. MULLER, hereinafter referred to as the “CNRS”,

CNRS acting on behalf of the Laboratory *Centre de Recherches sur les Macromolécules Végétales* (CERMAV) (UPR 5301), managed by Laurent HEUX, hereinafter referred to as the “LABORATORY”,

WHEREAS both Institutions are interested in the development of Higher Education, scientific knowledge and research, and technology,

WHEREAS the proposal for the joint research project “Catalytic regeneration and reactive compatibilization of PP/EVOH blends using organometallics anchored by Cellulose Nanocrystals”, filed by the researchers mentioned in Section 2 hereof, has been selected under the call International Research Booster (IRB) *Année 2024*, organized by the *Université Grenoble Alpes*,

WHEREAS they wish to formally establish an institutional relationship between them, aiming to promote their continuous strengthening, enhancement and advancement by jointly developing academic, scientific, technical and cultural activities in the area of and/or regarding topics on Materials Engineering, particularly the development of the research project mentioned above, for the interest of their respective academic and/or research unities involved,

ENTER INTO THIS AGREEMENT, which will be governed by the following terms and conditions:

SECTION 1 – Purpose

This Agreement establishes and governs academic, scientific, technical and cultural cooperation between the Parties in the area of and/or regarding topics on Materials Engineering, for the explicit interest of the Department of Materials Engineering of UFSCar.

Said collaboration may comprise the development of the following activities:

- I. Exchange of professors and researchers, so as to give lectures and workshops, teach courses and/or carry out or participate in research activities at the host institution.
- II. Joint development of research projects, like the project “Catalytic regeneration and reactive compatibilization of PP/EVOH blends using organometallics anchored by Cellulose Nanocrystals” (see Annex A), which work plans shall be timely attached hereto.
- III. Sharing and exchange of scientific, technical and cultural information, as well as joint production of academic, scientific and technical publications.

SECTION 2 – Coordination

In order to coordinate the implementation of this Agreement and the pursuit of its purpose, UFSCar indicates Dr. Lucas Henrique STAFFA, professor of its Department of Materials Engineering, and CNRS (through LABORATORY) indicates Dr. João Paulo COSAS FERNANDES, as lead scientists.

The coordinators shall supervise the research plans corresponding to the exchanges under this Agreement, as well as seek solution for the academic and administrative issues referring hereto from its effective date.

SECTION 3 – Exchange of professors and researchers

When promoting the exchanges provided in the First Clause hereof, both Parties shall observe the following rules, to the extent of their respective rules and regulations on international academic mobility:

- I. The maximum number of exchange professors and researchers from any institution in mobility at the other, as well as the length of their respective stay at the host institution, will be set forth timely by the Parties, in accordance with what is possible and feasible for them, subject to the limits stipulated in their by-laws.
- II. The exchange of professors and researchers requires formal invitation by professor or researcher from the host institution.
- III. For each professor and researcher a research plan and/or work plan shall be elaborated in order to be executed at the host institution, but before the arrival of the corresponding professors and researchers at said institution.
- IV. Professors and researchers accepted by the host institution will be subject not only to the rules and regulations in force there, but also to the immigration law of the country where said institution is situated.
- V. Before arriving in the country of the host institution, accepted professors and researchers must purchase health, personal accident, civil liability, and medical and mortal remains repatriation insurances featuring coverage for the whole period of their respective exchange.
- VI. Both institutions shall facilitate the access and use of its own facilities, equipments, laboratories and library material by exchange professors and researchers, so as to enable the proper development of their respective activities.
- VII. The host institution shall waive the academic fees (*e.g.*, bench fees), where required, regarding the mobility of professors and researchers from the other institution.

- VIII. Participants in the exchanges will bear the costs referring to their own participation in said activity, *e.g.*, travels, housing, food, transportation, insurance, visa, and others.
- IX. Where necessary or requested, the host institution shall send to the home institution document(s) informing the academic and scientific activities developed by each of its professors and/or researchers during his/her respective exchange and, where applicable, informing also the result of the evaluation of his/her performance in such activities.
- X. Participation in any activity under this Agreement does not generate any formal employer-employee relationship between any person from either Party and the other Party.

SECTION 4 – Financial resources

Unless otherwise agreed in an amendment hereto, this Agreement does not create any financial obligation from either Party to the other. Each Party shall bear the costs of its own effective participation in the development hereof.

The Parties may carry out activities hereunder using funds granted from agencies and organizations devoted to funding research and development, as well as from companies and other private and public institutions.

SECTION 5 – Confidentiality of information, intellectual property rights and publications

- I. Both Parties ensure that themselves, their respective employees and agents, as well as any other person in connection with the Parties, will respect the confidentiality of all the information, data, projects, know-how and any other information or documents provided by either Party to the other under this Agreement. Both Parties shall not disclose such information, documents, data, projects and know-how to third parties without the prior written consent of the Disclosing Party.
- II. Throughout the duration of this Agreement and for five (5) years after its termination, both Parties shall keep strictly confidential the confidential information exchanged between them or generated by them hereunder. Both Parties shall not directly or indirectly disclose such confidential information to third parties or make it public without the prior written consent of the Disclosing Party, or use such confidential information for purposes not set forth in this Agreement, except under a legal rule or court order.
- III. Notwithstanding the previous provisions, information will not be deemed confidential if:
 - a) it is publicly known or is known by the Receiving Party before its receipt, without any breach of this Agreement;
 - b) it becomes publicly known in the future, without either Party being responsible for its disclosure.
- IV. If a court order requires the Parties to disclose confidential information to third parties, the Party receiving the court order shall communicate the Disclosing Party about such court order and take all the appropriate legal actions, at its own expenses, in order to prevent disclosing said confidential information or, where it is not possible, disclose only the *piece of information that is strictly necessary to comply with such court order*.
- V. Any data, technology, technical and commercial information, software, procedure and routine, registered or not, belonging to any of the Parties and/or to third parties, but

under the responsibility of this Party, prior to the effective date of this Agreement, and which has been disclosed to the other Party for the sole purpose of supporting the development of programs, projects or activities hereunder, will remain belonging to the Party that has possessed such goods already.

- VI. The Parties hereby agree that any result able of being protected by intellectual property rights, resulting from programs, projects or activities developed under this Agreement, will be jointly owned by UFSCar and CNRS. Such intellectual property rights, as well as other rights and duties of the Parties, shall be set forth in a further specific agreement or contract, which shall observe the relevant legislation.
- VII. By signing this Agreement, CNRS explicitly acknowledges that UFSCar features an innovation agency, which is in charge of managing said university's policy on innovation. As a consequence, any further result arising from the development of this Agreement, which may become property of both Parties, shall be communicated to UFSCar Innovation Agency, so as to execute the appropriate procedures to protect such result. Likewise, CNRS is free to communicate confidential information or results with its affiliate CNRS INNOVATION for the same purposes.
- VIII. The Parties shall communicate each other about the generation of any new process and/or product able of being protected by intellectual property rights resulting from the development of programs, projects or activities hereunder.
- IX. Provided that clauses on confidentiality stipulated in this Agreement are observed, both Parties are entitled to publish or present results from the development hereof. Any publication or presentation resulting from this Agreement shall mention the cooperation set forth herein, as well as duly protect proprietary information or intellectual property regarding those results or confidential information disclosed by either Party.
- X. Any publication or presentation by any Party of any result jointly obtained under this Agreement requires the prior written consent from the other Party. Thus, the Party wishing to publish or present such results shall show the content of the publication or presentation to the other Party, which will give its consent or disallow the publication or presentation, along with the corresponding reasons, within sixty (60) days from the date when it receives the content of the publication or presentation in an electronic document. In the event that such decision is not communicated within the abovementioned period, the publication or presentation of said document will be deemed authorized.

SECTION 6 – Duration, amendments and termination

This Agreement is valid as from the date of the last signature by both Parties and will remain in force for five (5) years. The duration hereof may be extended by means of a duly signed amendment.

Any amendment hereto shall be agreed in writing and signed by the authorized representatives of both Parties.

Any Party can terminate this Agreement at any time by giving the other Party a reasoned termination notice in writing at least three (3) months in advance, along with return receipt. In the event of termination hereof, eventually ongoing activities will be duly concluded.

SECTION 7 – Settlement of disputes and language

In the event of any dispute which may arise between the Parties relating to the existence, validity, interpretation and/or performance of this agreement or of any one of its clauses, they shall attempt to reach an amicable solution to such dispute.

Should they fail to do so within a time limit of six (6) months, the dispute shall be settled in accordance with rules and principles of International Law.

In the case of legal disputes, the Parties may bring it before authorities and/or courts of the country having jurisdiction. The country of jurisdiction shall be that of the defendant.

This Agreement is originally drafted in English language. Any translations to other languages are for information purposes only.

This Agreement is signed in two (2) original copies in English language and two (2) original copies in Portuguese language. In the event of any conflicts, discrepancies or differences between the English version and the Portuguese version of this Agreement, the English version shall prevail.

São Carlos, São Paulo (Brazil), 12 JUN. 2025

for CENTRE NATIONAL DE LA RECHERCHE
SCIENTIFIQUE (CNRS)


Prof. Ana Beatriz DE OLIVEIRA, Ph.D.
Rector
Federal University of São Carlos



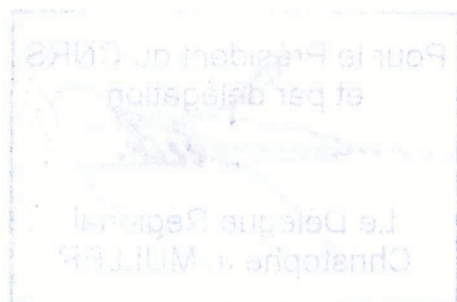
Pour le Président du CNRS
et par délégation


Le Délégué Régional
Christophe J. MULLER
Antoine PETIT
Chairman & CEO
And by delegation of signature
Christophe J. MULLER
Regional Delegate of CNRS ALPES (Grenoble
FRANCE)



ANNEX A – Proposal of the joint research project “Catalytic regeneration and reactive compatibilization of PP/EVOH blends using organometallics anchored by Cellulose Nanocrystals” in French and English languages.

See description in the following page.



International Research Booster (IRB)

Année 2024

Acronyme du projet	REGENCOMP
Titre du projet	Catalytic regeneration and reactive compatibilization of PP/EVOH blends using organometallics anchored by Cellulose Nanocrystals
Porteur du projet	João Cosas
Etablissement partenaire	Department of Materials Engineering (DEMa) of Federal University of São Carlos (UFSCar), Brazil
Montant de la demande	10 000€

Description du projet

■ Abstracts (2 pages)

- Résumé en français (1 page maximum)

L'utilisation croissante des matériaux polymères comme emballages à élimination rapide de faible biodégradabilité favorise un scénario de génération de déchets. Parmi ceux-ci, les matériaux multicouches tels que les emballages coextrudés, par exemple ceux formés de couches de polypropylène (PP) et de couches intermédiaires de copolymère d'éthylène-alcool vinylique (EVOH), font partie d'un contexte difficile en raison de la difficulté de circularité de ces matériaux. Il est connu que le principal produit du recyclage thermomécanique de tels produits est des mélanges polymériques. De plus, comme il s'agit de matériaux multicomposants incompatibles, des stratégies supplémentaires telles que la compatibilisation avec des copolymères à bloc ou maléatisés sont impératives dans le recyclage de ces matériaux. Cependant, comme le matériau de départ pour ce recyclage s'agit d'un matériau multirésine dégradé, l'ajout de compatibilisants habituels peut ne pas suffire pour la régénération des propriétés physico-mécaniques et pour permettre sa circularité. Dans ce contexte, une option intéressante est d'utiliser des additifs spécialisés pouvant fonctionnaliser une (ou plusieurs) phase(s) du mélange avec des monocouches organométalliques, pour soutenir un "lit de repolymérisation" par action catalytique (catalyse de type métallocène in situ). Ces agents de couplage réactifs sont basés sur des titanates et/ou zirconates néoalcoxy et réagissent avec des surfaces fonctionnalisées par OH via une coordination de protons in situ. Dans ce contexte, l'utilisation de matériaux à base de nanocellulose, tels que les nanocristaux de cellulose, peut être utilisée pour ancrer l'organométallique et repolymériser la phase environnante (PP), reconnectant les chaînes polymériques qui ont subi une scission précédente par dégradation thermomécanique. De plus, si le nanocristal de cellulose fonctionnalisé se positionne, via une localisation sélective, à l'interface PP/EVOH, il peut compatibiliser de manière réactive le mélange polymérique, améliorant l'adhérence et réduisant la tension interfaciale. Ce projet se concentre sur le recyclage et la circularité de matériaux multicomposants avec la régénération des propriétés mécaniques de la matrice dégradée, assistée par un renforcement mécanique simultané et une repolymérisation à l'aide d'additifs organométalliques sur des charges de nanocellulose. Ainsi, il est prévu de contribuer à l'utilisation de polymères recyclés en tant que matrice polymère dans un mélange, en fonction des nouvelles perspectives des agences réglementaires dans le mélange d'emballage. Une tentative d'illustrer les mécanismes de compatibilisation dans les mélanges PP/EVOH se trouve dans la Figure 1.

- **English Abstract** (1 page maximum)

The increasing use of commodities polymeric materials as low-biodegradability quick-disposal packaging fosters a scenario of increasing waste generation. Multi-resin materials such as co-extruded multi-layer packing, for example those formed by layers of polyolefins and intermediate layers of ethylene-vinyl alcohol copolymer (EVOH), are part of a challenging scenario due to the difficulty of circularity of these materials. It is known that the main product of thermomechanical recycling of such products is polymeric blends. Also, as these are incompatible multicomponent materials, additional strategies such as compatibilization with block or maleated copolymers are imperative in their recycling. However, as the starting material is a degraded multi-resin, the addition of usual compatibilizers may not be enough for the regeneration of physical-mechanical properties and to allow circularity. In this context, an interesting option is to use specialized additives that can functionalize one (or more) phase(s) of the mixture with organometallic monolayers, to support a “repolymerization bed” by catalytic action (*in situ* metallocene-type catalysis). These reactive coupling agents are based on neoalcoxy titanate and/or zirconates and reacts with OH-functionalized surfaces *via in situ* proton coordination. In this context, the use of nanocellulose-based materials, such as cellulose nanocrystals, can be used to anchor the organometallic and repolymerize the surrounding phase (PP), reconnecting polymeric chains that suffered previous scission by thermomechanical degradation. Moreover, if the functionalized cellulose nanocrystal positions itself, *via* selective localization, at PP/EVOH interface, it can reactively compatibilize the polymeric blend, improving adhesion and reducing interfacial tension. This project focuses on the recycling and circularity of multicomponent materials with the regeneration of mechanical properties of the degraded matrix, assisted by simultaneous mechanical reinforcement and repolymerization using organometallic additives on nanocellulose fillers. Thus, it is expected to contribute to the use of recycled polymer as a polymer matrix in a blend, in accordance with the new perspectives of regulatory agencies in the packaging mixture. An attempt to illustrate the compatibilization mechanisms in PP/EVOH blends is in **Figure 1**.

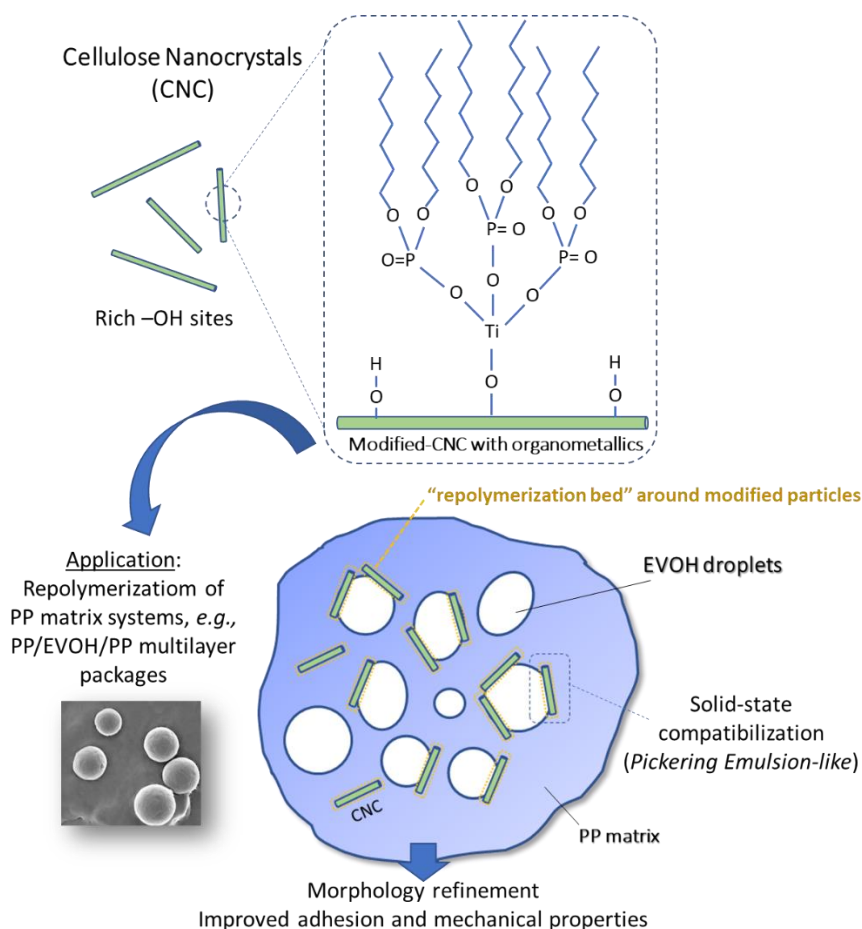


Figure 1. Illustration of the compatibilization mechanism of the PP/EVOH mixture, based on modified-CNC with organometallics.

Contenu du projet (5 pages maximum)

1. State of the art and originality of the project

The widespread use of polymeric materials, especially in consumer packaging, has led to a significant rise in waste production. Despite global plastic production reaching 322 million tons in 2015, recycling rates remain dangerously low. For example, in Europe, less than 30% of plastic waste is recycled, and in Brazil, only 1.3% was recycled in 2019, well below the global average, posing challenges for landfills and marine ecosystems due to the chemical resistance and poor biodegradability of packaging polymers. To address this, the European Commission introduced a 2017 directive aiming for all plastic packaging in the EU to be 100% recyclable or from recycled materials by 2030, ending single-use plastics. This directive mandates prioritizing reuse and recycling, prompting research efforts to facilitate recycling and promote circularity in plastic lifecycles by using recycled materials in new packaging designs.

Multi-resin polymeric products, notably multi-layer co-extruded materials, are common in packaging, with ethylene-vinyl alcohol copolymer (EVOH) often serving as an intermediate layer (between PP layers), due to its excellent barrier properties, ideal for flexible packaging like fresh meat and sliced cold cuts.¹ However, while multi-layer packaging is effective for food preservation, it presents sustainability challenges, particularly in recycling due to immiscibility and incompatibility, resulting in limited mechanical properties during thermomechanical recycling. Post-consumer recycling of multi-resin materials is even more complex due to degradation (photo-oxidized, thermally degraded, or partially biodegraded "starting materials")², requiring additional methods beyond conventional recycling. Photo-oxidation is influenced by various factors, including interactions between degradation products of different polymers, the impact of third components like physical compatibilizers, and the inadequacy of traditional compatibilization methods.

To enhance mechanical properties in degraded multi-resin mixtures, innovative strategies are needed. One promising approach involves utilizing specialized additives to functionalize phases of the mixture with organometallic monolayers.³ These additives facilitate *in-situ* macromolecular catalysis, enabling smaller chains resulting from degradation to react or copolymerize in the presence of organometallic compounds. Supported by the functionalization of dispersed phases, these additives create a coating with organometallic monolayers that facilitate a "repolymerization bed", catalyzing the surrounding polymeric phase's improvement and seeking to restore properties similar to virgin polymer. This "repolymerization" is a rheological effect in thermoplastics, independent of cross-linking, aimed at reconnecting molecular chains fragmented during plastic degradation.³

The aim of this work will be the development of a polymeric blend (recycled PP/EVOH) with regenerated properties, simulating the recycling of a multi-layer packaging of PP and EVOH, aiming at increased circularity. It is expected that organometallic additives based on transition metals such as titanium, zirconium, or zirconium aluminates will act as catalysts in polyolefin blends, enabling the circularity of multi-resin materials. Another environmentally friendly solution showing great potential for this compatibilization consists of the use of cellulose-based nanomaterials. Nanocellulose in the form of nanocrystals (CNCs) or microfibrillated cellulose (MFCs) is interesting for their intrinsic characteristics, such as a fibrillar morphology, with a large surface area and a high aspect ratio, reactive surface chemistry, high stiffness, low density, biomass origin and abundance. Furthermore, the intrinsic high aspect ratio of the nanocellulose materials is advantageous for the stress transfer and reinforcement of nanocomposites. The surface of CNCs/MFCs consists of many hydroxyl groups, responsible for a strong hydrophilic nature, and this reactive chemical surface can be tailored by surface functionalization to achieve strong interfaces between filler and matrix.⁴ The addition of cellulose grafted with the organometallic additives could allow the creation of more sites supporting "repolymerization beds" in the nanocomposites, precisely because of its high density of hydroxyl groups. Thus, it will be possible to contribute to the mechanism of repolymerization. Simultaneously it can provide mechanical reinforcement to the material and stabilize the polymer blend by the presence of the CNC particles at the PP/EVOH interface. This phenomenon is explained by "solid compatibilization", suppressing coalescence and reducing EVOH droplet size, in a phenomenon similar to the "Pickering effect" in emulsions.⁵

Originality of the project:

This project aims to contribute to different problematics of materials science and engineering, such as:

- Unlike typical industry methods for blend compatibilization, this project will employ organometallic additives, like neoalkoxy titanates and/or zirconates, grafted onto nanocellulose and EVOH, which will act as coupling agents, catalyzing repolymerization of the degraded matrix.
- Neoalkoxy organometallic additives are considered interface bonding agents, that can enhance adhesion between phases by chemical bonds via *in situ* proton coordination coupling (metallocene-type catalysis) in the polymer melt, without the need for corresponding polarities and condensation waters.
- The innovative approach involves functionalizing the dispersed phases (nanocellulose and EVOH) to form a "repolymerization bed," catalyzing the repolymerization of the surrounding phase, regenerating physical-mechanical properties.
- Nanocellulose crystals will offer triple benefits to the nanocomposite: stabilizing the polymer blend morphology at the PP/EVOH interface, aiding in the formation of a "repolymerization bed" through their functionalization with organometallic additives, and providing mechanical reinforcement.

2. Scientific or technological challenges

This research project will revolve around three scientific challenges:

- **1) Control of the functional properties of the cellulose nanocrystals:** It will be a question of controlling their chemical modification with the organometallic additives to give them the ability to contribute to the "repolymerization bed" in the triphasic material.
- **2) The preparation of the blends and the incorporation of compatibilizers:** The main challenge lies in the control of the parameters of the process for the proper dispersion and the effective functionalization of the dispersed phases of EVOH and CNCs with the organometallic additive. This step is essential for the formation of a repolymerization bed of the surrounding polymer (PP), to achieve suitable mechanical properties.
- **3) Understand the structure-property relationships:** Development of a multi-scale and multi-technique approach for the advanced characterization of these materials, in particular based on near-field techniques and electron microscopy, for the nanoscale measurements of the interfaces, up to the characterization of macroscopic properties, focusing on the rheological and mechanical properties.

3. Scientific approach and work plan

This research project will be divided into **5 Work Packages (WP)**, as shown in **Figure 2**.

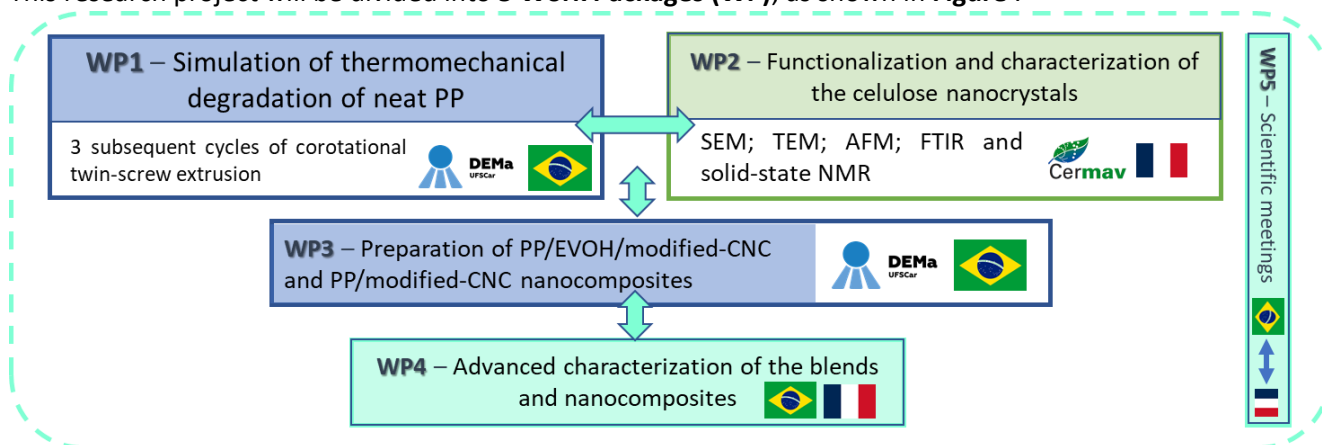


Figure 2. Technical diagram of work packages

3.1. WP1 – Simulation of thermomechanical degradation of the matrix

The thermomechanical degradation of pure PP will be done by 3 subsequent cycles of corotational twin-screw extrusion (200 rpm, 200°C profile). Here, an HP 523 J isotactic homopolymer PP will be used, supplied by Braskem, with a melt flow index (230°C/2.16 kg) of 3.1 g/10 min and suitable for application in the packaging sector. The degradation levels will be monitored indirectly through melt flow index tests (MFI,

230°C, 2.16 kg). Previous investigations made it possible to confirm that this procedure results in a 25% reduction in viscosity.

3.2. WP2 – Functionalization and characterization of the cellulose nanocrystals

Nanocellulose crystals will be produced by acid hydrolysis of different cellulose sources, e.g., cotton linters and tunicate, yielding crystals with different characteristic sizes (~100 nm to > 1µm in length). The morphology and size distribution of the nanocelluloses will be determined using transmission electron microscopy (TEM) observations, and height measurements will be performed using atomic force microscopy (AFM). Chemical modifications with the organometallic additive will be performed in lab conditions to assess the kinetics and grafting efficiency. To follow the chemical modifications, surface chemistry analyses such as FTIR and solid-state NMR will be carried out. Morphological changes of the CNCs before and after chemical modifications will be performed using electron microscopies (SEM, TEM) and AFM. This will provide important information on the success of the protocols. To adequately modify the nanocelluloses' surfaces, we will take advantage of the CERMAV's expertise in surface chemistry and characterization. An intern is envisioned during this task, supported by this project.

3.3. WP3 - Preparation of functionalized blends and nanocomposites

This work package is defined by the preparation stage of the mixtures and the incorporation of compatibilizers. Polymeric blends of degraded PP/EVOH (80/20% by mass) will be prepared via incorporation with 1, 1.5 and 3 wt% of the organometallic additive, a neoalkoxy titanate (CAPS® KPR® 12/LV supplied by Kenrich Petrochemicals). Functionalized cellulose nanocrystals (or not) will be added to the system (with and without EVOH) to provide additional anchoring sites for the organometallic additive together with mechanical reinforcement. The content of modified crystalline nanofilaments will be varied systematically towards the filler percolation limit to assess its effects on the coalescence of the EVOH phase and the final performance of the material. The preparation of the blends and nanocomposites with nanocellulose will be done at DEMa-UFSCar, with the aid of an intern supported by DEMa-UFSCar.

3.4. WP4 - Advanced characterization of the blends and nanocomposites

The properties of blends and nanocomposites result from the intrinsic properties of each component, the interfaces generated and the mixing methods, demanding multi-scale and multi-technique analyses to describe the dynamic phenomena occurring in these complex multiphase materials. We aim to combine local mechanical information at the cross-sections of the interfaces and bulk rheological characterization for estimating interface parameters, to provide insights into the mechanisms of compatibilization and repolymerization of the degraded matrix.

WP4.1 - Multiscale and multi-characterization of morphology and local properties

In-situ studies of the morphology and interfaces present in the nanocomposites will be carried out at CERMAV using AFM in nanomechanical mode, scanning electron microscopy (SEM) and transmission (TEM). The characterization of the nanomechanical properties of the nanocomposite by AFM will reveal the morphology in a non-destructive way by the difference in modulus between the polymer matrixes (PP ~1.3 GPa, EVOH ~2.2 GPa) and the nanocrystals (>20 GPa), as well as the effect of chemical modifications on the nanofiller/matrix interface. To access the morphology, interface properties and property profiles in the core of the blends and composites, the materials will be prepared by cryo-ultramicrotomy. The proper control of the surface chemistry of the CNCs and EVOH should improve the dispersion of the particles, avoid agglomeration and promote a better interface adhesion with the PP, while promoting the repolymerization of the degraded matrix by the catalytic action of the grafted organometallic additive. These analyzes will be carried out at CERMAV, using the AFM and the SEM/TEM of the microscopy platform of the *Institut de Chimie Moléculaire de Grenoble* (ICMG).

WP4.2 - Studies on thermo-mechanical properties and rheological behavior

To verify the utility gain of the polymeric recycled material by analyzing its mechanical behavior through tensile testing. The samples will be pressed and stamped according to ASTM D1708:18 standards. **Fourier**

Transform Infrared Spectroscopy (FTIR) will be used to ascertain the appearance or shift of characteristic bands related to the chemical bonds originating from the reactive compatibilization of the organometallic additive with the hydroxyl groups of the nanocellulose and/or EVOH via in situ proton coordination. The immiscibility between the phases will be studied by **Dynamic Mechanical Analysis (DMA)**. curves of storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) as a function of temperature will be determined in dual-cantilever mode. Shifts in the glass transition temperature and changes in crystallinity will be investigated by **Differential Scanning Calorimetry (DSC)** to verify the influence of surface-modified cellulose nanocrystals on the thermal behavior of PP and EVOH. The loss of molar mass after simulating the degradation of PP and any potential gains in molecular weight after the addition of the organometallic additive will be studied by **Size Exclusion Chromatography (SEC)**. The rheological behavior under steady-state (flow sweep) and oscillatory conditions will be evaluated by **Parallel Plate Rheometry**. The steady-state rheological approach will be used to determine the viscosity ratio and the oscillatory approach for estimating **the interfacial tension** via nonlinear regression of the viscoelastic response (G' and G'') of the blend during shear oscillatory rheometry. The aim is to obtain interfacial tension values to quantify the degree of adhesion between the phases of the PP/EVOH polymeric blend and the effect of the organometallic molecules and/or functionalized cellulose nanocrystals in the mixture.

These analyzes will be carried out at DEMa-UFSCar (São Carlos – Brazil), with the aid of an intern supported by DEMa-UFSCar. All equipment and techniques proposed here are available at DEMa-UFSCar. Additionally, multi-user laboratories at UFSCar are available, such as the Structural Characterization Laboratory (LCE) and the Analytical Center of the Chemistry Department (DQ), if necessary.

3.5. WP5 – Scientific coordination and missions at DEMa-UFSCar and CERMAV

To promote international collaboration and foster new projects in partnership with other groups of the department, a visit to DEMa-UFSCar is envisioned from the 15th – 30th of August 2024. Prof. Dr. Lucas Henrique Staffa will be directly involved in the reception of Dr. João Cosas. The visiting researcher from CERMAV (João Cosas) will teach class sessions for a short-term course at the Graduate Program in Materials Science and Engineering ([PPGCEM](#)), “**Special Topics in Atomic Force Microscopy Applied to Polymeric Materials**”, together with Prof. Dr. Lucas Henrique Staffa. Dr. Cosas will be responsible for 4 hours of theoretical classes and 4 hours of practical classes. During the stay, besides the teaching activities, the visit will also focus on scientific meetings to align this current project, discuss results, and provide new strategies for the project's improved progress. Eventually, meetings with other groups at DEMa-UFSCar may rise to foster new future collaborations. Following the same logic, the reception of Prof. Dr. Lucas Henrique Staffa from DEMa-UFSCar at CERMAV is also envisioned in 2025, comprising seminars and scientific meetings with other groups from CERMAV.

4. Results and deliverables

The scientific results issued from the project will be valued in the form of publications in peer-reviewed scientific journals, and presentations in scientific congresses, as well as popularized in actions intended for the general public. Finally, this project will be a driving force for setting up projects financed at an international level, also contributing to the training of students. The main deliverables envisaged in the project and the Gantt chart are shown below.

WP	ID	Deliverable	Partner
1	1.1	Thermomechanical degradation of PP matrix	DEMa
2	2.1	Chemical modifications of the surface of nanocelluloses	CERMAV
3	3.1	Preparation of PP/EVOH/modified-CNC and PP/modified-CNC nanocomposites	DEMa
4	4.1	Morphological characterization of nanocomposites by electron microscopies	CERMAV
	4.2	Characterization of local properties at the PP/EVOH/CNC interfaces by AFM	CERMAV
	4.3	Bulk chemical & thermo-mechanical properties (Tensile tests, DMA, Shear Rheology, FTIR, ...)	DEMa
5	5.1	Report on the scientific stay at DEMa-UFSCar	CERMAV
	5.2	Report on the scientific stay at CERMAV	DEMa
x	x.1	Writing of publications	CERMAV/DEMa

Tasks of the project	3	6	9	12	18
Task 1 : Thermomechanical degradation of PP matrix			Deliverables		
Task 2: Chemical modifications of the surface of nanocelluloses			Intern		
Task 3 : Preparation of PP/EVOH/CNC nanocomposites					
Task 4 : Understanding interfaces and structure-properties relationships					
Task 5 : Project management, missions and dissemination of results					
	Mission		Mission		

5. International positioning of the project; current state of international collaboration and its strengths

The recognized scientific competence of the *Centre de Recherches sur les Macromolécules Végétales* ([CERMAV](#) – Grenoble), in particular the surface functionalization of cellulose nanocrystals/nanofibrils, will be used in synergy with the Department of Materials Engineering ([DEMa](#)) of Federal University of São Carlos (UFSCar – São Carlos - Brazil), the pioneer department in the field of materials science and engineering in Latin America, particularly in the fields of processing and characterization of polymer materials and multicomponent polymeric systems.

This project was built as a first collaboration between Dr. João Cosas and Prof. Dr. Lucas Henrique Staffa, former colleagues from the Federal University of São Carlos, both graduated in 2014. [Dr. João Cosas](#) built a strong expertise in morphological and local properties characterization, particularly in the field of multiphase polymer systems, e.g., nanocomposites and rubber blends ([ORCID](#)). He joined CNRS in **October 2023** as a **Chargé de Recherche** and is currently focusing on designing, developing, and characterizing biosourced materials at CERMAV. He is now seeking opportunities to establish a new international collaboration between CERMAV and DEMa-UFSCar. [Prof. Dr. Lucas Henrique Staffa](#) has been an **Assistant Professor at DEMa-UFSCar since July 2022** and conducts research in the fields of interface, compatibilization, degradation and recycling of multicomponent polymeric systems with transversality with interfacial rheology ([ORCID](#)). He has developed expertise in estimating interfacial parameters using rheological method during his visiting scholar period in the *Soft Matter, Rheology and Technology (SMART)* group at Katholieke Universiteit Leuven supervised by Professor emeritus Paula Moldenaers.

This will open a new international collaboration with a project having a **transverse and multidisciplinary character**. The techniques of chemical modification and structural characterization which are developed at CERMAV (surface chemistry of nanocellulose, atomic force microscopy, scanning and transmission electron microscopies) will be perfectly complementary to the skills developed at DEMa (polymer blends, recycling, and composite processing), allowing a fine **understanding of the structure-properties relationships** of these recycled materials. The development of these functional nanofillers and compatibilization strategies using organometallic additives will help to establish the relationship between the structure of cellulose nanocrystals, EVOH and their surface chemistry with the promoted repolymerization of the PP matrix and consequent improvement of mechanical properties of recycled materials.

This project proposal is partially supported by a grant from **The São Paulo Research Foundation (FAPESP)** (process 2023/05519-6), a public taxpayer-funded foundation that has the mission of supporting research in all fields of knowledge within the State of São Paulo, Brazil. The Principal Investigator for this grant is Prof. Dr. Lucas Henrique Staffa. The focus of this project is on the mechanical recycling of multilayer packaging composed of PP and EVOH, utilizing reactive compatibilizers. The aim is to collaborate with CERMAV-CNRS to foster circularity in multicomponent polymeric systems, through the incorporation of biopolymers, seeking to facilitate the anchoring of organometallics and promoting the repolymerization and compatibilization of recycled polymeric materials more efficiently.

6. Funding demand: 3 800 € for the acquisition of consumables (reagents, AFM tips, sample preparation, ...) and access to the characterization platforms (electron microscopies, AFM, NMR, ...). 1 650 € for an internship student at CERMAV for 3 months. 4 550€ for mission-related expenses (plane tickets between France-Brazil, accommodation, workshop organization).

7. References

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4. Dominic, M. *et al. Carbohydr Polym* **230**, (2020).
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- Validation du projet au sein du laboratoire (1 page maximum)



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Grenoble, February 22nd, 2024

OBJET: Support letter for IRB joint project CERMAV-UFSCar

I, the undersigned Dr Laurent HEUX, CNRS Researcher and Director of the CERMAV laboratory, hereby attests that our Institute strongly support the project "Catalytic regeneration and reactive compatibilization of PP/EVOH blends using organometallics anchored by Cellulose Nanocrystals" proposed by Dr Joao Cosas (CERMAV) and Pr. Dr. Lucas Henrique Staffa (UFSCar). This project will be a unique opportunity to initiate a collaboration between the two Institutes that have complementary skills. The researchers involved in this project will be provided with all the facilities available at CERMAV in terms of acces to office, internet network, experimental room and scientific equipment .

Best Regards,

D' Laurent HEUX
Directeur du CERMAV

Sous la tutelle du



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