



# Lyon Polymer Materials Science

Master internships  
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## PFAS-Free Biomaterials for dental applications

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**Laboratory:** LMI

Polytetrafluoroethylene (PTFE) cords and tapes have recently gained attention as alternative gingival retraction materials for optical impression procedures. Their use is primarily justified by their low friction coefficient, high malleability, and satisfactory clinical handling characteristics. Nonetheless, PTFE belongs to the class of per- and polyfluoroalkyl substances (PFAS), which are currently undergoing re-evaluation due to increasing concerns regarding their long-term biocompatibility and environmental persistence. These considerations are of particular relevance in dental applications, given the repeated and intimate contact of PTFE-based materials with gingival tissues, as well as the forthcoming European “universal PFAS” restriction. This project aims to (i) clarify the regulatory and toxicological status of PTFE when used as a gingival retraction device, (ii) compare its biological safety and clinical performance with conventional retraction cords, and (iii) preliminarily identify and evaluate PFAS-free alternatives. In this context, two additional candidate materials, polydimethylsiloxane (PDMS) and polyurethane (PTU), will also be investigated for their suitability as gingival retraction devices in terms of handling properties, biocompatibility and mechanical properties. The expected outcome is to provide evidence-based guidance for potential substitution of PTFE gingival retraction devices with effective and biocompatible PFAS-free solutions, in line with evolving European regulations and public health concerns. This Master internship project is conducted as part of the PhD research program of Corentin Laboisseret, focusing on the development of safe, biocompatible, and regulatory-compliant alternative materials to conventional gingival retraction devices. In this respect, a series of assessments will be carried out, including physicochemical and topographical characterizations. Mechanical properties will be evaluated using conventional normalised testing as well as by means of a masticatory simulator. Finally, the biological behaviour of the selected candidate materials will be assessed in accordance with ISO 10993 standards. We aim to investigate the biocompatibility and *in vitro* performance of PTFE and PFAS-free alternative materials as a prerequisite for any subsequent clinical study.

### **Key words:**

Gingival retraction, PFAS-free biomaterials, Biocompatibility, Medical devices regulation, Mechanical and physicochemical characterization

## Multiscale characterization of polyurethane nanocomposites for hydrogen storage applications.

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Laboratory: IMP

### *Background*

KEMICA COATINGS (Orléans, France) aims to develop a high-performance hydrogen barrier coating formulated from a bio-based, VOC-free polyurethanes, in which innovative lamellar nanofillers such as graphene and boron nitride (BN) will be dispersed. Designed as a multilayer system, this coating seeks to drastically limit hydrogen permeation and protect metallic or composite substrates against hydrogen-induced embrittlement, while ensuring excellent mechanical and chemical durability. Within this project, a certification-ready formulation suitable for industrialization will be delivered. The expected benefits are multiple. From a technical perspective, the combination of graphene, recognized for its near-total gas impermeability, and boron nitride, which is thermally and chemically stable, makes it possible to obtain an effective barrier even under high pressure, with a targeted reduction of more than 90% in hydrogen permeation. From an economic standpoint, this solution aims to extend the service life of hydrogen storage and transport equipment (tanks, pipelines, hoses) while reducing costs associated with leaks and premature failures. The targeted application areas include hydrogen energy (infrastructure, stations, tanks).

### *Objectives of the internship*

Within the frame of this project, an internship of 3 months is proposed at IMP. The role of the intern will be to characterize the aforementioned polyurethane formulations showing the most promising barrier properties through a multiscale approach:

- DSC (differential scanning calorimetry) will be considered to characterize thermal transitions and formulation stability.
- DMA (dynamic mechanical analysis) and mechanical testing will be used to evaluate stiffness, fatigue resistance, and the viscoelastic behavior of the coatings as a function of temperature.
- Solid State NMR will provide insight of the molecular mobility and eventual crosslink density of the formulations at the molecular scale.
- Small and wide angle X-ray scattering will be used to analyze the orientation and crystallinity of graphene and boron nitride sheets, in order to couple these results with the hydrogen permeation properties as well as on the thermomechanical behavior of developed materials.
- If time allows, SEM investigations could assess filler distribution within the matrix, the condition of interfaces between layers, and film morphology.

## Design of centimeter-scale hydrophobicity gradients via sol–gel processing

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### Laboratory : LMI

Interactions between liquid droplets and solid surfaces play a key role in many everyday applications (inkjet printing, self-cleaning surfaces, superhydrophobic textiles, anti-fog glazing...). Recently, the ability to control the positioning and motion of a water droplet along a defined path has further expanded the field of application and is of even greater interest in microfluidics ("lab on a chip") and 3D printing of biological tissues.

A promising strategy for controlling droplet motion relies on anisotropic surfaces exhibiting spatial gradients of surface energy. Such gradients can induce directed droplet displacement without external actuation.

The objective of this Master's project is to develop functional coatings presenting centimeter-scale gradients of chemical functionality and wettability using sol–gel chemistry. The sol–gel process is based on the formation of an inorganic polymer network obtained through hydrolysis and condensation reactions of silicon-based molecular precursors (alkoxysilanes). These reactions progressively transform a solution of molecular precursor into a sol, defined as a colloidal suspension of nanoparticles, and finally into a gel consisting in a three-dimensional inorganic polymer network.

In this project, hydrophobic sol–gel thin films will be deposited and subsequently modified to create controlled gradients of hydrophobicity through localized post-degradation using UV irradiation or air plasma treatment.

### Main objectives

The student will:

- Prepare inorganic polymer sols via hydrolysis–condensation reactions from silicon-based precursors,
- Synthesize hydrophobic coatings using liquid-phase deposition techniques (dip-coating),
- Generate spatial gradients of chemical functionality through controlled UV or plasma post-treatment,

Characterize surface properties using wettability measurements and surface energy calculations, microscopy techniques (optical microscopy, SEM, AFM) and physicochemical analyses (FTIR spectroscopy, etc.).

### Skills and learning outcomes

This project will allow the student to acquire expertise in:

- inorganic polymer chemistry and sol–gel processing,
- structure–property relationships in polymer-derived coatings,
- solid–liquid interfacial interactions (hydrophilicity/hydrophobicity),
- advanced physicochemical surface characterization techniques.

## Development and characterization of chitosan nanoparticles and filaments

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**Laboratories : IMP and LAGEPP**

According to the increasing trend towards the “zero waste”, there is a huge demand of the cosmetic market for solid cosmetics, as well as multifunctional products able to be both make-up and skincare products. Thus, the global face compact market size valued at \$1.3 billion in 2021, is projected to reach \$2.2 billion by 2031, with a Compound Annual Growth Rate of 5.7% (Ref). However, cosmetic brands are currently facing two main problems: (i) talc powder, the main ingredient in their powders, is being phased out, while lawsuits related to the development of cancer have been multiplying for the past ten years and (ii) consumer demand for natural, sustainable, biodegradable and safe materials continues to grow. In this context there is a growing interest in developing environmentally friendly and healthy cosmetic formulations (Ref). Among available bio-material, chitosan, a linear polysaccharide composed of  $\beta$ -(1 $\rightarrow$ 4)-linked D-glucosamine and N-acetyl-D-glucosamine units, has become a highlighted biopolymer. This natural polysaccharide is industrially obtained by N-deacetylation of chitin, which is the second most abundant biopolymer in biomass, mainly present in crustacean and insect exoskeletons. Because of its numerous properties, *i.e.* non-toxic, water-soluble, biodegradable, biocompatible, antimicrobial, antifungal and antioxidant, chitosan has found many applications in cosmetics, biomedical, food additives and water treatment fields (Ref). Furthermore, the various chemical modifications offered by the primary amine group of D-glucosamine units, as well as the hydroxyl groups in the backbone of chitosan may be used for the grafting of anti-aging active substances such as ferulic acid which possesses antioxidant properties.

A thesis project intending to develop new powdered skincare face compacts containing a high level of biopolymers for replacing mineral compounds, has begun since November 2024 in collaboration between IMP and LAGEPP laboratories. Before the powder formulation process and the compaction phase required for the elaboration of the compact, the conception of a smart biopolymer has been considered through two strategies: *i.* covalent grafting of ferulic acid on chitosan, and *ii.* encapsulation of ferulic acid in chitosan microparticles.

The first part of the thesis has focused on the study of the covalent grafting of ferulic acid on chitosan. The best results were obtained through a carbodiimide-mediated coupling reaction (Ref). Nevertheless the grafting rate may be improved by varying some experimental parameters such as amine to carboxylic acid molar ratio, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) and N-hydroxysuccinimide (NHS) amounts, employed as coupling agents, temperature and reaction duration. Then we propose a five months-long internship at M1 level for accompanying the PhD student in the study of the influence of these parameters on the grafting rate of ferulic acid on chitosan.