French Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes one of the PhD subjects proposed by the French Polytech network. The network is composed of 15 engineering schools/universities. The document also provides information about the supervisor. Please contact the PhD supervisor by email for further information regarding your application.

Supervisor information	
Family name	MICHELET
First name	VERONIQUE
Email	veronique.michelet@univ-cotedazur.fr
Web reference	https://icn.univ-cotedazur.fr/axes-de-recherche/aromes-parfums-synthese-et-modelisation/catalysis-methods-for-organic-synthesis-fine-chemistry
Lab name	INSTITUT de CHIMIE de NICE
Lab web site	https://icn.univ-cotedazur.fr/
Polytech name	Cliquez ou appuyez ici pour entrer du texte.
University name	UNIVERSITE COTE D'AZUR
Country	France

PhD information	
Title	**Limonene-based Recyclable, Repairable and Reprocessable Resins**

Main topics regards to CSC list (3 topics at maximum)	Green chemistry / Biomaterials and polymer materials / Sustainable development engineering and lower cost manufacturing
Required skills in science and engineering	Chemistry

Subject description (two pages maximum including biblio)

Limonene-based Recyclable, Repairable and Reprocessable Resins

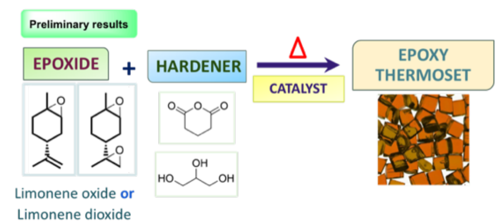
The epoxy resins are the most commonly used resin systems in the composite sector for **structural applications** (sectors such as **construction** and **automotive**) due to important advantages including dimensional stability, chemical resistance and thermo-mechanical performances. The global market for epoxy resins records around 3 million tons in annual sales.[1] Nevertheless, due to their cross-linked architecture, current thermosets cannot be reprocessed, and are very difficult to be repaired and recycled. A**t the end of their use life, thermosets are treated as wastes and incinerated,** increasing significantly the overall material cost and causing grave **environmental concerns**.[2] Another important drawback of epoxy resins is that the majority of the commercial epoxy resins are produced by reacting **bisphenol A** (BPA) with epichlorhydrin (ECH) obtaining the diglycidyl ether of bisphenol A (DGEBA). Besides all the DGEBA performances, increasing environmental concerns are due to the bisphenol A, highly debated molecule owing to ecology and human risks[3] BPA may be released when DGEBA is washed during manufacturing of epoxy resins. It has been estimated that a total of 572 kg/year of non-reacted dissolved BPA could leave the wastewater treatment plant and be disposed of via the sewages in the whole Europe.[4]

The challenge is to synthesize new, greener, epoxy resins with at least equivalent performances as petroleum bisphenol A resins, from bio-based products and presenting the 3R characteristics. With respect to **circular economy and** REACH regulations, we envisage on a first approach the valorization of the **limonene**, a citrus by-product. More than 13.6 million tons of orange peel waste is produced every year, leading to reportedly more than 60 000 tons of *(R)*-(+)-limonene, mainly obtained by extraction.[5-8] The (*R*)-isomer is commonly used in chemical syntheses as a precursor to carvone, chiral carvo-lactone and as a renewable-based solvent.[9]

The monoterpenes are versatile class offering more than 1500 renewable molecules with biological and chemical potential use. This PhD program aims to use this research as a proof of concept on the aptitude of limonene, as monoterpene, to generate thermosets.

We envisage during this PhD program to address the two main challenges and limitations of commercial thermoset resins, which are the toxicity of BPA and the non-reprocessability of such materials: valorization of chiral limonene, by producing original key building blocks, polymerization using bio-based hardeners leading to epoxy thermosets.

There are very few reports on the synthesis of limonene-based epoxy thermosets, and these studies do not consider the potential effect of its chirality.[10] The main studies were devoted to the alternating copolymerization of LO (limonene oxide) with CO_2 to produce biodegradable polycarbonates (PC).[11-13] Coates *et al.*[14] reported a highly selective copolymerization of *trans*-LO with CO_2, using a zinc catalyst. **The literature is very poor on reports regarding the use of LO or LDO in the synthesis of thermosetting resins.**[15-17] The authors studied the curing of LDO and of model reagents with different diamines and found incomplete reactions. In a preliminary study we showed a successful anionic copolymerization of limonene dioxide to produce thermosets (but brittle!) by direct crosslinking with glycerol or glutaric anhydride. DSC analyses confirmed that the polymer was completely cured.[18]



We intend to develop during this PhD program novel polymers via original methodologies. The group of Université Côte d'Azur has gained international notoriety for polymers[19] and catalysis.[20]

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