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Biosourced thermoset polymers: from orange peel to 3D-printing

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PURPOSE OF THE ABSTRACT

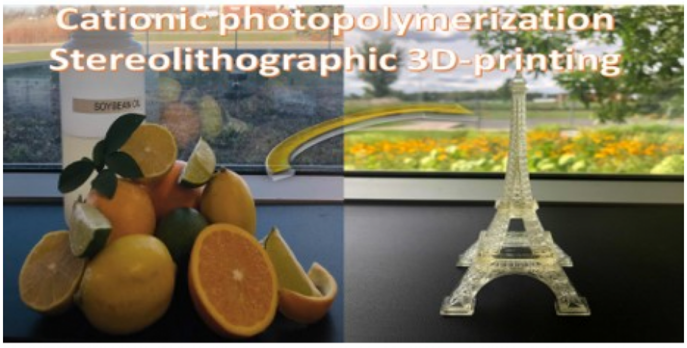
This poster presents the work done separately at the University of Côte d'Azur (Professors Mija and Michelet), and at the University of Sherbrooke (Canada) (Professor Claverie) on the valorization of limonene for the manufacture of biobased thermosetting polymers.

Biobased (+)-limonene is a natural terpene which is extracted from the peels of citrus fruits. Since it is directly valorized from a major food waste and since it can be epoxidized directly with oxygen (ideal atom economy), (+)-limonene fulfills many of the criteria that are desirable for the preparation of green materials. Our research groups have explored various routes to transform limonene dioxide (LDO, the bis epoxide of limonene) into epoxy thermosetting polymers.

LDO is a mixture of four isomers, two of which (trans-LDO) are actually difunctional while the others (cis-LDO) have one epoxide group which is significantly less reactive, as revealed by Fourier transformed infrared spectroscopic analysis of formulations cross-linked with polyethylene imine. Thus, LDO was initially found by one of us to be hardly polymerizable. To investigate the racemic LDO's potential to generate thermosets, the living anionic copolymerization strategy was applied, by reacting it with different nucleophilic molecules as glycerol (Gly), 2,2-dimethylglutaric anhydride (DGA), maleic anhydride (MA), phthalic anhydride (PhtA), itaconic anhydride (IA) and succinic anhydride (SA). Our studies showed that the best hardeners for the racemic LDO are the glutaric and dimethylglutaric anhydrides leading to thermosets with high Tg values (?98 °C) and good mechanical properties: ? = 27 MPa; ? = 3.5%; E = 1150 MPa; E' = 1650 MPa, Shore D = 78. Furthermore, the LDO/AG thermoset was found to disaggregate in some solvents which demonstrates the reversibility, and thus, the recycling potential of this material. We have therefore succeeded the unprecedented preparation of 100% bio-based and reprocessable thermosets, starting from a racemic LDO and biobased glutaric anhydride.

Another strategy was explored by one of us, who devised a scheme to photochemically polymerize LDO. In particular, LDO and biosourced epoxidized vegetable oils were conveniently copolymerized. These formulations led to the fabrication of the first biosourced stereolithographic formulation for 3D-printers.

FIGURES



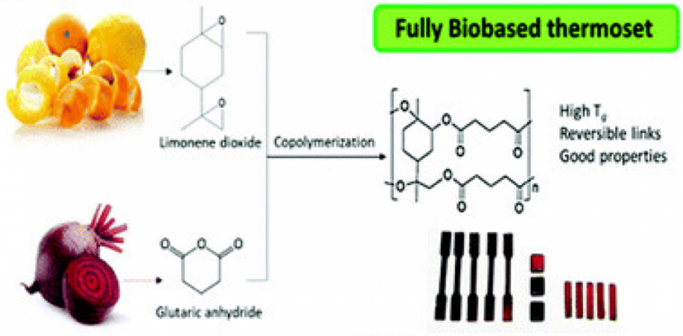


FIGURE 1
Photocationic 3D-printing of epoxy thermosets

3D printing with orange peels and linseed oil.

FIGURE 2
Biobased epoxy thermosets

Epoxy thermosets from LDO and glutaric acid

KEYWORDS
limonène | polymère | époxy | thermodurcissable

BIBLIOGRAPHY