

Make it greener: Exploring novel biobased materials in photopolymerization processes

*Original*

Make it greener: Exploring novel biobased materials in photopolymerization processes / Noe', Camilla. - (2022 May 03), pp. 1-147.

*Availability:*

This version is available at: 11583/2962960 since: 2022-05-09T10:16:35Z

*Publisher:*

Politecnico di Torino

*Published*

DOI:

*Terms of use:*

Altro tipo di accesso

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# Summary

In a continuously evolving world, the invention of plastics can be considered one of the greatest revolutions. From their first discovery, it was clear that polymers can replace different natural materials like wood, stones, and metals since they are lightweight, strong, and flexible and can be shaped in many ways. Over time, polymers have progressively changed how we live, playing, nowadays, a fundamental role in our life. For those reasons, plastic production has exponentially increased over the years and it is expected to overcome 400 million metric tons in 2022. Unfortunately, their production is causing increasing environmental concern due to the high greenhouse emission and toxic products released into the water, soil, and air giving rise to potential threats to human health. Therefore, many scientists are currently working to find greener and more sustainable replacements for fossil-fuel-based polymers. Among the available substituted, biobased polymers stand out since they are based on renewable resources and their production can have lower CO<sub>2</sub> impact. Currently, the biobased market is dominated by thermoplastic while there remains a huge need for the development of green thermosets.

In this context, this thesis presents the development of new biobased thermosetting polymers by means of the UV-curing process.

Chapter 1 presents a brief introduction to biobased polymers and the most common photopolymerization techniques, while the experimental part, which represents the main body of the thesis, is divided into three major topics: UV-curable starch-based hydrogels and organo/hydrogels (Chapter 2), Biobased UV-curable coatings (Chapter 3) and Biobased UV-curable composites (Chapter 3).

The first experimental work focuses on the modification of maize starch with methacrylic groups to make it light processable. The obtained methacrylated starch (MA-Starch) was initially used to produce photocrosslinkable hydrogels that can be 3D-printed *via* a digital light processing (DLP) printer and have good cell cytocompatibility, therefore they possess promising applicability in tissue engineering and as cell carriers (Chapter 2.1). Subsequently, the MA-Starch was mixed with acrylated cyclodextrin to produce a new class of UV-curable bio-sorbents for the removal of methylene blue from wastewater (Chapter 2.2).

The second experimental work is based on the development of UV-curable biobased coatings. This work is divided into two sections; the first one is focused on the investigation of cationically photocurable epoxy-based coatings, while the second one is based on radical photocurable methacrylate-based coatings.

In the initial part of the chapter, the reactivity and the mechanical properties of three different biobased epoxy monomers deriving from phloroglucinol, vanillin, and castor oil are investigated (3.1.2). Then the possibility to successfully UV-cure three different epoxy cardanols derivatives is presented. The mechanical properties of the obtained thermosets were analyzed considering the chemical structures of the monomer (3.1.3). Subsequently, 12 epoxidized vegetable oils (EVOs), derived from different resources and differing according to their glycidyl index, were selected and crosslinked. The scope of this investigation was to demonstrate the existence of a correlation between the number of epoxy rings and the final thermo-mechanical properties of the thermosets (3.1.4). Further developments of this study are then presented. Moreover, the influence of the starting glycidyl

index on the metal adhesion and corrosion protection effectiveness of three EVO- based coatings is analyzed in section 3.1.5.

The second part of Chapter 3 is dedicated to the study of UV-curable MA-starch films. The obtained films possess a high adhesion to glass and are biodegradable. Their biodegradability was assessed by studying the enzymatic degradation of the coatings by  $\alpha$ -amylase from *Bacillus licheniformis* (3.2.1).

Chapter 4 presents the last experimental work that was conducted, which was based on the study of two different classes of fully biobased composites. The first class consists of the DLP 3D-printing of acrylated soybean oil composites, reinforced with a lignocellulose waste derived from the macadamia nut industry. The cytotoxicity, adhesion and cell proliferation with human fibroblast cells of the 3D-printed objects were investigated to demonstrate their suitability as scaffolds for bioengineering purposes (4.2). The second part of Chapter 4 instead concerns the radical induced cationic frontal photopolymerization (RICFP) of diglycidylether of vanillyl alcohol, reinforced with two types of fabric mats: unidirectional non-woven cellulose fibers and flax woven fibers. The RICFP reaction considerably reduced the curing time and thus improved the efficiency of composite fabrication. Moreover, the mechanical properties of these fully bio-based composites were compared with the one obtained by other epoxy composites that were RICFP cured with a petroleum-based resin and reinforced with the same biobased fabrics (4.3).

Altogether the results presented in this manuscript show new possible strategies to produce and expand the biobased thermosetting polymer field.