Towards a more sustainable world: UV-curing & 3D printing of bio-based monomers

Synthesis and characterization of bio-derived monomers for cationic and radical UV-curing

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Abstract

Sustainable development is one of the main challenges of our time, underlined by the United Nations which embraced the 2030 Agenda for Sustainable Development by adopting 17 Sustainable Development Goals. Economic, social, environmental, and governance dimensions are crucial factors to international agreements to face these challenges. The limitation of climate change needs to handle multiple challenges such the use of fossil-based resources, the reduction of greenhouse emission, and the minimization of the carbon foot print. To meet these challenges, important innovations have to be done in material science to create and develop new materials aiming to a circular economy. Bio-based polymers can represent a promising avenue towards a more sustainable future, being the natural substitute of fossil-based plastic. Indeed, speaking of plastics, the impressive achievable properties make these materials exploitable in a wide spread of applications making the global market one of the most profiting over the world. However, the plastic production is causing, apart from the depletion of fossil resources, an increasing environmental concern due to the high greenhouse emissions and toxic products released into the environment giving rise to potential threats to human health and climate change. Thus, the industrial processes become crucial to reach sustainability. Progress has to be reached in all the different steps of the material production processed aiming for a sustainable future.

In this view, this thesis aims to show possible innovations in the world of bio-based polymers and UV-curing. The Introduction to the world of green materials and sustainability (**Chapter 1**) points out the potential benefits in the exploitation of natural resources to create new materials. Lignocellulosic biomass is one of the main platforms that can generate a wide palette of several monomers suitable for material production. Industrial and food side streams are under deep investigation,

being valuable source of monomers which, after suitable treatment, can be reused to produce further value chemicals. Moreover, environmentally green and efficient processes are required to make a further step toward a more sustainable development. The synergy between natural monomer and UV-curing (**Chapter 2**) can move toward this scope showing interesting benefits in term of energy, cost and time production.

After this brief introduction about general principles and fundamentals, the first part of the scientific contribution is devoted to UV-cationic curing of bio-based monomers. The multiple works presented in **Chapter 3** aim to highlight the great potential of different classes of biopolymer in distinct areas, from coatings to 3D printing. The first part is focused on furan-based monomers and three possible uses of this class of monomers. Specifically, hybrid coatings were accomplished to illustrate the benefits of a dual network, then an innovative cross-linking of monofunctional furan-based monomer was investigated by two-step curing approach. Lastly, a breakthrough in 3D printing is presented, where bio-based epoxy resins are successfully 3D printed, exploiting the Hot-lithography technology.

Moreover, the second part of the chapter is dedicated to different bio-based epoxy-functional monomers employed in different applications covering adhesives, coatings, and 3D printings. The ferulic-based epoxy shows remarkable adhesive properties and a versatility in the possible curing mechanisms which can be used to achieve the formation of green thermosets. This open the possibility to obtain a wide spectrum of different thermo-chemical properties. Then, the great potential of isosorbide-based epoxy in coating application is presented, highlighting the possible reinforcement given by the addition of bio-derived macadamia fillers. Lastly, the 3D printing field is once more area of focus exploiting this time epoxy vegetable oils (EVOs). The innovation using Hot-lithography is presented in the successfully 3D printing of fully bio-based composites generating by bio-based polymer matrix and bio-derived filler based on wall-nut shell powders.

After this excursus on cationic UV-curing, the focus changes to radical mechanism with a particular attention to thiol-ene chemistry (**Chapter 4**). In this case several works present the innovation in coating applications using ferulic acid, isosorbide and furan-based monomers as platform to synthetize several allyl derivatives. Remarkably, a deep investigation of the influence of the chemical structure is carried out to find the main important features responsible for the thermo-mechanical properties of the resulted thiol-ene networks. The new horizons

open by 3D printing are investigated adopting levoglucosenone-based monomers to develop bio-based photocurable green resins. Lastly, a different application of the thiol-ene chemistry is shown, the surface functionalization of a green coating is investigated highlighting a further use of UV-light in the field of post-functionalization.

In general, the presented works aim to show the efficacy in the use of bio-based polymers in different applications spacing from coatings to 3D printing. Furthermore, the different syntheses performed were evaluated aiming to understand possible benefit of using green reagents or criticism caused by less green reagents. Chemical and kinetic aspects of the UV-curing were carefully analyzed aiming to better understand the process. A thermo-mechanical characterization of the different thermosets was performed all through the studies aiming to increase the knowledge of structure-properties relationship and to verify the possibility to use this bio-based monomer instead of fossil-based ones. Overall, these works present significant steps toward the realization of the SDGs contributing in a more sustainable, and circular economy.