Doctoral Dissertation
Doctoral Program in Material Science and Technology (37th Cycle)

Exploitation of Polyphenols from Industrial Food By-Products for the Design of New Materials

Rossella Sesia
* * * * * *

Supervisors
Prof. Silvia Spriano,Supervisor
Prof. Marco Sangermano, Co-Supervisor
Prof. Sara Ferraris, Co-Supervisor

Politecnico di Torino
2025

Summary

As underlined in the 2030 Agenda for Sustainable Development, the global adoption of unsustainable development practices needs the establishment of greener and more sustainable alternative approaches. The concept of green chemistry aligns with the Sustainable Development Goals by promoting environmentally friendly practices, including CO_2 reduction and circular economy principles. The development of bio-based polymers exemplifies these goals, exploiting renewable raw materials, like natural resources, and represents an alternative to fossil-derived polymers. Polyphenols can be extract from plant sources and agro-food waste and include different types of compounds, like phenolic acids and tannins. In detail, tannins exhibit wide-ranging industrial, environmental and biomedical applications due to their interesting characteristics, including antioxidant, antimicrobial, and corrosion-inhibiting properties.

This Doctoral research, supported by the European PON REACT-EU program, contributes to the SDGs through the development of innovative natural polyphenols-based materials. The project is in collaboration with Centro Ricerche per la Chimica Fine (CRCF S.r.l.) and bridges academia and industry to encourage sustainable technological advancements, addressing environmental challenges and promoting a circular economy. Exploiting greener experimental approaches, like eco-friendly synthesis and photopolymerization, the study demonstrates the versatility of natural polyphenols, in particular tannins, and their phenolic groups in multiple applications, including coatings, 3D printing, composites manufacturing and water remediation.

Innovative industrial applications of natural tannins and gallic acid were investigated. The reaction of (meth)acrylation was performed *via* innovative and eco-friendly processes, which proved effective to achieve photopolymerizable monomers. Microwave-assisted methacrylation reaction was particularly advantageous compared to conventional thermal method, as it offered faster reaction time and higher product yields and substitution degrees, which were related to viscosity and photoreactivity of the achieved polyphenols-based UV-curable monomers.

Microwave-assisted functionalized polyphenols were investigated for two different applications, demonstrating the feasibility of greener materials based on natural polyphenols. Methacrylated tannic acid was successfully used as UV-curable coating. This green polyphenol-based coating demonstrated remarkable thermal and surface properties and corrosion protection performance on the steel substrate, which was previously pre-treated *via* the eco-friendly plasma technique. Additionally, methacrylated gallic acid was proposed for additive manufacturing. In particular, it exhibited its potential as a bio-based resin alternative for the Digital Light Processing 3D printing.

Unmodified tannins were explored as potentially anticorrosive primers and adhesion promoters on low carbon steel substrate.

Different types of natural tannins and several pre-treatments of steel surface and deposition methods were investigated to achieve a green tannin-based anticorrosive primer layer on low carbon steel. However, the corrosion resistance measurements showed the necessity of future further optimizations.

The incorporation of tannic acid into the UV-curable epoxidized soybean oil was studied as adhesion promoter. The addition of tannic acid proved to accelerate the photopolymerization kinetic by means of activated monomer mechanism and remarkably enhance the adhesion of the coating system.

The natural polyphenolic groups were exploited to achieve novel bio-based epoxy resins. The two-steps method involving microwave-assisted O-allylation and epoxidation reactions implied the use of several chemicals and the production of waste and led to low product yields, in contrast to the direct glycidylation reaction with epichlorohydrin. The glycidylated polyphenols-based monomers proved suitable for advance reprocessable thermosets produced *via* thermal curing. These materials, combined with carbon nanotubes, demonstrated electrical conductivity, Joule heating, and piezoresistive properties, opening pathways for smart bio-based composite applications.

Finally, the use of tannins in water treatment applications was studied. The introduction of tannic acid into UV-cured chitosan-based hydrogels improved copper ions adsorption. Moreover, the interaction between tannin and chitosan functional groups enhanced the mechanical performance, and thus the recycling capacity, contributing to cost-effective and sustainable water management.

In conclusion, this Ph.D. research aims to demonstrate the versatility of natural polyphenols in developing novel eco-friendly materials through green methods. New strategies to produce natural polyphenols-based materials for several applications are presented to address global challenges in sustainability and environmental protection.