Abstract

In modern society plastic pollution represents a major global challenge; in fact, despite the high production quantities, only a fraction of plastic is recycled and reutilized. Polymers can be classified into thermoplastics and thermosets. While thermoplastic polymers can be normally recycled to some extent, with only a small downgrade of their properties, thermoset polymers, commonly used in high technology sectors, like aeronautical, wind turbines and automotive, are inherently difficult to recycle due to their permanently cross-linked covalent networks. As a result, thermosets are typically disposed of by incineration, leading to loss of valuable materials. Additionally, thermoset polymers are conventionally made of petrol-derived chemicals, such as bisphenol A and epichlorohydrin, which raise significant environmental and health concerns. To address these challenges, increasing efforts have focused on the development of bio-based thermosets and more sustainable processing technologies. However, bio-based alternatives still face limitations related to variability, performance, and scalability. At the same time, additive manufacturing technologies, such as 3D printing, offer opportunities to reduce material waste and energy consumption. Among these, Liquid Deposition Modeling (LDM) is particularly suitable for processing highly filled thermoset formulations. The environmental performance of these materials and processes can be quantitatively assessed through Life Cycle Assessment (LCA).

In this scenario, this thesis aims to develop bio-based epoxy thermosets with enhanced sustainability, combining reprocessability and 3D printability.

Firstly, various bio-based formulations based on epoxidized cardanol and amine-containing cross-linkers were developed. Natural fillers (i.e., cellulose and clay) were incorporated to tailor mechanical and rheological properties, enabling successful processing by LDM 3D printing. Subsequently, to fabricate reprocessable epoxy thermosets, covalent adaptable networks (CANs), specifically vitrimers, were designed. Epoxidized cardanol-based vitrimers were developed in combination with bio-based cross-linkers (i.e., itaconic acid and cystamine). These materials exhibited dynamic bond exchange behavior, enabling mechanical reprocessing while maintaining thermoset-like properties. Also in this case, cellulose fillers imparted the proper rheological behavior for LDM, making selected formulations suitable for 3D printing. Eventually, LCA was employed to evaluate the environmental performance of the developed materials and processes. The results demonstrate the potential of combining bio-based feedstocks, vitrimer chemistry, and additive manufacturing to reduce the environmental impact of thermoset polymers, providing a promising route toward more sustainable materials.