Development and fabrication of self-healing hydrogels via vat photopolymerization 3D printing technology

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There is a growing attention in the scientific community towards the successful modeling and shaping of functional three-dimensional (3D) hydrogels, which could significantly and positively impact future developments in the biomedical field, but not only. Their main potential application would be as artificial substitutes for human tissues, but they must be able to replicate the natural functionalities. The two most peculiar characteristics of living tissues are the sophisticated architectures, which could be reproduced by 3D printed structures, and the ability to restore their properties after a damage, called self-healing. This property could push 3D printed hydrogels beyond their structural role, extending their lifetime performance limited by irreversible failures and expanding their application to many different fields, from soft robotics and sensors to energy harvesting and storage. Up to now, many studies in the literature have been focused on the development of self-repairing hydrogels that could be 3D printed with extrusion-based printing, which are limited in the design complexity achievable. Vat photopolymerization (VP) 3D printing can guarantee superior resolution and accuracy with a good trade off with the object size. However, there seems to be an incompatibility between the requirements for successful VP printing and efficient self-healing in the printed hydrogels. In this context, the experimental studies reported in this thesis are aimed to the development of suitable and easily adaptable approaches to combine VP printability and healability based on various different mechanisms into self-repairing hydrogels with complex three-dimensional architecture.

After a broad and comprehensive overview on self-healing fundamentals and mechanisms description and a general discussion on additive manufacturing with a detailed investigation on vat photopolymerization, focused on principles, technologies, reactions and materials involved, the current state-of-the-art of the field of self-healing vat VP 3D-printed systems, including both dry systems and hydrogels, is reviewed. The experimental section is preceded by an outline of the specific goals pursued in the following studies based on what was missing in the field at the start of the investigation and a commentary on the major critical aspects of the research to be faced (chapter 4).

In the first research presented we aimed for an autonomous and rapid restoration based on dispersive forces, occurring at room temperature and without any external trigger to avoid water evaporation. The system was designed as a semi-interpenetrated network by including poly (vinyl alcohol) (PVA), exploited as a healing agent to provide repairability since it can establish extensive hydrogen bonding, within an independent covalent network fabricated during the printing process. The large volume of water embedded favors PVA chain mobility and diffusion across the rejoined interface to promote interactions beyond the surface. In our second study we evaluated cooling below room temperature as trigger for self-healing and favor water retention, which is an inverse strategy with respect to the most common and easier approach to heat up the system to promote diffusion of chains across a fracture interface. Thermoreversible Pluronic block copolymer was selected as healing agent since it shows an inverse gelation behavior and forms micelles, capable of entangling and forming

electrostatic interactions, that are trapped within a covalent network bearing pendant PEG chains acting as plasticizers with an influence on micelle aggregation. In the last experimental work reported, light, already used as polymerization stimulus during printing, was also used as a trigger for self-healing by exploiting a customized dye as healing agent embedded within the network. The dye goes from an auxiliary role of light confinement for resolution enhancement to being a major and active element responsible for restoration by acting as photoactivated switch capable of establishing dynamic boronate ester bonds with the covalent network. Light-mediated activation of labile covalent chemistries can enable controlled and localized repair of complex features or fine elements even in areas not easily accessible.

These works, achieved mainly by using commercially available compounds or molecules synthesized with simple chemistry and a commercial Digital Light Processing (DLP) printer, want to be proof of concepts taking the best of both self-healing and additive manufacturing worlds to open new possible paths.