SELF-HEALING HYDROGELS 3D-PRINTED VIA VAT PHOTOPOLYMERIZATION

Matteo Caprioli[a,b], Ignazio Roppolo[a], Candido Fabrizio Pirri[a], and Shlomo Magdassi[b]

[a] Department of Applied Science and Technology, Politecnico di Torino,
10129 Turin, Italy
[b] Casali Center for Applied Chemistry, Institute of Chemistry,
The Hebrew University of Jerusalem, 9090145 Jerusalem, Israel

3D-printed soft materials, such as hydrogels, are limited in their lifetime by irreversible failures. Intrinsic self-healing (SH) ability could push the hydrogels beyond their structural applications because they would autonomously repair minor damages due to embedded functional groups interacting across the severed interface. The processing of self-healing hydrogels in complex 3D shapes is challenging unless it is performed through additive manufacturing (AM) fabrication methods. Extrusion-based 3D printing technologies are the most used but are limited by poor resolution, constraint design, and the need for supports. On the contrary, vat photopolymerization (VP) allows precise fabrication of unsupported 3D complex structures. Interpenetrated network (IPN) hydrogels, combining non-reversible bonds with reversible interactions, enable combining VP printability and SH, apparently incompatible.

In this work, we successfully fabricated 3D printed hydrogels with complex architectures and self-healing ability at room temperature, without any external stimuli. This was achieved using a waterborne system based on commercial materials processed using a commercial Digital Light Processing (DLP) printer, combining a covalent network made of photocurable materials, acrylic acid, poly (ethylene glycol) diacrylate, and a water-soluble photoinitiator, with a physical network of poly (vinyl alcohol), which is able to effectively interact via strong hydrogen bonding. Complex objects were printed and could withstand bending and stretching deformation after restoration without failing. The SH properties were characterized with dumbbell-shaped samples, which showed a 72% recovery of their initial tensile strength after 12 hours of healing. This study offers a versatile approach to develop self-repairing hydrogels with complex 3D architecture via vat photopolymerization for applications in diverse fields, ranging from biomedicine to soft robotics.