DLP 3D-printed self-healing hydrogels

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Self-healing (SH) hydrogels are smart soft materials able to autonomously recover their properties after mechanical damage without requiring the presence of an adhesive. Those materials are of increasing importance especially in scaffolds, actuators and sensors [1].

Up to now, the processing of these materials through stereolithographic additive manufacturing technologies (such as Digital Light Processing - DLP) has been challenging because of their opposite requirements in terms of cross-linking density [2]. It would be of great impact to build complex 3D structures with SH hydrogels for their application in biology and underwater environments. In this work, we overcame the incompatibility between 3D printing and self-repairing properties by using an interpenetrated double network, made of chemically cross-linked Acrylic Acid (AAc) and an electrostatically cross-linked Polyvinyl Alcohol (PVA). We propose the use of PVA as mending agent, that provides self-healing behavior thanks to its strong hydrogen bonding [3]. A waterborne formulation, containing a PVA solution, AAc, and a water-soluble photoinitiator, was used to print complex soft samples using a commercial DLP system. Healed samples showed a 72% recovery in mechanical strength, which increased to 91% with the addition of Polyethylene Glycol (PEG) in the formulation. The proposed solution opens the way for new relevant applications of 3D printing such as mendable soft robotics.

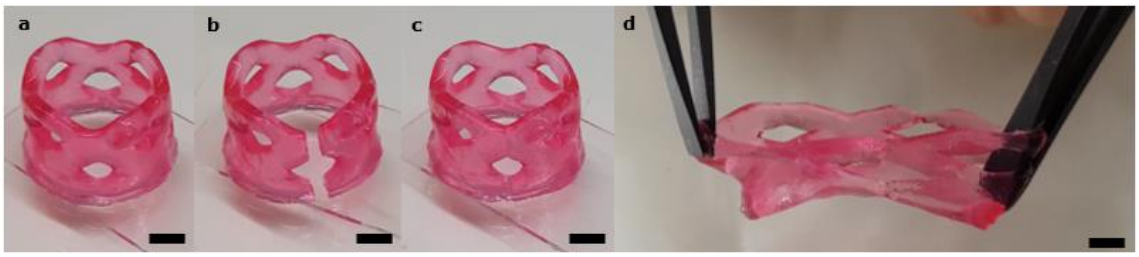

Figure 1: Cylindrical sample (a) as printed (b) cut (c) rejoined (d) stretched after 8 h healing (reference bar 4 mm).

[1] L. Shi, P. Ding, Y. Wang, Y. Zhang, D. Ossipov, and J. Hilborn, *Macromol. Rapid Commun.* **40** (2019) art. no. 1800837.
[2] D.L. Taylor and M. in het Panhuis, *Adv. Mater.* **28** (2016) 9060-9093.
[3] H. Zhang, H. Xia, and Y. Zhao, *ACS Macro Lett.* **1** (2012) 1233-1236.