3D PRINTING OF MOLECULARLY IMPRINTED POLYMERS BY DIGITAL LIGHT PROCESSING FOR ANTIBIOTICS RECOVERY

E. Camilli[a,b], *W. Tang*[d], *I. Roppolo*[a], *F. Frascella*[a], *V. Bertana*[b], *M. Cocuzza*[a,b,c], *T. Minami*[d], *S L. Marasso*[b,c]

[a] Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy

[b] Chilab-Materials and Microsystems Laboratory, Department of Applied Science and Technology (DISAT), Politecnico Di Torino, Via Lungo Piazza d'Armi 6, 10034 Chivasso (Turin), Italy

[c] CNR-IMEM, Parco Area delle Scienze, 37a, 43124, Parma, Italy

[d] Institute of Industrial Science, The University of Tokyo, 4–6-1 Komaba, Meguro-ku, Tokyo 153–8505, Japan

e-mail: elena.camilli@polito.it

Molecularly Imprinted Polymers (MIPs) as artificial receptors have received considerable scientific attention in the past few decades, as material for biomimetic molecular recognition [1]. The preparation of an imprinted polymer involves the complexation, through covalent or non-covalent interactions, between a template molecule and a functional monomer, followed by polymerization in the presence of an excess of a crosslinking agent. The removal of the template from the resulting matrix leaves behind imprinted cavities, complementary at the atomic scale to the template molecules, thanks to the binding sites exhibited by the functional monomer. MIPs are nowadays employed in a large number of applications and fabricated in a variety of techniques, including photopolymerization methods [2], even though fabrication through additive manufacturing (AM) appears mostly as an unexplored field. The challenge of this work is in the employment of AM technology to realize 3D-printed MIP-based objects. A new composite photocurable resin was developed to be suitable for a Digital Light Processing (DLP) printer, and optimized in order to reach reproducibility. The resin includes Oxytetracycline (OTC, a broad-spectrum antibiotic) as the template molecule, methacrylic acid (MAA) as the functional monomer, Dipropylene Glycol Diacrylate (DPGDA) as the photopolymerizable crosslinker and Dimethyl sulfoxide (DMSO) as the solvent. The interaction mechanism between the carboxylic group of MAA and the hydroxyl and amide groups of OTC was computationally investigated through density functional theory (DFT) calculations [3], including the presence of DMSO.

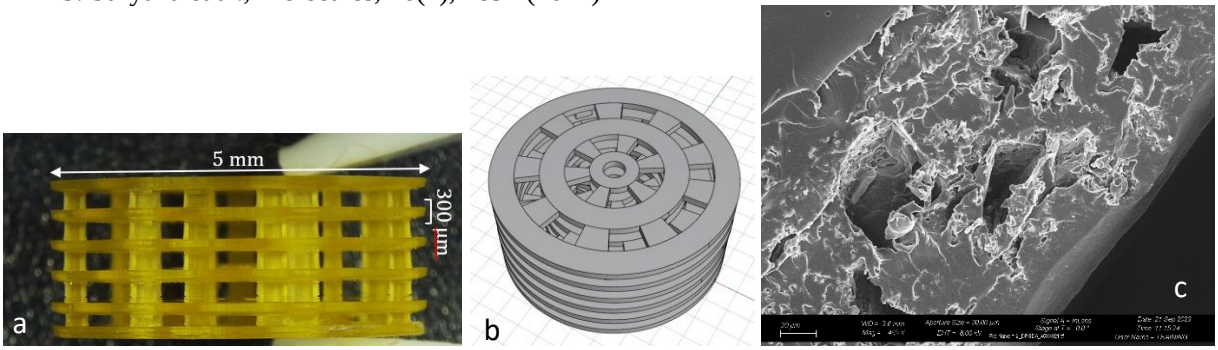
Different geometries were printed and tested, starting from multi-material disks consisting of a MIP 50 µm thick layer on a 500 µm thick support base of DPGDA. The thickness of the MIP layer was minimized to mimic a functionalization layer on a surface. Then, complex 3D filters were printed, entirely made of MIP resin (Figures (a) and (b)). Lastly, some porous samples were printed, thanks to the addition of salt in the resin, in order to increase the surface area (Figure (c)). The samples were tested for OTC recovery from aqueous media, and the target adsorption was characterized by UV-Vis spectrophotometry.

In this work, DLP was employed to fabricate microstructured samples suited to characterize the material and investigate its capability in target recovery. Nonetheless, the described approach may be applied to develop a resin printable with a higher resolution technique, namely Two-Photon Polymerization, to obtain the patterning of MIPs at the nanoscale and the integration of MIPs in micro and nanosystems.

[1] J. J. Belbruno, Chemical Reviews, 119(1), 94–119 (2019)

[2] E. Paruli et al., ACS Applied Polymer Materials, 3(10), 4769–4790 (2021)

[3] S. Suryana et al., Molecules, 26(7), 1891 (2021)



Figures: (a) Side view picture of the printed MIP filter, and (b) the perspective view of the CAD drawing. (c) SAM image of the cross-section of a porous MIP sample.