

# BOOK OF ABSTRACTS

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Light mediated AM / Vat photopolymerization, polyimide, latex

# FOCUSING A SUSTAINABILITY LENS ON ADDITIVE MANUFACTURING: ASKING MORE FROM SCIENCE AND ENGINEERING

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This lecture begins with our motivation for sustainability and polymer circularity, suggesting the necessity for monomaterialization and dematerialization as pathways to achieve more facile recycling processes and reduced polymer consumption. Additive manufacturing (AM) allows for unprecedented three-dimensional form factors with micron-scale geometric complexity to reduce polymer consumption with enhanced mechanical performance. Our research has focused on the printing of high-performance engineering polymers whose thermal, rheological, and chemical characteristics generally complicate legacy processing modalities; however, 3D printing micron-scale organogels allows polymerization in the printed structure with process intensification. Polyimides offer exceptional thermal, chemical, flame, and radiation resistance for many emerging transportation, electronic, and aerospace applications. Thus, recent efforts involve the vat photopolymerization (VPP) of aqueous polyimide latexes and complete removal of organic solvents. (Fig. 1) Printed aromatic polyimides enables conversion to carbonaceous objects from water upon pyrolysis as confirmed with various measurements [1]. The lecture will conclude with hot lithographic printing of unsaturated polyesters to impose a lens of sustainability.

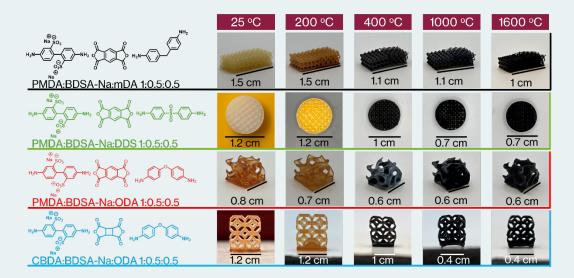


Fig. 1: Vat Photopolymerization of Diverse Polyimide Latexes with Subsequent Carbonization

(1) Weyhrich, C. W.; Nayyar, G.; Stovall, B. J.; Long, T. E. 3D printing carbon from aqueous all aromatic polyimides. Carbon 2024, 230. DOI: 10.1016/j.carbon.2024.119682.

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4 YRS -PL

Extrusion based AM /

Gallic acid, Alkaline oxidation, Gelatin

## GALLIC ACID AS A GREEN CROSSLINKER FOR GELATIN 3D PRINTED SCAFFOLDS

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Many crosslinkers, like glutaraldehyde or carbodiimide, have been explored for 3D printable inks. These crosslinkers present difficulties in scaling up because of the complex protocols or toxicity issues that limit cell viability. Gallic acid, a natural phenolic compound, has been found to crosslink proteins at basic pH, inducing protein-polyphenol conjugates and, thus, stabilizing proteins. In this study, a 15 % (w/v) gelatin solution with 1.5 % (w/v) gallic acid was prepared at pH 10 and printed using an extrusion-based 3D printer. The ink exhibited solid-like behavior and self-supporting ability, suitable for 3D printing. The shear-thinning properties enabled extrusion at 28 °C, with a printing platform temperature of 15 °C. The 3D printed scaffolds replicated the designed geometry with precision and had high shape fidelity. Crosslinking was initiated by exposure of scaffolds to oxygen during the drying process and was effectively monitored through colorimetric analysis and FTIR spectroscopy. Amide I/II ratio confirmed that new interactions between the protein and the gallic acid occurred. The scaffolds were treated with NaOH, HCl or PBS to ensure cell growth. NaOH treatment yielded the best results, achieving the highest cell confluence in direct and indirect cytotoxicity tests. In particular, aligned and elongated human fibroblasts were observed around the pores of the scaffolds. These results demonstrate the feasibility of using gallic acid to crosslink gelatin to develop cytocompatible scaffolds with potential applications in tissue engineering.

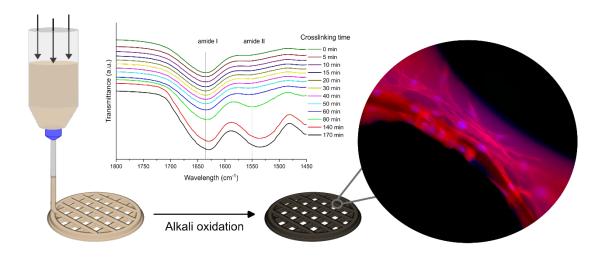


Figure: Crosslinking monitoring by FTIR and cell spreading in the 3D printed scaffold.

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Emerging AM technologies / Soft material, Fluorinated polymer, Microfluidic chip

# 3D PRINTED ELASTIC FLUOROPOLYMER WITH HIGH STRETCHABILITY AND ENHANCED CHEMI-CAL RESISTANCE FOR MICROFLUIDIC APPLICATIONS

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Elastomeric materials, such as polydimethylsiloxane (PDMS), are essential for the fabrication of microfluidic systems, but suffer from poor chemical resistance and leaching in organic solvents like acetone, dichlormethane, and tetrahydrofuran(THF)[1] limiting their use in chemistry-on-chip applications. Therefore, fluorinated elastomer, which possess a higher chemical resistance[2], would be ideal materials utilized in such applications with aggressive solvents. However, shaping fluorinated elastomers on microscale and their embedding by covalent bond onto microfluidic chips remains challenging. Here, our research group presented the first successful use of a custom-synthesized fluorinated resin for fabrication of fluorinated elastomeric membranes for microfluidic applications, which can be structured using a commercial digital light processing (DLP) 3D-printer[3]. The printed structure show exceptional stretchability (523%) and retains its elastic properties even after immersing in THF for 24 hours[3]. The material's high chemical resistance enables the fabrication of a wide range of microfluidic components, including pneumatic valves and peristaltic pumps, while maintaining complex designs with hard and soft segments combined via multi-material printing strategies. This work advances the potential of functional materials for chemistry-on-chip applications, offering new possibilities for emerging technologies through additive manufacturing.

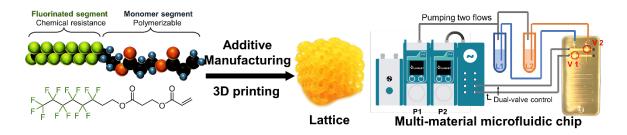


Figure: Chemical structure of the proprietary fluorinated resin. The resin enables additive manufacturing of elastic Kelvin lattices and multi-material microfluidic through additive manufacturing utilizing the fluorinated elastomer as membranes in quake valves.

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stimuli-responsive materials, functional polymers, sustainable polymers

## NEW PROGRAMMABLE POLYMERS FOR LIGHT-BASED 4D PRINTING

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#### Abstract:

Light-based four-dimensional (4D) printing has emerged as transformative strategy to fabricate intricate 3D architectures that change shape or other properties over time in response to external stimuli. This is typically achieved by 3D printing stimuli-responsive polymers such as hydrogels, liquid crystal elastomers, and shape memory polymers. However, other promising responsive polymers remain unexplored for this strategy, including the class of self-immolative polymers (SIPs).

SIPs are programmed to disassemble spontaneously in response to an external stimulus. This feature has been exploited in different applications ranging from molecular imaging to drug delivery and recyclable materials. Nevertheless, their broader application has been constrained by synthetic challenges and the limited options for bulk materials fabrication [1].

Herein, we present the successful integration of SIPs into light-based 4D printing. In detail, we synthesize a small library of photopolymerizable SIPs and employ digital light processing to fabricate complex, high-resolution 4D structures on the centimeter scale. Upon exposure to a chemical trigger, the SIP depolymerizes within the printed objects, resulting in significant changes in mass, volume, mechanical stiffness, and optical transparency. Subsequently, in a "living" 4D printing approach [2], these changes are partially reversed by repolymerization of the SIP. This proof-of-concept work opens the door to new possibilities in the field of 3D/4D printing.

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Drug-delivery, Implant, Grayscaling

## 3D-PRINTED DRUG-ELUTING IMPLANTS FOR THE TREATMENT OF PERIODONTITIS

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Periodontitis is a chronic inflammatory disease that affects a significant portion of the adult population and is a leading cause of tooth loss due to its progressive destruction of the alveolar bone. Traditional treatments often fail to restore the lost bone structure, which limits the long-term success of dental rehabilitation. Recent advances in additive manufacturing and biomaterials offer a promising pathway for the development of personalized, bioactive implants designed to regenerate bone tissue and improve patients' quality of life [1]. In this work, we propose a digital light processing (DLP) 3D printing approach to fabricate patient-specific scaffolds for periodontal regeneration. Our formulation is based on biofunctional gelatin methacryloyl (Gel-MA) known for its regenerative properties, complemented with low-molecular-weight poly(ethylene glycol) diacrylate (PEGDA) to enhance mechanical strength while preserving biodegradability [2]. Curcumin and dexamethasone are incorporated as active pharmaceutical ingredients, with curcumin also serving as a photoblocker and radical scavenger to improve printing resolution and cytocompatibility [3]. Nanohydroxyapatite is included to promote osteoconductivity by mimicking native bone mineral content. Overall, we evaluated how parameters such as crosslinking density, porosity, and infill patterns (e.g. gyroid, diamond) as well as the design of functionally graded structures influence the mechanical performance, degradation behavior, and drug release profiles of the resulting 3D-printed drug-eluting implants. In addition, we developed a reversible cell microencapsulation method using ionically crosslinked alginate shells to provide a temporary protective environment for cells during 3D-printing [4].

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Extrusion based AM / Photoreactor, reproducibility, modular

# STANDARDIZING LIGHT: A MODULAR PHOTOREACTOR FOR CONTROLLED, REPRODUCIBLE AND HIGH-THROUGHPUT PHOTOCHEMICAL REACTIONS

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Despite the growing relevance of photochemical processes for applications such as synthetic chemistry, coatings, and additive manufacturing, the field still lacks economically accessible and standardized equipment for conducting reproducible batch photochemistry. Indeed, key photonic parameters—such as light intensity, photon flux, and irradiation dose—are often uncontrolled, making experimental replication difficult and thus hampering fast and efficient progress. Our work provides a solution through a 3D printed, cost-effective design in the form of a concentric modular photoreactor (CMP).[1]

The system ensures excellent reproducibility (<1% errors in conversions *via* NMR in exemplar photopolymerization reactions) due to its innovative architecture. Its modular construction supports various reaction vessel types and permits a wide range of wavelengths, enabling versatile, low-cost, high throughput and standardized experimentation. Thus, this innovation provides a reliable and accessible set-up for reaction screening, kinetic analysis, and reproducible photochemical transformations across disciplines.

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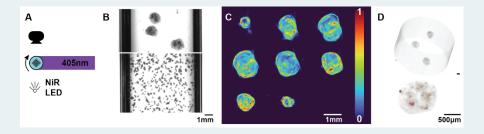
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Light mediated AM / Volumetric Printing, Bioprinting, Biofabrication

# NEAR INFRARED TOMOGRAPHY FOR DENSITY BASED ADAPTIVE CONTEXT-AWARE VOLUMETRIC PRINTING

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Tomographic volumetric printing (VP), also termed tomographic volumetric additive manufacturing, is an emerging 3D printing technique that rapidly (~60 s) fabricates complex, centimeter-sized geometries by projecting light into a photosensitive resin, thereby inducing threshold polymerization. However, a key limitation of this process, is that the printed design is superimposed onto the resin vat, with no awareness of the actual position of particles or objects suspended in the resin, including living cells in the context of bioprinting. A key step in enabling context-aware printing within VP is registration the process of accurately locating objects within the resin. Spatial coordinates of embedded features can then be used to generate parametric CAD models that guide the integration of new printed structures. We recently introduced Generative Adaptive, Context-Aware 3D Printing (GRACE) (1), a novel workflow which utilizes a multi-wavelength light sheet system to perform in situ registration of objects in the vat, and produces targeted designs which automatically adapt to the nature and position of the embedded objects. Expanding this workflow to different imaging modalities can greatly increase the resolution of the technology, as well and increasing the depth of information that can be extracted from the imaging data. In this study, we paired a volumetric printer with a diffuse near-infrared backlight (1040 nm), and a camera to capture the attenuation images at different angles as the vat rotates. This dataset enables volume reconstruction using filtered back projection. This approach facilitates the precise registration (>20 µm) of biological constructs (e.g., organoids, spheroids, pancreatic islets, etc.) without the need for fluorescent staining, thereby enhancing compatibility with a more extensive array of biologically relevant samples. Furthermore, the NIR-based system enhances the precision and autonomy of object-specific fabrication within complex microenvironments by integrating quantitative, density-based reconstruction with downstream classification. This integration enables parametric print generation based on biological discrimination. Our work presents a novel, label-free strategy for object registration in the vatbased tomographic VP, with the added benefit of machine learning-driven classification based on intrinsic density profiles obtained via infrared tomography.

Figure: A) Setup for the two step process of near-infrared registration followed by printing. B) Blood vessel organoids (BVOs, top) and iPSC derived pancreatic islets (bottom) as seen by the camera. C) Slice view of the density registration of a BVO D) Reconstruction and registering of a BVO for Generative Adaptive, Context-Aware 3D Printing (GRACE) printing.

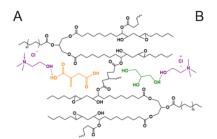
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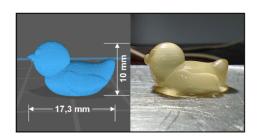
Eutectogel, 3D printing, soybean oil

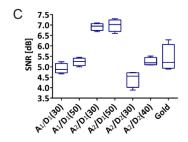
# 3D-PRINTABLE BIOBASED EUTECTOGELS DERIVED FROM SOYBEAN OIL AND NATURAL DEEP EUTECTIC SOLVENTS FOR UNDERWATER ELECTROMYOGRAPHY RECORDING

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Bioelectronics based on eutectogels are gaining increasing attention due to their conductivity, low volatility, and thermal stability [1]. In this work, we developed biobased eutectogels suitable for underwater body signal recording by combining a hydrophobic polymer network made of acrylated epoxidized soybean oil (AESO) with biocompatible deep eutectic solvents (DES) (Figure A). Two acrylation degrees of AESO were studied (AESO1 y AESO2) in order to tune mechanical and water-repellent properties. Choline chloride:glycerol (Ch-Cl:Gly) (DES 1) and a mixture with ChCl:itaconic acid (IA) (DES 2) were used as DES in diferent contents (30, 40, and 50 wt% based on AESO). The formulations were codified by indicating the AESO (A) and DES (D) employed, and the weight percent of DES in the mixture with respect to the AESO. For example, A1/ D1(30) is a formulation prepared with the AESO1 and 30 wt % of DES1. These formulations were processed as inks for VAT photopolymerization 3D printing to create electrodes with predesigned shapes. The printed eutectogels exhibited good resolution (Figure B), remarkable mechanical and rheological properties, and ionic conductivity. Underwater electromyography (EMG) tests confirmed their excellent performance and stability (Figure C), suggesting great potential for marine biology, exploration, and environmental monitoring.

Figure: Schematic representation of molecular structure of AESO network (black) and DES (color) (A), 3D piece printed from  $A_2/D_1(30)$  formulation, and SNR for underwater EMG recordings from wet eutectogel electrodes and a control gold electrode (C)

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Light mediated AM / Photopolymerization, wavelength-selective, multimaterial

## WAVELENGTH-SELECTIVE ONE-POT MULTIMATERIAL DLP 3D PRINTING

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Biological structures such as human teeth, squid beaks, bone-tendon interfaces, and nacre exemplify how nature uses mechanical gradients and microstructural organization of multiple materials to achieve highly specialized functionality [1]. However, synthetically recreating these multimaterials remains challenging with major obstacles including seamlessly interfacing soft and hard materials, balancing strength with elasticity, and increasing manufacturing speeds [2]. This work addresses these challenges by designing and optimizing resin systems for one-pot wavelength-selective multimaterial digital light processing 3D printing. One-pot multimaterial systems offer simplified hardware and scalable design, but they require precise control over resin reactivity. Both multiwavelength and grayscale strategies are leveraged as selective activation tools to achieve spatially controlled material differentiation within a single vat. By tuning resin formulation, light wavelength, and intensity, we enable the fabrication of complex biomimetic structures with large stiffness contrasts and programmable mechanical gradients. These findings highlight chemistry's integral role in advancing additive manufacturing and provide a roadmap for the scalable design of multimaterials for functional components in soft robotics, wearable electronics and prosthetics [3].

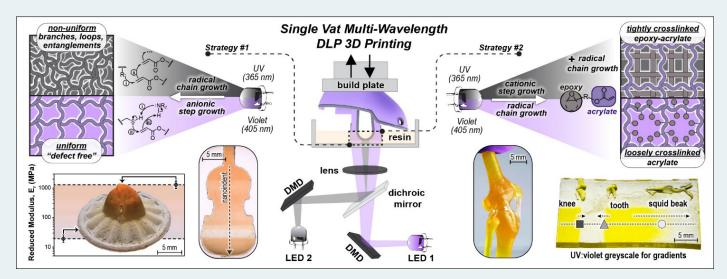


Figure: Single-vat dual-wavelength DLP setup (center) enabling multimaterial 3D printing via wavelength-selective photopolymerization. Strategy 1 (left) contrasts radical chain growth (365 nm) with anionic step-growth (405 nm). Strategy 2 (right) uses 365 nm to trigger both radical and cationic polymerization, while 405 nm initiates only radical polymerization. Bioinspired structures and grayscale control yield spatial mechanical gradients with tunable stiffness for both systems.

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Extrusion based AM /

Fused Granulate Fabrication, conductive TPS, soft sensors

# CONDUCTIVE TPS FOR PELLET-BASED 3D PRINTING: PROCESSING, CHARACTERIZATION AND SENSOR APPLICATION

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Fused Granulate Fabrication (FGF) is a promising technique for 3D printing of thermoplastic pellets, offering broader material compatibility and overcoming the limitations associated with filament-based FDM, particularly for soft materials [1]. In the field of elastic 3D-printing, thermoplastic polyurethanes (TPUs) have been widely studied, while TPS (styrenic block copolymers) have received comparatively less attention—despite offering a broad hardness range, excellent elastic recovery and thermal processability [2]—partly due to the greater challenges they present during printing.

This work investigates the use of FGF to print TPS materials, aiming to develop elastic and conductive components for soft robotics and wearable electronics. For this purpose, TPS composites loaded with carbon black (5–45 wt%) were developed to achieve electrical conductivity while maintaining mechanical compliance. The materials were characterized using thermal analysis (thermogravimetry, differential scanning calorimetry), mechanical testing (tensile strength, Shore hardness), and electrical conductivity evaluation. The composites exhibited percolation behavior consistent with studies on carbon-black-filled polymers [3]. Optimized processing parameters enabled the fabrication of multimaterial conductive 3D-printed sensors. This work highlights the potential of TPS-based composites to broaden the range of printable materials in FGF, enabling the production of soft, functional parts for advanced applications such as soft robotics grippers [4].

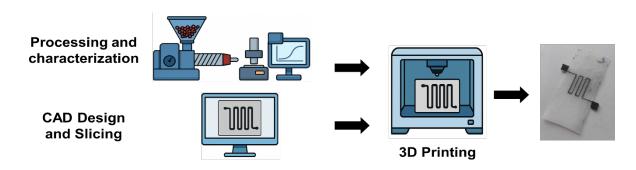


Figure: Processing, characterization, design and sensor printing scheme.

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Light mediated AM / Bioprinting, hydrogels, biosensors

## DEVELOPMENT OF GELMA-BASED BIOINK FOR BACTERIAL DETECTION

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Antimicrobial resistance (AMR) remains one of the major global health challenges today, demanding novel approaches beyond conventional drug development. In addition to the long and costly process of discovering new antimicrobials, there is a critical need for advanced tools that enable precise detection and monitoring of bacterial behavior. Achieving this requires in vitro systems that accurately replicate the complexity of the in vivo bacterial microenvironment [1]. Within this framework, bioprinting has emerged as a powerful technology for creating 3D in vitro models that closely mimic the morphology, microstructure and cell-bacteria interactions of specific tissues. Moreover, it offers the advantage of integrating sensors directly into the bioinks, enabling real-time, in situ monitoring of bacterial infections [2]. Among the different sensor types used for infection monitoring, conjugated polymers (CPs) stand out due to their opto-electronic properties, exhibiting colorimetric and fluorescent responses upon exposure to bacteria or biomarkers. Polydiacetylenes (PDAs) are a unique class of CPs synthesized through the polymerization of self-assembled diacetylene monomers. This process yields vesicles that exhibit an intense blue color (non-fluorescent), which undergo a visible transition to red (fluorescent) upon interaction with microorganisms or biomolecules [3]. In this work, by combining sensors with hydrogel-based bioinks we aim to create 3D cells models for bacteria sensing (Figure 1). As PDAs, 10,12-pentacosadiynoic acid (PCDA) is proposed for its commercial viability and extensive study in sensing applications. As hydrogel, gelatin methacryloyl (GelMa) is proposed for its biocompatibility and printability. Preliminary results indicate successful incorporation of the sensors into the GelMa matrix, exhibiting a strong and reliable sensing response. In addition, the developed bioink enable the printing of simple structures.

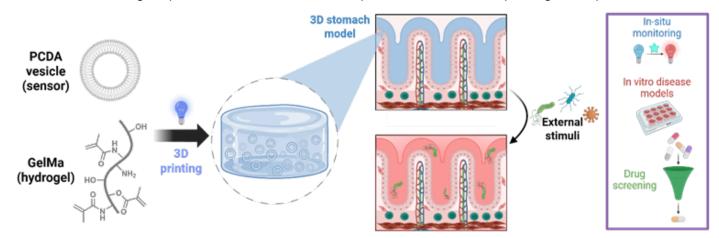


Figure 1. General scheme of 3D model of hydrogel bioink with incorporated sensors.

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Volumetric additive manufacturing, Functional composite, In-situ synthesis

## **VOLUMETRIC ADDITIVE MANUFACTURING OF COMPOSITES VIA HYDROGEL INFUSION**

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Volumetric additive manufacturing (VAM) is an emerging polymer-based 3D printing technique that surpasses conventional layer-by-layer additive manufacturing (AM) methods in terms of printing speed, surface finish, and the ability to fabricate complex, support-free structures. Despite these advantages, VAM is currently limited to highly transparent photoresins, as the presence of particle fillers induces significant light scattering and absorption, rendering the direct printing of polymer composites infeasible. To address this challenge, we introduce a post-fabrication, in-situ nanoparticle synthesis strategy that enables composite fabrication without compromising the optical requirements of the VAM process. Specifically, VAM-printed hydrogels were infused with metal precursor solutions, followed by controlled precipitation to form magnetic or conductive inorganic particles in-situ, achieving filler loadings up to 65 wt%. Furthermore, applying multiple post-processing steps facilitates the creation of multi-material architectures with tunable functionalities and mechanical properties. This versatile strategy not only overcomes the material transparency constraints inherent to VAM but also holds promise for adaptation to other AM techniques requiring optically clear resins, thereby broadening the scope of functional material fabrication in volumetric and photopolymer-based additive manufacturing.

Light mediated AM / CNT, Scaffold, Biomedicine

#### 3D PRINTABLE CNT SCAFFOLDS FOR NEURONAL TISSUE ENGINEERING

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Lesions in the central nervous system, such as spinal cord injuries (SCI), lead to the loss-of-function of the neural tissue. In the field of tissue engineering, 3D scaffolds containing carbon nanotubes (CNTs) have emerged as promising conductive materials to interface with electrically active tissues due to their unique electric and mechanical properties [1,2]. We aim to utilize CNT containing hydrogels as therapeutic implants in the SCI lesion site to regain the functionality of the spinal cord. In order to achieve this objective, we printed CNT hydrogels based on (Hydroxyethyl)methacrylate (HEMA) and Poly(ethylene glycol) diacrylate (PEGDA) by Vat photopolymerization, using a SLA printer. We later studied their mechanical and electrical properties and tested them in vitro, by culturing neuroblastoma SH-SY5Y cells and performing cell viability assays (LDH) and confocal imaging to study cellular morphology, attachment and cell coverage on our materials. The CNT-based scaffolds showed a significantly better performance *in vitro* than the control hydrogels, showing the potential of CNTs for tissue engineering.

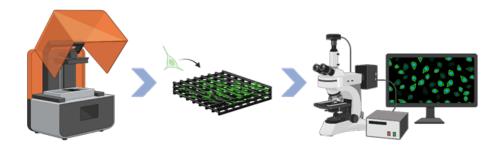


Figure: Schematic representation of the in vitro experimental design.

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Light mediated AM / functional peptides; hydrogels; two-photon laser printing

## REVERSIBLE COILED-COIL PEPTIDE FUNCTIONALIZATION OF 3D-MICROPRINTED HYDROGELS

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The development of novel responsive soft materials holds the potential to revolutionize external control of biochemical systems. By changing material properties according to deliberately triggered stimuli, the desired functionality can be achieved at arbitrary temporal resolution.[1,2] In parallel, with the emergence of high-resolution 3D printing techniques, such as two-photon laser printing, high spatial resolution can be achieved for soft (bio-)materials.[3]

In our approach, these two aspects of material design were combined by covalently incorporating coiled-coil-forming peptides into two-photon laser printed hydrogels. We synthesized a set of two peptide monomers which assemble into heterodimeric coiled coils in solution.[4] First, by acrylation of monomer 1 and addition of it to a polyethylene-glycol-based ink, we printed microstructured hydrogels containing one of the coiled-coil-forming strands. Second, the complementary monomer 2 was chemically decorated with a desired cargo unit (e.g. a fluorophore). By addition of a solution of monomer 2 onto the hydrogel, in-material assembly of the two strands into coiled coil structures was promoted. The cargo-loaded strand 2 could be non-covalently trapped in the hydrogel and only released upon denaturation of the coiled coil fold *via* eligible stimuli. Ultimately, orthogonal loading and release of cargo, promoted by coiled-coil assembly and disassembly, could be achieved with precise spatial and temporal control.

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Light mediated AM / photo-crosslinkable PCL; photo-crosslinkable gelatin; VAM/2PP/DLP

# LIGHT-BASED 3D PRINTING OF TUNABLE THIOL-ENE POLYMERS: FROM SUBMICRON PRECISION TO RAPID FABRICATION OF BIODEGRADABLE IMPLANTS

<u>Sandra Van Vlierberghe</u>\* (1), Quinten Thijssen (1), Bo Van Durme (1), Astrid Quaak (1), Hayden Taylor (2), Steven Ballet (3), Kristyna Kolouchova (1), Laurens Parmentier (1)

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- (3) Vrije Universiteit Brussel, Brussels, Belgium.

Current biodegradable, cross-linkable polymers largely rely on acrylate cross-linking, which, despite its fast kinetics, results in brittle materials with limited use. This work presents photo-cross-linkable synthetic poly( $\epsilon$ -caprolactone) (PCL) and semi-synthetic gelatin networks using orthogonal thiol-ene chemistry. These step-growth polymerized networks offer tunable, predictable mechanical properties—surpassing those of acrylate-based counterparts—by varying the molar mass between cross-links (Mc). The impact of Mc on thermal, mechanical, and degradation behavior is evaluated. Volumetric 3D-printing capabilities are demonstrated with record-small features for thiol-ene systems. In vitro and in vivo assessments confirm the biocompatibility and regenerative potential of these constructs. Progress in two-photon polymerization printing is also discussed.

In addition, to mimic nature's cell adhesion, a single-step method is introduced where thiol-ene chemistry enables both network formation and simultaneous incorporation of cell-binding motifs (C(-linker-)RGD) via cysteine sites. The effect of linker variations was analyzed using contact angle measurements and X-ray photoelectron spectroscopy, confirming successful and uniform cell-adhesive functionalization.

This approach combines mechanical stability, tunability, biocompatibility, and rapid fabrication without post-processing, paving the way for bedside manufacturing of patient-specific biodegradable implants. Case studies using digital light processing and indirect 3D-printing of (CT-traceable) scaffolds will also be presented as well as highlights involving real-time in vivo implant monitoring. The in vivo angiogenic potential of recombinant versus animal-derived gelatin hydrogels is also explored.

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18 D1 -PL

Light mediated AM / Biofunctional resins, 4D printing, in vitro models

#### BIOFUNCTIONAL RESINS FOR 4D PRINTING AND THEIR APPLICATION IN VITRO MODEL DESIGN

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3D bioprinting is a powerful technique for replicating complex tissue architectures. However, creating biocompatible, printable resins that closely mimic the mechanical and biological properties of soft tissues remains a major challenge. To address this, we have developed a range of hybrid resins that enable the biofabrication of dynamic, optically responsive 4D tissue models. These advanced *in vitro* systems serve as valuable tools for investigating the fundamental mechanisms governing native tissue functions and simulate cellular mechanotransduction—the process by which physical stimuli are translated into biochemical signals that influence cell function. This is especially relevant for cardiovascular and pulmonary models, where rhythmic motions such as heartbeats and breathing are critical to physiological function.

By incorporating plasmonic nanoparticles (NPs) into thermoresponsive polymer-based resins, we have achieved precise, light-triggered cyclic expansion and contraction, effectively mimicking natural tissue movements. These plasmonic NPs act as nanoscale antennas that convert light into localized heat, enabling finely controlled actuation. Additionally, the presence of NPs enhances the compatibility of these models with multimodal imaging techniques, facilitating detailed structural and functional characterization.

During the talk, two different examples of bioresins developed for 4D bioprinting will be presented: one used to fabricate an alveolar model and the other to create vascular-inspired architectures. These structures were produced using different printing techniques such as Liquid Crystal Display (LCD) 3D printing and volumetric printing. We will emphasize the role of plasmonic NPs included in the resins, in both the design and characterization of these dynamic in vitro 4D models, highlighting the unique advantages they offer over conventional bioprinting materials.

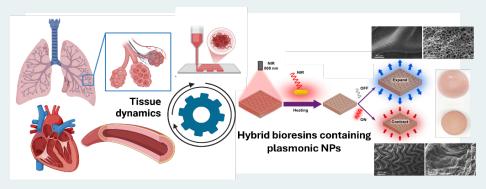


Figure: Printable hybrid bioresing containing plasmonic NPs to reproduce tissue dynamics.

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19 D1 -S1 -01

Light mediated AM / recycling, sustainability, vitrimers

# BIOBASED PHOTOPOLYMER RESIN FOR 3D PRINTING CONTAINING DYNAMIC IMINE BONDS FOR FAST REPROCESSABILITY

Jules Stouten (1), Geraldine H. M. Schnelting (2), Jerzy Hul (3), Nick Sijstermans (1), Kylian Janssen (2), Tinashe Darikwa (1), Chongnan Ye (4), Katja Loos (4), Vincent S. D. Voet, **Katrien V. Bernaerts\*** (1)

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Acrylic photopolymer resins are widely used in stereolithographic 3D printing. However, the growing demand for such thermosetting resins is weighing on global issues such as waste management and fossil fuel consumption. Therefore, there is an increasing demand for reactive components that are biobased and enable recyclability of the resulting thermoset products. In this work, the synthesis of a photo-cross-linkable molecule containing dynamic imine bonds based on biobased vanillin and dimer fatty diamine is described [1]. Using the biobased building blocks, formulations containing reactive diluent and a photoinitiator were prepared. The mixtures could be rapidly cross-linked under UV light, yielding vitrimers. Using digital light processing, 3D-printed parts were prepared, which were rigid, thermally stable (see Figure), and reprocessed within 5 min at elevated temperature and pressure. The addition of a building block containing a higher concentration of imine bonds accelerated the stress relaxation and improved the mechanical rigidity of the vitrimers. This work will contribute to the development of biobased and recyclable 3D-printed resins to facilitate the transition to a circular economy.

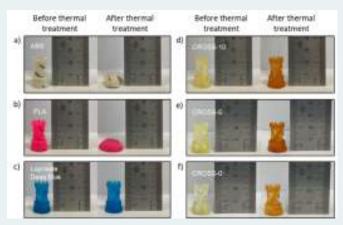


Figure. Photograph of 3D printed Rook Tower test specimens before and after thermal treatment at 200 °C for 10 minutes. The evaluated specimens are composed of thermoplastics ABS and PLA (a and b), thermoset Liqcreate Deep Blue (c) and vitrimers CROSS-0, CROSS-5, and CROSS-10 (d-f).

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20 D1 -S2 -01

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DAY 1 / TUESDAY OCTOBER 7

Light mediated AM / Architectures, reconfigurability, self-healing

# SELF-HEALING POLYMERS FOR RECONFIGURABLE ARCHITECTED MATERIALS

# Disha Bandyopadhyay

## DISCLAIMER

The abstract is not included as per author's request.

21 D1 -S1 -02 DAY 1 / TUESDAY OCTOBER 7

Light mediated AM /

biofabrication, microarchitected hydrogels

# SUBTRACTIVE TWO-PHOTON MICROPRINTING OF ARCHITECTED HYDROGELS TO GUIDE CELL NETWORK FORMATION

# Margherita Bernero

## **DISCLAIMER**

The abstract is not included as per author's request.

22 D1 -S2 -02

Light mediated AM / volumetric printing, biofabrication, bioprinting

# LIGHT-BASED VOLUMETRIC BIOPRINTING AND IMAGING-DRIVEN MANUFACTURING: SHINING A NEW LIGHT ON ENGINEERED TISSUES AND ORGANOIDS

#### Riccardo Levato (1,2,3,\*)

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In the quest to capture the complex environment of living organs within lab-made tissues, light emerged as a uniquely powerful stimulus for enabling dynamic and spatio-temporal control over cell and biomaterial properties, opening new avenues in regenerative medicine and tissue engineering. Light-responsive moieties permit to non-invasively trigger mechanical actuation and shape-changes in cell-laden constructs, to modulate stiffening or softening of the extracellular milieu, and to enable spatio-temporal control over cell behavior. Previously, we introduced volumetric bioprinting (VBP), an ultra-fast, layer-less visible light-based biofabrication approach, to resolve virtually any 3D geometrical patterns in less than 20 seconds by projecting tomographic patterns onto photosensitive hydrogels making it possible to sculpt cell-laden materials with unprecedented geometrical freedom into high resolution architectures. Using visible light volumetric bioprinting technologies and protein-derived photoresponsive hydrogels, complex mini-organ models, also termed organoids, can be safely assembled into centimeter scale living tissues in a matter of few seconds. Herein, the most recent advances in light-driven biofabrication will be presented, together with our efforts to engineer functional blood vessels, breast gland tissue, and pancreatic tissues as advanced biological models, using organoids as living building blocks. Challenges in recreating vascularized environments can be addressed converging light-based volumetric printing with microgel-based printable materials, as well as via combining VBP other fabrication techniques, such as extrusion-based bioprinting and melt electrowriting. Moreover, spatial-specific functionalization with growth factors and biochemical signals can be achieved via a secondary VBP process to graft bioactive proteins in specific locations. Further advancing this technology, precise imaging strategies are leveraged to for enhanced metrology, quality control, and for introducing the concept of context-aware printing. In context-aware manufacturing, making printers that are able to detect objects, cells and features of interest within the printing vat, enables the creation of constructs that match the metabolic demands of the embedded cells, facilitates multi-material printing and overprinting, and permits to print across opaque, light-occluding elements, allowing for the creation of complex composite materials and living tissues. Overall, introducing anisotropic, multicellular/multimaterial patterns within volumetrically bioprinted constructs enables the biofabrication of freeform tissue models that more closely mimic the complex biochemical and structural composition of native tissues, to more precisely guide cell fate and maturation.

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23 D1 -S1 -03

Adaptive microstructures, Stimuli-responsive materials, Shape memory polymers

## 4D PRINTING WITH LIGHT: FUNCTION MEETS SUSTAINABILITY

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4D printing has become a promising tool for the fabrication of dynamic and adaptive structures. During the last years, promising examples of defined 4D microstructures employing stimuli-responsive materials have been shown using two-photon 3D laser printing. Herein, we present our recent work on the field with emphasis on new responsive materials enabling the preparation of adaptive and structures. In particular, shape memory polymers as well as liquid crystal elastomers have been explored. In the first case, a simple and versatile formulation has been developed enabling complex microstructures with remarkable shape memory properties. Also, multi-responsive structures using photo responsive liquid crystal elastomers, are demonstrated. Furthermore, we have exploited the inclusion of dynamic and living bonds in a printable formulation enabling the creation of microstructures with "life-like" characteristics such as adaptability by tunable shape and mechanical properties. In addition, we demonstrated at the macromolecular sequence, specifically the positioning of the crosslinkable group, plays a critical role in both the printability and final properties of the printed material. We envision that careful and precise design of new printable materials will open new opportunities for the additive manufacturing of functional devices in the near future.

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24 D1 -S2 -03

DAY 1 / TUESDAY OCTOBER 7

## Light mediated AM

# SUSTAINABLE PHOTOLUMINESCENT MATERIALS BASED ON SOYBEAN OIL-PHOTOCURABLE INKS FOR DIGITAL LIGHT PROCESSING

<u>Cristian Mendes-Felipe</u> (1)\*, Bárbara Cruz (2,3), Daniela Correia (2), Senentxu Lanceros-Mendez (1,3,4)

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The growing demand for additive manufacturing, particularly digital light processing (DLP) printing, calls for sustainable alternatives to petroleum-based resins, which pose environmental and resource depletion concerns [1]. Bio-based photocurable materials have emerged as a suitable solutions to reduce fossil dependency while maintaining high performance [2]. Among them, soybean oil derivatives stand out for their renewability, biodegradability, and compatibility with light-based curing technologies [3].

In this work, bio-based photocurable inks were formulated using soybean oil derivatives, optimizing viscosity and photopolymerization kinetics to ensure high-quality printing with a high biorenewable carbon content. The formulation strategy balanced printability and mechanical integrity while offering a sustainable alternative to commercial resins. Beyond sustainability, functional fillers allowed to endow functional photoluminescent characteristics to the developed 3D-printed objects. Photoluminescent lanthanide-based salts and ionic liquids (Eu³+, Tb³+, Tm³+, Yb³+, Nd³+) enabled tunable emission in the visible and near-infrared regions, achieving efficient luminescence at low concentrations (5 wt.%) for security and smart display applications. The curing parameters, specially curing rate and gelation time are slightly affected by the addition of photoluminescent salts except to Eu-based one. Additionally, thermal properties, i.e. T<sub>g</sub>, are maintained for all samples and the functional fillers are well dispersed in the cured materials observed by SEM-EDX analysis. Challenges such as light absorption effects on photopolymerization, viscosity and material adhesion optimization were successfully addressed to ensure print reliability, obtaining 3D parts with details at millimeter scale. This study advances bio-based functional materials for DLP printing, demonstrating their potential for next-generation sustainable and multifunctional additive manufacturing.

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25 D1 -S2 -04

DAY 1 / TUESDAY OCTOBER 7

Light mediated AM

Two photon polymerization - Shape memory - Poly-e-caprolactone

# ADVANCED FABRICATION OF THERMO-RESPONSIVE SCAFFOLDS FOR TISSUE ENGINEERING: TAILORED RESIN DEVELOPMENT AND 4D MICROPRINTING

**Bo Van Durme** (1), Astrid Quaak (1), Joost Brancart (2), Clara Vazquez Martel (3), Samantha Olivia Catt (3), Eva Blasco (3), Vincent Van Rompaey (4), Sandra Van Vlierberghe\* (1)

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- (3) Blasco Group, Heidelberg University, 69120 Heidelberg, Germany
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Multiphoton lithography is a powerful and versatile structuring tool capable of creating 3D micro- and nanometer features from various materials with high spatial resolution down to the nm-scale. It has gained significant interest in tissue engineering and medical device manufacturing for its ability to print sophisticated structures that traditional methods cannot easily achieve. A notable trend is the shift towards active printable materials, often referred to as 4D microprinting, allowing enhanced control within printed systems. Hence, this study develops a biodegradable and biocompatible photosensitive resin based on a thiol-ene photo-crosslinkable poly( $\epsilon$ -caprolactone) designed to yield thermo-responsive scaffolds with a shape transition near body temperature ( $T_m = 34.4 \, ^{\circ}$ C) [1].

Tailored specifically for 2PP printing, the resin's printing parameters - including photo-initiator concentration (1–2.5 wt%), writing speed (100–600 mm s<sup>-1</sup>), laser power (50–200 mW), and voxel size - were thoroughly optimized. Post-processing is improved using methoxyperfluorobutane, achieving > 95 % CAD/CAM mimicry due to its lower surface tension compared to conventional solvents such as acetone, chloroform, and THF. The shape memory properties are evidenced both qualitatively and quantitatively through dynamic mechanical analysis and nanoindentation, showing a shape shift near body temperature along with excellent shape fixity and recovery, making the scaffolds highly suitable for minimally invasive TE strategies.

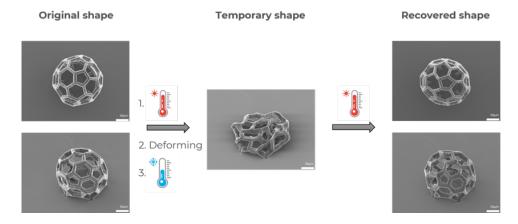


Figure: Proof of concept showing shape memory properties of 2PP printed constructs. Scale bars represent 50 microns.

[1] A. Quaak, Q. Thijssen, S. Van Vlierberghe, Exploiting the network architecture of thiol–ene photo- cross-linked poly(ε-caprolactone) towards tailorable materials for light-based 3D-printing, Polym. Chem., 2023,14, 3392-3403

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26 D1 -S1 -04

Extrusion based AM / Rheology, FDM, Conductivity

# INFLUENCE OF 3D PRINTING ON THE ELECTRICAL PROPERTIES OF CONDUCTIVE NANOCOM-POSITES

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The 3D printing of conductive nanocomposites has emerged as a promising approach for fabricating customizable components with tailored electrical properties. Achieving optimal conductivity, however, depends heavily on processing conditions, as shear forces and cooling during printing influence the formation of the conductive network. [1] Numerous studies have demonstrated that nanocomposites exhibiting electrical conductivity when produced by compression molding often lose this property when processed via injection molding (Figure 1). This study investigates how extrusion-based 3D printing affects the electrical properties of a nanocomposite composed of a biopolymer and carbon nanotubes (CNTs). To further explore the relationship between shear and conductivity, both linear (SAOS) and non-linear (LAOS) rheological tests were conducted in tandem with electrical conductivity measurements.

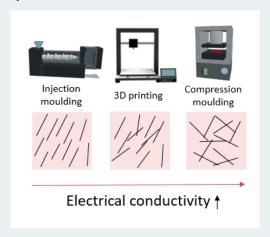


Figure 1: Processing effect on CNT orientation and resulting conductivity scheme.

[1] Fangming Du, John E. Fischer, Karen I. Winey "Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites", *Phys. Rev. B*, **2005**, 72 (12), 121404, DOI: 10.1103/Phys-RevB.72.121404.

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27 D1 -S2 -05

biomedical applications, antimicrobial materials, devices

# DESIGNING POLYMERS FOR ADDITIVE MANUFACTURING FOR BIOMEDICAL APPLICATIONS: FROM ANTIMICROBIAL MATERIAL TO BIOMEDICAL DEVICES

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- (1) Polymer Functionalization Group (FUPOL) Institute of Polymer Science and Technology (ICTP-CSIC), Madrid, Spain.
- (2) Facultad de Ingeniería, Arquitectura y Diseño, Universidad San Sebastián, Santiago 8420524, Chile
- (3) Departamento de Química, Facultad de Ciencias Naturales, Matemáticas y del Medio Ambiente, Universidad Tecnológica Metropolitana, Santiago 7800003, Chile.

Additive manufacturing offers unprecedented alternatives to design and fabricate intricate 3D structures. In particular, biomedical applications benefit from these advantages for those cases in which patient customization is also a requirement. In this contribution we will present, on the one hand, the design of novel polymeric materials in view of their use as scaffolds or as tissue engineering platforms. On the other hand, we will present recent collaborative projects in which biocompatible devices have been designed to improve current spinal cord injury treatments as well as for the regeneration of articular cartilage through cell therapy based on thermosensitive hydrogels.

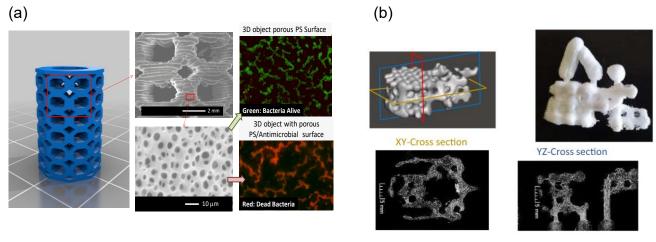


Figure: (a) Preparation of functional and porous 3D scaffolds with antibacterial properties (b) Desing of 3D printed molds for the fabrication of entirely porous and biocompatible scaffolds

- [1] Sanz-Horta, Raul et al. "Breath Figures makes porous the "so-called" skin layer obtained in polymer foams prepared by supercritical CO2 treatments" Journal of Supercritial Fluids, **2021**, 167, 105051. [2] Sanz-Horta, Raul et al.. Polycaprolactone with multiscale porosity and patterned surface topography prepared using sacrificial 3D printed moulds: towards tailor-made scaffolds. Biomaterials Advances. 151, 213465, **2023**.
- [3] Sarabia-Vallejos, Mauricio A. et al. Biocompatible and bioactive PEG-Based resin development for additive manufacturing of hierarchical porous bone scaffolds Materials and Design, 234, 112315, **2023**.

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28 D1 -S1 -05

biobased monomers, cationic photopolymerization electricla conductivity

## BIOBASED SUSTAINABLE 3D-PRINTABLE UV-CURABLE FORMULATIONS

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Additive manufacturing has become a widely used technology in materials production exploited for both academia and industrial applications ranging from biomedical to electronic or aerospace industry. While this technique is well mastered by exploiting acrylates or methacrylates monomers, there is not any report in literature on the use of epoxy monomer for 3D-printing.

We have investigated the printing properties of furandimethanol diglycidyl ether (FDE) and resorcinol diglycidyl ether (RDE), two biobased epoxy resin synthesized on purpose [1]. The hot Lithography 3D printing process was exploited both to enhance the reactivity towards UV-irradiation as well as to reduce viscosity. The photocuring process was fully characterized. The thermo-mechanical properties of the final thermosets were investigated by DMTA and tensile test. Finally, the 3D printing of complex shapes was carried out to demonstrate the possibility to obtain arbitrary self-standing shapes. The investigation pursued exploring the possibility to 3D printing bio-derived composites by adding bio-based fillers, such as wall-nut shell. The benefit of the addition of the filler was confirmed and explained by investigating the surface modification of the filler which had an incredible impact on the properties of the composite [2].

Biobased polyglycerolate monomers containing acrylic groups were also investigated in 3D-printing, in the presence of CNTs as conductive fillers to achieve 3D-printed functional objects. The formulations incorporating CNTs were processed via a Digital Light Processing (DLP) 3D printer for an assessment of their printability [3].

Acrylated, epoxidized soybean oil (AESO) reinforced with bioactive glass was investigated in DLP 3D-printing technology to achieve scaffold for biomedical applications, enabling precise resolution and the possibility to manufacture a hollow and complex structure. The resin formulation was optimized with a biobased, reactive diluent to adjust the viscosity for an optimal 3D-printing process. The in vitro biological evaluation of the 3D-printed scaffolds, combined with showed a good cytocompatibility and cell proliferation. This work highlights the effect of the vitrimeric polymer matrix and doped, bioactive glass in manufacturing biocompatible, biobased, and antibacterial scaffold used in hard tissue application. [4]

- [1] L. Pezzana, R. Wolff, G. Melilli, N. Guigo, N. Sbirrazzuoli, J. Stampfl, R. Liska, M. Sangermano, Polymer, **2022**, 254, 225097.
- [2] L. Pezzana, R. Wolff, J. Stampfl, R. Liska, M. Sangermano, Additive Manufacturing, 2024, 79, 103929.
- [3] M. Porcarello, S. Bonardd, G. Kortaberria, Y. Miyaji, K. Matsukawa, M. Sangermano, ACS Appl. Polym. Mater., **2024**, 6, 2868–2876.
- [4] M. Bergoglio, M. Kriehuber, B. Sölle, E. Rossegger, S. Schlögl, Z. Najmi, A. Cochis, F. Ferla, M. Miola, E. Vernè, M. Sangermano, Polymers **2024**, 16, 3614.

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29 D1 -S1 -06

3D laser nanoprinting, multi-photon absorption, two-step absorption

## 3D LASER NANOPRINTING

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- (2) Institute of Nanotechnology, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany.

3D printing using light has become a vast field [1]. In this lecture, I will give an introduction into 3D laser printing on the micrometer or nanometer scale based on using some sort of nonlinearity, e.g., two-photon absorption. I will also review selected recent results from my research group.

[1] P. Somers, A. Münchinger, S. Maruo, C. Moser, X. Xu, and M. Wegener, "The physics of 3D printing with light", *Nature Rev. Phys.*, **2024**, 6, 99-113.

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30 D1 -PL

two-photon lithography, biomaterials, bone

## 3D PRINTED BONE ARCHITECTURES FOR MEDICINE

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Bone is a complex tissue that is hierarchically organized across several length scales. This hierarchical organization is essential for cell-mediated skeletal remodeling in response to mechanical loading. Despite recent progress, current *in vitro* models of bone lack the structural and functional complexity found in native bone. In this talk, I will present our efforts in developing advanced biomaterials and 3D (bio)printing techniques to create novel 3D bone tissue models across length scales. Specifically, I will highlight these examples: 1) designing a synthetic dynamic photoresin for fast tomographic volumetric bioprinting of permissive hydrogel constructs within 5-20 seconds; 2) new photoresins for additive two-photon printing of bioactive hydrogel constructs on demand; and 3) photocleavable hydrogels for subtractive two-photon patterning for spatiotemporal tissue engineering at subcellular resolution. Finally, I will provide a personal perspective to the current challenges and future directions.

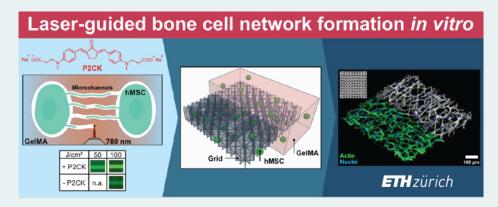


Figure: Illustration of laser-printed living bone cell networks.

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31 D1 -S3 -01

Light mediated AM / Multimaterial, Wavelength-Selective, Photochemistry

## COLOR- AND DOSE-CONTROLLED MULTIMATERIAL DIGITAL LIGHT PROCESSING 3D PRINTING

Zachariah A. Page(1), Elizabeth A. Recker(1), Keldy S. Mason(1), Ji-Won Kim(1), Marshall J. Allen(1), Meghan T. Kiker(1)

(1) The University of Texas at Austin, Austin, Texas, USA

Natural structures have evolved to integrate hard and soft materials in precise 3D configurations, imparting unique bulk properties and functionalities that remain challenging to replicate synthetically. The development of biomimetic analogues capable of seamlessly combining hard and soft materials offers vast potential for applications in fields such as soft robotics, sealants, and medical devices – including prosthetics and wearable health monitors. This demand has catalyzed the exploration of new chemistries and manufacturing methods. This presentation will highlight the ZAP research group's efforts to address these challenges [1-3]. We will discuss multicomponent resins that selectively respond to different wavelengths and intensities of light, enabling high-resolution, rapid 3D printing using digital light processing (DLP). The focus will be on the optimization of resin formulations and their influence on feature resolution, mechanical properties, and the creation of multimaterial structures.



Figure: Representative Structures from Multimaterial 3D Printing

- [1] Meghan T. Kiker, Elizabeth A. Recker, Ain Uddin, Zachariah A. Page "Simultaneous Color- and Dose-Controlled Thiol–Ene Resins for Multimodulus 3D Printing with Programmable Interfacial Gradients", Advanced Materials, 2024, 36, 2409811, DOI: 10.1002/adma.202409811
- [2] Ji-Won Kim, Marshall J. Allen, Elizabeth A. Recker, Lynn M. Stevens, Henry L. Cater, Ain Uddin, Ang Gao, Wyatt Eckstrom, Anthony J. Arrowood, Gabriel E. Sanoja, Michael A. Cullinan, Benny D. Freeman, & Zachariah A. Page, "Hybrid Epoxy-Acrylate Resins for Wavelength-Selective Multimaterial 3D Printing", *Nature Materials*, 2025, *in-press*, DOI: 10.1038/s41563-025-02249-z
- [3] Keldy S. Mason, Ji-Won Kim, Elizabeth A. Recker, Jenna M. Nymick, Mingyu Shi, Franz A. Stolpen, Jaechul Ju, & Zachariah A. Page "Multicolor Digital Light Processing 3D Printing Enables Dissolvable Supports for Freestanding and Non-Assembly Structures", *ACS Cent. Sci.*, 2025, in-press.

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32 D1 -S4 -01

LCD printing, dynamic, alveolar model

# ENGINEERING DYNAMIC LUNG MODELS: 4D LCD PRINTING OF THERMORESPONSIVE ALVEOLAR SCAFFOLDS

Ane Urigoitia-Asua (1,2), Irune Villaluenga (2,3), Dorleta Jimenez de Aberasturi\* (1,3)

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- (2) POLYMAT, Basque Center for Macromolecular Design and Engineering, 20018 Donostia, Spain.
- (3) IKERBASQUE Basque Foundation for Science 48013 Bilbao, Spain

Advances in 3D *in vitro* alveolar models are necessary for accurate disease modeling and drug screening. Replicating native lung geometry and breathing dynamics is essential for functional tissue maturation [1]. We applied 4D printing to fabricate scaffolds mimicking alveolar cavities and support dynamic expansion and contraction to simulate breathing motions. Building on previous work in our group [2], we developed a stimuli-responsive, biocompatible, hybrid material for Liquid Crystal Display (LCD) vat-photopolymerization by integrating the thermoresponsive monomer vinyl caprolactam (VCL) and near-infrared (800 nm) plasmonic gold nanorods (AuNRs), functionalized for biocompatibility and improved cell adhesion. The material exhibited tunable actuation via NIR laser-triggered heating and cooling across its Lower Critical Solution Temperature (LCST), 34°C. We 4D-printed and characterized honeycomb-patterned scaffolds (400 µm diameter) resembling native alveoli. The hybrid polymer supported 16HBE lung epithelial cell growth, with the AuNRs functionalization being critical, as positively charged AuNRs promoted more uniform monolayer formation than negatively charged ones. This LCD 4D-printable material offers significant potential for developing physologically relevant, dynamic alveolar models for respiratory disease research and high-throughput drug testing.

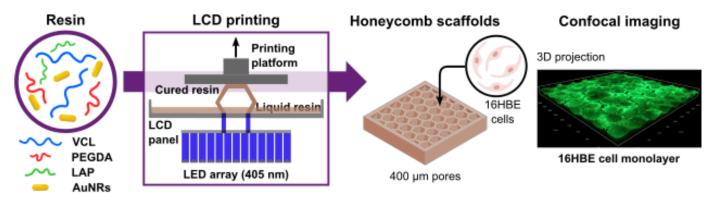


Figure: Workflow from liquid resin to LCD-printed scaffolds, and 16HBE cell monolayer formation.

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33 D1 -S3 -02

<sup>[1]</sup> Laura Fallert, Ane Urigoitia-Asua, Amaia Cipitria, Dorleta Jimenez de Aberasturi "Dynamic 3D *in vitro* lung models: applications of inorganic nanoparticles for model development and characterization", *Nanoscale*, **2024**, 16, 10880, DOI: 10.1039/d3nr06672j

<sup>[2]</sup> Uxue Aizarna-Lopetegui, Clara García-Astrain, Carlos Renero-Lecuna, Patricia González-Callejo, *et al.* "Remodeling arteries: studying the mechanical properties of 3D-bioprinted hybrid photoresponsive materials", *J. Mater. Chem. B*, **2023**, 11, 9431, DOI: 10.1039/d3tb

DAY 1 / TUESDAY OCTOBER 7

Light mediated AM

depolymerisation, sustainable ink, macro- to micro-scale printing

## TUNEABLE DEPOLYMERISATION OF LIGHT-BASED 3D PRINTED STRUCTURES

## ON THE MACRO- AND MICRO-SCALE

Pia S. Klee (1), Samantha O. Catt (1), Eva Blasco\* (1)

(1) Institute for Molecular Systems Engineering and Advanced Materials, Heidelberg University, Heidelberg, Germany.

3D printing offers great potential as a modern sustainable manufacturing technique for polymer materials [1]. Light-based methods in particular, provide high resolution on both the macro- and micro-scale. Conventional inks, however, currently rely mostly on (meth)acrylates as the photopolymerisable component which results in thermosets that are difficult to depolymerise and recycle [2]. Therefore, there has been an increasing interest in finding alternative photopolymerisable units. Dithiolanes have proven to be promising candidates, as they can be found in thioctic acid which is naturally sourced. Herein, a dithiolane-based ink has been developed for both macro-scale printing using digital light processing and micro-scale printing, using two-photon 3D laser printing. The ink has proven to be successful on both scales without the need for a photoinitiator and the incorporated dithiol linkages have facilitated the depolymerisation of the printed structures. Further, it has been optimised to undergo depolymerisation at relatively low temperatures. This widens the potential for further applications of this system and allows for selective depolymerisation of multimaterial prints and sacrificial materials. The presented ink, therefore, demonstrates a versatile alternative to (meth)acrylates as initiator-free photopolymerisable units for light-based 3D printing on both the macro- and micro-scale.

- [1] Eva Sanchez-Rexach, Trevor G. Johnston, Coralie Jehanno, Haritz Sardon, Alshakim Nelson, "Sustainable Materials and Chmical Processes for Additive Manufacturing", *Chem. Mater.*, **2020**, 32, 7105–7119, DOI: 10.1021/acs.chemmater.0c02008.
- [2] Vincent S. D. Voet, Jarno Guit, Katja Loos, "Sustainable Photopolymers in 3D Printing: A Review on Biobased, Biodegradable, and Recyclable Alternatives" *Macromol. Rapid Commun.*, **2021**, 42, 2000475, DOI: 10.1002/marc.202000475.

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34 D1 -S4 -02

DAY 1 / TUESDAY OCTOBER 7

Light mediated AM

Tomographic volumetric bioprinting; in vitro modeling; millifluidic systems

#### **VOLUMETRIC ADDITIVE MANUFACTURING OF COMPLEX CONSTRUCTS FOR IN VITRO MODELING**

<u>Viola Sgarminato</u> (1), Riccardo Rizzo (1), Felix Wechsler (1), Turan Badalli (2), Wouter R. Karthaus (2), Christophe Moser (1)

- (1) Laboratory of Applied Photonics Devices, EPFL, Switzerland
- (2) ISREC Swiss Institute for Experimental Cancer Research, EPFL, Switzerland

Pancreatic ductal adenocarcinoma (PDAC) is a highly lethal cancer, as often during diagnosis patients present with advanced metastatic disease. Understanding PDAC initiation and progression therefore is key to enable early detection and treatment. PDAC initiates in the ductal cells of the pancreatic exocrine compartment, a process that can be studied *in vitro*. However, conventional *in vitro* models fall short in recapitulating the cellular, structural and physiological complexity of the exocrine gland [1]. While organoids have emerged as powerful tools for modeling human tissue development capturing epithelial cell heterogeneity, they still lack key features of the native tissue microenvironment, including authentic architecture, vascularization, and consistent organization. To address these limitations, we present a novel approach using tomographic volumetric additive manufacturing (TVAM) [2] to rapidly fabricate perfusable constructs that replicate the intricate tubuloacinar morphology of the pancreatic exocrine niche. This platform provides a biomimetic environment that supports organoid growth and promotes tissue-like organization, offering a more physiologically relevant model for pancreatic disease.

Using a GelMA-based bioink, we printed complex hydrogel architectures including multi-acinar microcavities, directly into perfusable squared chambers equipped with different inlets and outlets. Pancreatic epithelial organoids were introduced through these inlets and successfully colonized the 3D microcavities, adhering to and lining the inner walls to form a biomimetic epithelial layer. In parallel, we fabricated interconnected microchannels and seeded them with human umbilical vein endothelial cells (HUVECs), which formed endothelial monolayers as confirmed by confocal microscopy.

This integrated platform, enabled by TVAM and supported by a recently developed open-source optical simulation framework (Dr. TVAM) [3], establishes a new paradigm for 3D bioprinting within microfluidic systems. By enabling the direct fabrication of perfusable, geometrically complex environments that support multi-cellular seeding and organization, our approach advances the field of biofabrication. The successful integration of organoids and vasculature within these constructs paves the way for more physiologically relevant models, with potential applications in studying early tumorigenesis and evaluating therapeutic responses *in vitro*.

- [1] Handschin, C. et al. "Biotechnological advances in 3D modeling of cancer initiation. Examples from pancreatic cancer research and beyond". *Biofabrication*, **2025**, 17, 022008, doi: 10.1088/1758-5090/adb51c
- [2] Loterie, D., Delrot, P. & Moser, C. "High-resolution tomographic volumetric additive manufacturing". *Nat Commun*, **2020**, 11, 852, https://doi.org/10.1038/s41467-020-14630-4
- [3] Nicolet, B., et al. "Inverse Rendering for Tomographic Volumetric Additive Manufacturing." *ACM Transactions on Graphics (TOG)*, **2024**, 43, 1-17.

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35 D1 -S3 -03

two-photon polymerization, nanoimprint lithography, microfluidics

# ADAPTIVE RESOLUTION TWO-PHOTON POLYMERIZATION AS MASTERING TOOL FOR NANOIM-PRINT LITHOGRAPHY FOR THE FABRICATION OF LARGE-AREA MICROFLUIDIC DEVICES

Stjepan Perak (1), Sonja Kopp (2), Viktorija Jonaityte (2), Marta Bonora (3), Michael Muehlberger (2), Francesco Moscato (3), **Markus Lunzer**\* (1)

- (1) UpNano GmbH, Vienna, Austria.
- (2) PROFACTOR GmbH, Steyr-Gleink, Austria.
- (3) Center for Medical Physics and Biomedical Eng., Medical University of Vienna, Vienna, Austria.

UV-nanoimprint lithography (NIL) is a micro- and nano-replication technology that offers high-resolution and process flexibility [1]. A critical step in the process chain is the production of high-quality masters, which are essential for the fabrication of NIL stamps. We use two-photon polymerization (2PP), a high-precision 3D printing technology to produce various complex masters. To show the potential of combining NIL and 2PP, we investigate microstructured surfaces as antithrombogenic tools. Cardiovascular devices, such as implantable blood pumps, trigger the activation of platelets through repeated contact between blood cells and artificial device surfaces. Microstructures can help reduce platelet adhesion and thus prevents blood clotting on these surfaces. We test the hemocompatibility of microstructured surfaces in both semi-static and dynamic flow conditions. Thus, master microstructures were fabricated using the 2PP system NanoOne 1000 (UpNano) and a 40× objective in Vat mode. The master microstructures and flat reference surfaces, each with an area of 4 x 4 mm<sup>2</sup> (Figure 1a-b), were printed using UpNano's Adaptive Resolution 2PP technology. This approach enables the selective and dynamic application of high-resolution and high throughput printing parameters, significantly reducing print time while preserving localized high-resolution. By combining 2PP and NIL, multiple samples were produced to evaluate the antithrombogenic potential of various micropatterns with blood platelets in low-shear experiments. Dynamic experiments were then performed within microfluidic chips to simulate in vivo pump flow shear conditions. Thus, several 20 x 2 mm<sup>2</sup> large microfluidic devices were fabricated by 2PP and replicated in a manual step & repeat NIL process using PDMS stamps and OrmoComp® as imprint material (Figure 1c). Combing 2PP and NIL allows to obtain many samples with different geometries for single-use experiments as well as the production of complex microfluidic test devices for the investigation of the interaction of blood and microstructures.



Figure 1: 2PP 3D printed microstructures are replicated by NIL to produce microfluidic test devices.

[1] Michael Muehlberger "Nanoimprinting of Biomimetic Nanostructures", *Nanomanufacturing*, **2022**, 2, 17-40, DOI: 10.3390/nanomanufacturing2010002

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36 D1 -S4 -02

Light mediated AM / polycarbonates; extrusion; VAT

## ADDITIVE MANUFACTURING WITH TRIBLOCK POLYCARBONTES

**Emily B. Pentzer**, Chia-Min Hsieh, Mani Sengoden Naushad Ahmed, Donald J. Darensbourg, and Peiran Wei

Texas A&M University, College Station, TX USA

Additive manufacturing has the opportunity to be a disruptive processing technique and enable rapid prototyping and production of bespoke parts on demand.¹ With few exceptions, many feedstocks for additive manufacturing are derived from petroleum and printed parts contribute to the plastics problem, being neither biocompatible nor biodegradable. This presentation will address the development of polycarbonates in additive manufacturing for both extrusion based direct ink write (DIW) and vat digital light processing (DLP).²-⁴ The use of ABA triblock copolymers allows for the impact of polymer architecture and thermal and mechanical properties of each block to be evaluated.

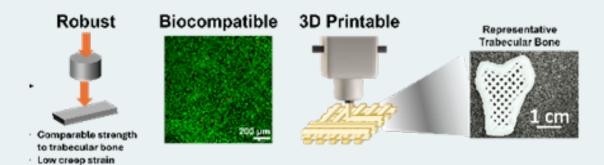


Figure: Triblock polycarbonates can be printed to produce biocompatible materials with tailored mechanical properties.

- [1] Peiran Wei; Ciera Cipriani; Chia-Min Hsieh; Kamani; Simon Rogers; Emily Pentzer. Go with the flow: Rheological Requirements for Direct Ink Write Printability. *Journal of Applied Physics*, **2023**, *134*, 100701. DOI: 10.1063/5.0155896
- [2] Krista Schoonover; Chia-Min Hsieh; Mani Sengoden; N. Ahmed; M. S. Kalairaj; Taylor Ware; D. J. Darensbourg; Emily Pentzer; Peiran Wei. Bridging Polymer Architecture, Printability, and Properties by Digital Light Processing of Block Copolycarbonates. *Chemical Science*, **2024**, *15*, 14228-14240. DOI: <u>10.1039/d4sc04593a</u>
- [3] Peiran Wei; Gulzar Bhat; Ciera Cipriani; H. Mohammad; Krista Schoonover; Emily Pentzer; D. J. Darensbourg. 3D Printing CO<sub>2</sub>-Based Triblock Copolymers and Post-Printing Modification. *Angewandte Chemie*, **2022**, e202208355. DOI: <u>10.1002/anie.202208355</u>
- [4] Chia-Min Hsieh; Mani Sengoden; Soon-Mi Li; Justin Smolen; N. Ahmed; Karen Wooley; Don Darensbourg; Emily Pentzer; Peiran Wei. Printable, Biocompatible, and Bioderived Polymer-Composite Scaffolds. *submitted*

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37 D1 -S5 -01

Light mediated AM / photopolymerization, bioprinting, photoinitiators

## WATER-SOLUBLE RADICAL PHOTOINITIATORS FOR MICROFABRICATED OF 3D PRINTED OBJECTS

Joanna Ortyl (1,2,3), Filip Petko (1,2), Andrzej Świeży (1,2), Mariusz Galek (2), Patryk Szymaszek (1), Agnieszka Sysło (1), Wiktoria Tomal (1), Patrycja Środa (1,2), Myong Joon Oh (1), Kasidid Yaemsunthorn (1)

- (1) Department of Biotechnology, Physical Chemistry Faculty of Chemical Engineering and Technology, Cracow University of Technology Warszawska 24, Cracow 30–155, Poland
- (2) Photo HiTech Ltd., Bobrzynskiego 14, Cracow 30–348, Poland
- (3) Photo4Chem Ltd., Lea 114, Cracow 30–133, Poland

The work concerns the development of new water-soluble type one photoinitiators that enable efficient photopolymerization of hydrogels. The goal is to create tools for precision microfabrication of 3D objects used in tissue engineering and regenerative medicine applications. The photophysical and photochemical properties of the initiators, their ability to generate radicals and their efficiency in printing high-resolution 3D structures were studied. The work highlights the importance of biological compatibility and efficiency under aqueous conditions and visible light.

Research financed within the framework of the competition no. 2024/ABM/03/KPO/ project no. KPOD.07.07-IW.07-0125/24 entitled: "Title of the Undertaking: Luminescent theranostic compounds with anticancer activity, i.e., combination of photodynamic therapy and diagnostics through imaging in a single molecule and development of 3D printed topical micro-needle systems to provide precise individualized cancer therapy" from the National Plan for Reconstruction and Enhancement of Immunity, part of Investment D3.1.1 Comprehensive Development of Research in Medical and Health Sciences, a project funded by the Medical Research Authority.

38 D1 -S6 -01

DAY 1 / TUESDAY OCTOBER 7

Light mediated AM / bioprinting, volumetric, organ-on-chip

## TOMOGRAPHIC BIOPRINTING: A UNIVERSAL APPROACH FOR BIOMIMETIC ORGANS-ON-CHIP

Riccardo Rizzo (1), Viola Sgarminato (1), Felix Wechsler (1), Christophe Moser\* (1)

(1) Laboratory of Applied Photonics Devices, École Polytechnique Fédéral Lausanne (EPFL), Lausanne, Switzerland

Animal testing for drug development and disease modeling is costly and time-consuming, often failing to predict human responses. The FDA Modernization Act 2.0, which includes organs-on-chip (OoC) among the technologies that can be used to determine drug efficacy and safety, represents a promising step towards better clinical mimicry.[1] However, due to the limitations of microsystems technologies, most OoC devices, although aiming to mimic biological tissues, are made of rigid materials (glass, plastics, or polysiloxanes) and feature simplistic 2.5 D models composed of channels with non-physiological square cross-sections, and on a single plane. In this study, we explore the use of tomographic volumetric additive manufacturing (TVAM)[2] to rapidly generate a variety of microfluidic models in soft biological matrices, opening to a new generation of OoCs that better mimics native tissue microarchitecture.

We leverage Dr.TVAM, our recently released open-source optical simulation framework,[3] to perform TVAM on pre-assembled, customized microfluidic systems with flat surfaces, ensuring ease of use and compatibility with standard imaging systems. Importantly, Dr.TVAM enables optimization in overprinting scenarios (printing around pre-existing objects) which is herein used to generate biomimetic vascular networks connected to light-occluding inlets/outlets. This results in leakage-free, contamination-free and ease-of-use TVAM compatible chips.

A wide variety of complex biomimetic microfluidic models, differing in number of channels, size, and network complexity were successfully printed, proving the high versatility of the proposed method. Endothelial and epithelial cells are seeded into the channels and monolayer formation monitored via confocal microscopy. The printing process is shown to be compatible with various crosslinking chemistries (methacrylate, thiol-norbornene, tyrosine dimerization), photoinitiating systems (Type I and Type II initiators), and biological matrices (PEGs, gelatin, hyaluronic acid, dECM). This approach paves the way to a new generation of human OoCs that better mimic native tissue microarchitecture, and (patho)physiology.

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39 D1 -S5 -02

Light mediated AM

Shape-Memory, Soybean oil, DLP printing

## DESIGN AND FABRICATION OF BIO-BASED MATERIALS FOR SHAPE MEMORY 3D PRINTING

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The versatility of polymers has driven the development of numerous synthetic materials, most of which originate from petroleum-based sources. However, in recent years, there has been growing interest in renewable-sources based polymers. Further, technological advanced incresasingly demand advanced materials with funstional and stimuli-responsive characteristics, such as shape memory polymers (SMPs), with the ability to "memorize" a permanent shape, be temporarily programmed into different forms, and recover their original shape when exposed to external stimuli such as temperature [1]. When SMPs are produced through 3D printing techniques like vat photopolymerization, specifically digital light processing (DLP), the time response is integrated into the material's behaviour, leading to the innovative field of 4D printing [2].

In this study, we present the development of formulations based on epoxidized-acrylated soybean oil (AESO) and isobornyl methacrylate (IBOMA), both derived from renewable sources. These formulations were synthesized in various molar ratios and combined with different photoinitiators. We evaluated their reactivity, rheological behavior, and optimal printing conditions. The resulting printed samples were analyzed for their thermal, thermomechanical, mechanical, and shape memory properties, as well as their capability to form complex structures. Our findings demonstrate that these formulations are suitable for low-volume DLP printing, offering a promising alternative to conventional fossil-based commercial resins. Notably, the formulation with a 1:5 AESO:IBOMA molar ratio, combined with 1 phr of Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), exhibited shape memory effect at working temperatures below 100°C, recovering 100 % of the shape in a total time of 145 s (*Figure 1*).

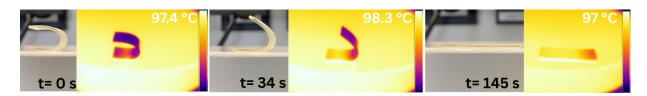


Figure 1: Demonstration of shape recovery form for the sample with 1:5 AESO:IBOMA molar ratio to 1phr of BAPO.

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40 D1 -S6 -02

Light mediated AM

Volumetric 3D-printing, radiopaque PCL, in vivo tracking

# FROM LIGHT TO LIFE: RAPID VOLUMETRIC 3D-PRINTING AND REAL-TIME TRACKING OF BIODE-GRADABLE SCAFFOLDS.

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Poly( $\epsilon$ -caprolactone) (PCL) is ideally suited for hard tissue engineering, yet real-time *in vivo* degradation monitoring remains a major challenge. Here, we present the first radiopaque PCL scaffolds that enable non-invasive, long-term tracking using micro-computed tomography ( $\mu$ -CT). This was achieved by covalently integrating the iodinated contrast agent (CA) 5-acrylamido-2,4,6-triiodoisophthalic acid (AATIPA) into a thiol-ene crosslinked PCL network [1-3], ensuring persistent radiopacity without leaching.

To fabricate these scaffolds with unmatched speed and precision, we employed volumetric additive manufacturing (VAM)—a cutting-edge light-based 3D-printing technology that creates entire 3D-structures in one single step. By projecting 2D-light patterns into a rotating resin vial, VAM enables rapid, high-resolution production of patient-specific implants, far surpassing traditional extrusion and point-by-point or layer-based techniques such as SLA, 2PP or DLP.

The resulting scaffolds maintained radiopacity over time and supported continuous μ-CT imaging of structural changes and degradation. This platform offers a powerful new strategy for creating smart, imageable, and clinically translatable biodegradable implants. For this research, Astrid Quaak gratefully acknowledges funding from Research Foundation Flanders (FWO, 1SHDP24N).

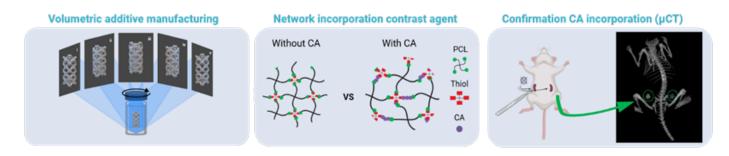


Figure: VAM-printing of radiopaque PCL scaffolds, enabling μ-CT-based in vivo degradation tracking.

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41 D1 -S5 -03

Extrusion based AM

Hot-melt extrusion, Polymer blends, Crosslinked networks

## EXPLORING PHASE SEPARATION, ALIGNMENT AND MOLECULAR ORGANIZATION IN 3D PRINTED POLYMER BLENDS AND CROSSLINKED NETWORKS

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Understanding the impact of extrusion-based additive manufacturing on the resulting microstructure of 3D printed samples is crucial to modulate their properties. The objective of our work is to investigate the behavior of blended thermoplastic and pi-conjugated blends using hot-melt extrusion, where the thermoplastic polymer acts as a matrix, which can eventually be replaced by a crosslinked network. More specifically, the first model system studied comprises a thermoplastic matrix, poly( $\epsilon$ -caprolactone (PCL) and poly(3-hexylthio-phene-2,5-diyl (P3HT). Rheological, spectroscopic and atomic force microscopy analyses conducted on the formulations and the 3D printed samples reveal that the blended formulations exhibit a composite-like behavior within the studied temperature range (printability window), with the aggregation state of P3HT remaining largely unaffected by the hot-melt extrusion process. [1,2] We are currently extending our exploration to other categories of matrices, including photo- and thermally crosslinked ones as model systems, which impact the phase separation, alignment and molecular organization of the components of the blends observed in the samples. Overall, we demonstrate that the use of a matrix to facilitate additive manufacturing of  $\pi$ -conjugated materials represents a promising strategy for fabricating 3D printed functional architectures, particularly within the framework of structure–processing–property relationships.

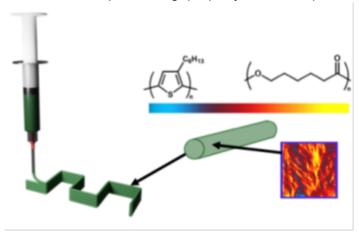


Figure: Investigation of the phase separation in hot-melt extruded PCL:P3HT blends

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42 D1 -S6 -03

Light mediated AM

carbon dots, photopolymerization, photocatalysts

## DEVELOPMENT OF CARBON DOT-BASED PHOTOINITIATING SYSTEMS FOR 3D PRINTING TECHNOLOGIES

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Carbon dots represent chemically stable nanomaterials that exhibit a range of properties, making them promising materials for use in both cationic and free radical photopolymerization processes. The use of environmentally friendly, green substrates for synthesising carbon dots is particularly beneficial, as it enables a simple and economical synthesis process with minimal environmental impact [1]. In this study, a one-step, solvent-free synthesis of carbon dots derived from citric acid is described. The obtained nanomaterials were purified to eliminate residual impurities and fluorophores [2]. Spectroscopic analyses and kinetic studies of the photopolymerization process were conducted to assess the impact of carbon dots on both the reaction kinetics and the material properties. Three-dimensional objects were successfully produced by digital light processing (DLP) printing [3]. The study's results highlight the significant potential of citric acid-derived carbon dots as components of photoinitiating systems for 3D printing. The developed methodology represents a step towards the development of efficient and sustainable strategies for the synthesis and application of carbon dots.

The research was financed by the Medical Research Agency under the project 'Onco-Lumi-3D,' No. KPOD.07.07-IW.07-0125/24, from the National Recovery and Resilience Plan (NRRP) program, Component D: Efficiency, Accessibility, and Quality of the Health-care System, Investment D3.1.1: Comprehensive Development of Research in Medical and Health Sciences. The NRRP program was funded by the European Union Recovery Instrument (NextGenerationEU) through the Recovery and Resilience Facility (RRF) for the period 2021–2026.

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43 D1 -S5 -04

Light mediated AM

SLA bioprinting, dECM bioinks, Stomach models

## DEVELOPMENT OF DECELLULARIZED EXTRACELLULAR MATRIX BIOINKS FOR SLA BIOPRINTING OF GASTRIC IN VITRO MODELS

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Gastric cancer is the fifth most common malignancy worldwide [1], primarily caused by recurrent *Helicobacter pylori* infection, lifestyle, and genetic factors [1]. Current *in vitro* models of the gastric mucosa lack the complexity of native tissue, limiting their relevance for studying the disease. This project aims to improve *in vitro* gastric mucosa models by combining high-resolution stereolithography (SLA) bioprinting with stomach-derived decellularized extracellular matrix (dECM). This approach replicates gastric pit geometry and provides a biologically relevant environment for cells. Figure 1 illustrates the target model. Porcine stomach tissue was decellularized to obtain three bioink bases: whole stomach (W-dECM), tunica muscularis (T-dECM), and mucosa (M-dECM). These were methacrylated for photocrosslinking compatibility with SLA printing. Functionalization was assessed by ¹H-NMR, and resulting dECM-MA hydrogels were characterized by photorheology to evaluate crosslinking kinetics and viscoelasticity. Preliminary biological testing confirmed the hydrogels are non-toxic and support cell adhesion and proliferation. Printing parameters were initially optimized using cell-free inks, based on methods from literature [2,3], with computational analysis and a design of experiments (DOE) approach. Selected compositions and settings will be used for future cell-laden constructs.

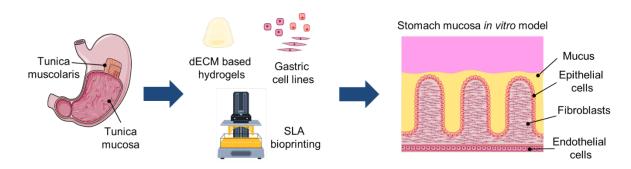


Figure: Graphical abstract of the proposed gastric in vitro model production.

[1] A.P. Thrift, T. N. Wenker, H.B. El-Serag, "Global burden of gastric cancer: epidemiological trends, risk factors, screening and prevention", *Nat Rev Clin Oncol*, **2023**, 20, 338–349, <a href="https://doi.org/10.1038/s41571-023-00747-0">https://doi.org/10.1038/s41571-023-00747-0</a>

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44 D1 -S6 -04

Light mediated AM / conductive polymers, ion conductive, functional devicess

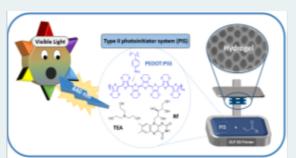
## 3D PRINTING OF IONIC AND ELECTRONIC CONDUCTIVE POLYMERS

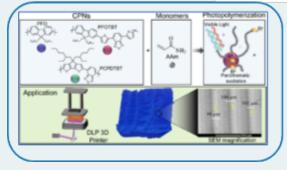
### **David Mecerreyes** (1)

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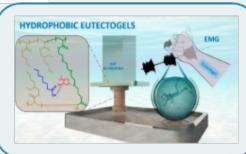
In this presentation we will show our recent developments in the additive manufacturing 3D printing of functional polymers. Our main goal is to develop active polymers to be used in functional devices. For this purpose, in the last years we optimize the 3D printing of ionic conductive polymers, electronic conductive polymers and optically active polymers. During our presentation the 3D-4D printing of different polymer systems will be showed as well as its different applications in bioelectronic devices, batteries or smart windows.

- Conductive polymers such as poly(3,4-ethylenedioxy thiophene) PEDOT.[1]
- Ionic conductive systems such as hydrogels, iongels and eutectogels. [2]
- The use of semiconducting polymer nanoparticles in 3D printing and its use in obtaining hydrogels with photodynamic properties. [3]









- [1] a) M. Criado et al. "Additive Manufacturing of Conducting Polymers: Recent Advances, Challenges, and Opportunities", *ACS Applied Polymer MaterialsI*, **2021**, 3,6, 2865-2863, DOI: <u>10.1021/acsapm.1c00252</u> b) N. Lopez-Larrea et al. "Fast Visible-Light 3D Printing of Conductive Polymer Hydrogels" *Macromolecular Rapid Communications* **2024**, 45, 1, 2300229
- [2] M.L. Picchio et al. "Mixed Ionic and Electronic Conducting Eutectogels for 3D printable sensors and Bioelectrodes" *Advanced Materials Technologies* **2022**, 7, 10, 2101680
- [3] a) G.E. Cagnetta et al. "Conjugated polymer nanoparticles as visible light panchromatic photoinitiators 3D printing of acrylic hydrogels" *Macromolecules* **2024**, 57, 1, 78-87, b) M. Criado et al. *Materials Horizons* **2025**, 12, 2524-2534. 10.1039/D4MH01802H

45 D2 -PL

Extrusion based AM / tissue regeneration, 4D printing, 3D printing

## FROM STATIC TO DYNAMIC: 3D AND 4D PRINTED MATERIALS FOR TISSUE REGENERATION

### Sandra Camarero-Espinosa\*

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- (2) IKERBASQUE, Basque Foundation for Science, 48009, Bilbao, Spain

3D printing emerged over 2 decades ago and quickly started to find application on the biomedical field. Early studies exploited 3D printing as tool to rapidly and reproducibly fabricate scaffolds that could withstand the loads applied to the targeted tissue and to guide cell attachment, distribution and, eventually, differentiation. Cells are capable of sensing characteristics such as patterned (bio)chemical, topographical and mechanical cues over their microenvironment and thus, these parameters have lately been introduce into 3D printed scaffolds. However, the lateral spacing and dimensions of the presented cues have to be carefully designed to achieve an efficient cell-material interaction.[1-3] Despite the knowledge generated so far, the difficulties to translate these systems to clinical environments have pushed us to slowly shift to other approaches based on the stimulation of cells by mimicking their function in the body.[4] Thus, a 4D or time dependant control of material properties can be achieved by the exploitation of sonic, magnetic or biological stimuli to biomaterial scaffolds that is then translated to cells.

We will review these two concepts highlighting a series of combined scaffold biofabrication approaches (3D printing, electrospinning, self-assembly, etc) that lead to the fine control of the cell microenvironment, as well as the development of smart materials responsive to sonic, magnetic or biological stimuli and their implication in tissue regeneration.

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- [2] Camarero-Espinosa S, et al., Advanced Healthcare Materials. 2023, 12, 2203023.
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46 D2 -S7 -01

SLS or Powder Bed Fusion AM/ PBF Feedstock design

## TAILOR MADE POLYMERIC FEEDSTOCKS FOR POWDER BED FUSION

## Kaizhong Guan, Akan George, Mahmud Hassan, Mark D. Dadmun

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Powder Bed Fusion (PBF) is crucial technology in polymeric additive manufacturing. However, there exist limited polymers available for PBF, where most efforts use nylon. This work seeks to understand and control the rational development of scalable processing protocols that use liquid-liquid phase separation (LLPS) to reproducibly fabricate polymer powders that are suitable for powder bed fusion from a broad range of polymers, including those in the waste stream. In this process, the solvent quality of a polymer solution is reduced by a temperature quench or addition of non-solvent, causing the polymer to precipitate via phase separation. This results in the formation of polymer particles suitable for PBF that can be easily recovered, which also enables reclamation and *reuse* of solvent. Understanding the fundamental driving forces that guide the variation of final particle size with polymer solution concentration, polymer crystallinity, solvent type, and quench temperature provides pathways to rationally control the size and manufacturability of the powder.

Work in our group has focused on providing fundamental insight into the powder formation process, to offer guiding principles to design suitable precipitation protocols for a broad range of polymeric materials. Initial studies clearly show that droplet coalescence governs the powder formation process in creating polypropylene powders [1] (*J. Polym. Sci,* 62, 2605). However, expansion of this protocol to other polyolefins, such as HDPE, emphasizes the importance of balancing the competition between precipitation of the polymer and the crystallization of the polymer from solution. (*Figure*) Thus, the time evolution of the solution as it goes from the cloud point temperature down to the crystallization temperature defines the thermodynamic trajectory that governs powder formation. With this guiding principle, processing protocols have been developed to create powders that are suitable for powder bed fusion from polymer blends, various grades of high-density polyethylene, and polymers from the waste stream, including PET, HDPE, PP.

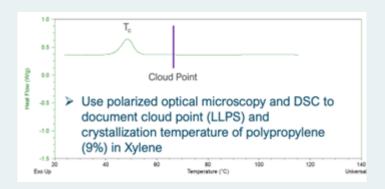


Figure: Cloud Point and Crystallization of PP from Solution, with SEM of PP powder (inset).

[1] Kaizhong Guan, Jackson S. Bryant, Akan George, Michael J. Bortner, Christopher B. Williams Mark D. Dadmun "Expanding polymeric feedstocks for powder bed fusion via rational control of liquid–liquid phase separation" *J. Polym. Sci,* **2024**, 62, 2605-2615 <a href="https://doi.org/10.1002/pol.20230286">https://doi.org/10.1002/pol.20230286</a>

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47 D2 -S8 -01

Light mediated AM / aerogels, sol-gel, alkoxysilanes

## SILICA AEROGELS BY 3D PRINTING VAT PHOTOPOLYMERIZATION

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- (2) POLYMAT, Basque Center for Macromolecular Design and Engineering, Donostia-San Sebastián, Spain.
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3D printing enables the precise and scalable fabrication of customized objects with personalized designs. Among the different 3D printing techniques, digital light processing (DLP) attracts special attention because a liquid photopolymer resin is selectively cured and solidified layer by layer using a light source (UV) creating a solid object. This technology represents a new challenge in the development of new materials, which will be based on the design and formulation of new photopolymerizable resins. In this project, VAT polymerization has been considered to develop high performance aerogels based on photopolymerization and sol-gel approach [1]. To achieve this, optimized acrylate-modified alcoxysilane sols have been gelified through an acid-base catalytic reaction, and subsequently VAT photopolymerized to obtain the final object (Figure 1). Finally, the printed objects were characterized to assess their structural and thermal properties, and potential application areas such as catalysis for these innovative materials were explored. Knowing the mechanisms involved in the sol-gel transition, the viscosity of the resin at each stage of the transformation, and the kinetics of photopolymerization are key points that highlights the key role of rheological control in additive manufacturing of advanced functional materials.

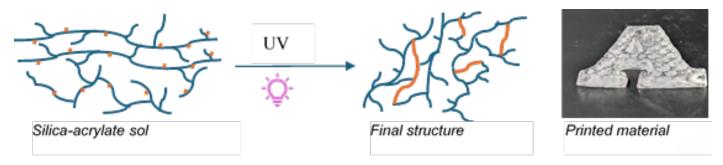


Figure 1: Established printing scheme for alkoxysilane printing

[1] W. Zou, Z. Wang, , Z. Qian, J. Xu, N. Zhao, *Advanced Science* ,**2022**, 9, 36, DOI: 10.1002/advs.202204906

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48 D2 -S7 -02

Light mediated AM / recycling, sustainability, end-of-life

## ADVANCED STRATEGIES FOR RECYCLING OF FUNCTIONAL 3D PRINTING MATERIALS

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- (2) School of Molecular Sciences, Biodesign Center for Sustainable Macromolecular Materials and Manufacturing, Arizona State University, Tempe, Arizona 85281, United States.
- (3) Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, Liege, 4000 Belgium.

3D printing technologies such as vat photopolymerization (VP) that rely on making permanently crosslinked structures are inherently non-circular due to their lack of post-use reprocessability. To realize more sustainable approaches for a future materials economy, new techniques must be devised with built-in-circularity. Under this new mindset of turning waste into valuable resources, it is vital to ensure that printed parts are designed to be recycled or reused with minimal energy into valuable materials or photoresins at the end-of-life (EOL). Two such approaches are presented in this communication. First, the use of dissociative bonds in 3D printed objects designed with dynamic reaction-induced phase-separation (DRIPS) allows the mechanical recycling of the crosslinked structures while enabling pluripotent behavior. Second, printing of polymer latexes containing high-molecular weight thermoplastics enables their re-extrusion and re-molding, opening new manufacturing and EOL options for these unique engineering materials.

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- [2] Jon Ayestaran, Xabier Lopez de Pariza, Fernando Vidal, Clara Vazquez-Martel, Alodi Pascal, Siwei Yu, Miren Aguirre, Alshakim Nelson, Jose R. Leiza, Eva Blasco, Timothy E. Long,\* Robert H. Aguirresar-obe,\* Haritz Sardon\*", *Advanced Functional Materials*, **2025**, (in press)

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49 D2 -S8 -02

Light mediated AM

## 3D printing *via* polymerization-induced microphase separation using acrylate macromonomers instead of macroRAFT agents

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Additive manufacturing, commonly known as 3D printing, has emerged as a versatile platform for fabricating materials with complex shapes and customizable properties. [1] Recent advances focusing on multiscale structural control, particularly at both the nano- and macroscale, have further expanded its potential. [2] Building on the early work of Seo and Hillmyer on polymerization induced microphase separation (PIMS)[3], novel 3D printing technology by integrating photoinduced reversible addition—fragmentation chain-trans fer (RAFT) with PIMS in photocuring 3D printing, enabling disordered nanostructured materials. [4] Traditionally, PIMS utilizes macromolecular chain transfer agent (macroCTAs) synthesized by RAFT polymerization. However, RAFT-based PIMS can introduce undesirable color and odor into the final materials. To address these limitations, the use of macromonomers, polymers terminated with acrylate or methacrylate groups, were explored as alternatives to usual macroCTAs. [5]

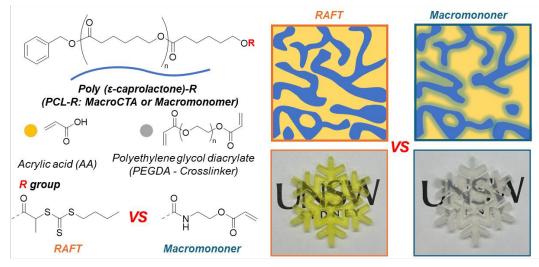


Figure: Illustration of PIMS Nanostructures: Classical RAFT macroCTA vs. Macromonomer Strategy.

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Extrusion based AM

## HYDROGELS, COVALENT NETWORKD, METALS

## RHEOLOGICAL INSIGHT ON 3D PRINTABLE DYNAMIC HYDROGELS

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- (2) CIDETEC, Basque Research and Technology Alliance (BRTA) Parque Científico y Tecnológico de Gipuzkoa, Miramon Pasealekua, 196, 20014Donostia-San Sebastián.
- (3) IIS Biogipuzkoa, Po Dr. Beguiristain s/n, 20014 Donostia–San Sebastián

The dynamic covalent bonds are mechanically stable but capable of exchanging, dissociating, or switching in response to external stimuli, providing the material with a responsive and adaptive nature, which gives hydrogels self-healing properties, injectability and suitability for post-processing and additive manufacturing. The study investigated the dynamic response of hydrogels based on thiol-functionalized hyaluronic acid formulated with coordinative gold (I) or silver (I), that meet all the requirements to be printed without the need for external stimuli. At rest, the hydrogel viscoelastic network was characterized by good macroscopic mechanical stability. The structure evolved to a liquid network under strain, facilitating the deformability and printability of these materials. The rheological analysis of these hydrogels will be discussed. Oscillatory shear in the linear viscoelastic regime (SAOS) and steady flow curves accounted for the soft-solid and still liquid nature of the network. In parallel superposition experiments, the steady and oscillatory shear motions were applied simultaneously, which allowed detection and quantification of the flow induced acceleration of the network relaxation modes. The specific signature of the large amplitude oscillatory shear (LAOS) was also dependent on the different interactions. The nonlinear parameters provided useful information related to the printability criteria of these materials.

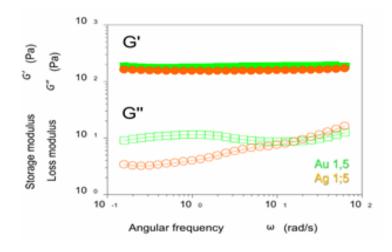


Figure 1: Gel like viscoelasticity of hyaluronic based disulfide-Au/ Ag dynamic hydrogels

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51 D2 -S8 -03

Light mediated AM / photoinitiators, photopolymerization, 3D printing

## NEW PHOTOINITIATING SYSTEMS FOR HIGH PERFORMANCE MATERIALS AND 3D PRINTING

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**Abstract:** Photopolymerization technology has been developing steadily benefiting from the characteristics of spatial and temporal controllability, **environmental protection**, and efficient processes.[1,2] However, the polymerization in shadow areas remains a huge challenge. In this work, new photoinitiating systems for radical, cationic or hybrid polymerization will be presented for different spectral ranges: near UV, visible, Near Infrared. **New non-cytotoxic photoinitiators for 3D printing will be presented.** This work will be extended to dual-cure processes as well as photopolyaddition reactions. Better depths of cure can be obtained. Some applications for coatings, 3D printing and photocomposites will be provided. The mechanical properties of the generated polymers/composites will be also investigated.

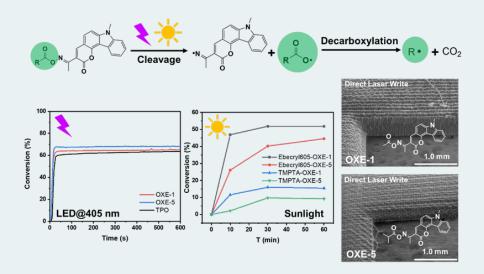


Figure. Example of new high performance photoinitiating systems.

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52 D2 -S7 -04

Extrusion based AM / Functional composite, toxicity reduction, rheology

## ADDITIVE MANUFACTURING FOR SELECTIVE ENVIRONMENTAL REMEDIATION

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There is significant interest to enable additive manufacturing (AM) of dense polymer matrix suspensions with high loading levels of rigid particles for enhanced functionality. Coupled with growing interest in unique methodologies for environmental remediation through selective contaminant adsorption/removal and/or degradation, material extrusion AM offers significant promise for on-demand, retrievable, and reusable technologies. This talk will present two case studies with different remediation mechanisms. Approach 1 investigates selective photocatalytic degradation of microcystin toxin associated with 3D printing of immobilized TiO2. Photocatalytic performance studies indicate printed composites retained comparable dye degradation efficacy to free TiO2 after UV exposure. The TiO2 composites further reduced the Microcystin toxin released from the cyanobacterium Microcystis aeruginosa below toxicity thresholds [1]. Approach 2 investigates contaminant adsorption using 3D printed polymer-zeolite composites to both isolate and enhance ammonia adsorption kinetics. Results demonstrated that incorporating different zeolite loadings (8-32% w/w) in printed, submersible structures improved ammonia removal, with the ability to reduce ammonia below toxic levels [2]. Through the adsorption studies, it was found that tuning processing parameters significantly alters the "quality" of the print and corresponding ammonia adsorption kinetics. These findings lead to an important question about how to broadly define "printability" and "requirements" for "successful" printing [3].

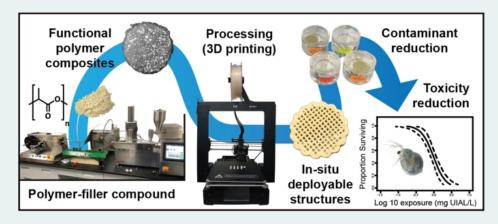


Figure: 3D printing for selective environmental remediation. From Kennedy et al. [2].

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53 D2 -S8 -04

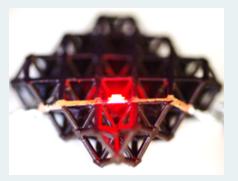
Emerging AM technologies / multi-modal, multi-axis, high-performance polymers

# PRINTING OUT OF THE BOX: MAKING THE IMPOSSIBLE BY MULTI-MATERIAL, -MODAL, -AXIS ADDITIVE MANUFACTURING

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Additive Manufacturing (AM) has been often hyped as an all-in-one manufacturing process capable of directly fabricating end-use products within a single step. However, this holds AM to a higher standard than all other manufacturing processes, which require additional processing steps to refine material properties, surface finish, etc. To fully realize the potential of AM, the processes are in need of further advancements in material selection, performance, and process capability, which can be aided by additional post-processing steps. The aim of this talk is to highlight how multi-functionality can be achieved by expanding our view of AM processing to expand outside of the printer's box to incorporate multiple AM modalities and post-processing steps. Examples include enabling AM of (i) hybrid electronics via photopolymerization of fully-aromatic polyimides [1], (ii) multifunctional high-performance elastomers via printed latexes [2], (iii) composite structures featuring optimized topology and toolpathing via multi-axis robotic deposition [3], and (iv) complete mechatronic systems via autonomous, robotic, hybrid AM [4].



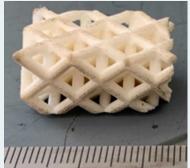




Figure: Fabricating multi-functional parts with multi-modal additive manufacturing

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54 D2 -S9 -01

Light mediated AM / Multi-material 3D printing, greyscale lithography, multi-temperature printing

## EXPANDING MATERIAL FRONTIERS IN 3D PRINTING VIA MULTI-MATERIAL STEREOLITHOGRAPHY

## **Katharina Ehrmann** (1)

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Modern-day devices such as medical prostheses or information storage devices typically require the intricate interplay of several material properties to operate. Manufacturing of such macroscopic multi-property parts typically relies on several manufacturing techniques and corresponding engineering solutions to assemble the multi-property constructs from several individually manufactured single-property parts.

Therefore, true multi-material printing from one photosensitive resin has recently become one of the focus areas in the light-based 3D printing community. This talk will explore the advancement of multi-material printing beyond the current scope. New interpretations of the traditional multi-material printing techniques greyscale and multi-wavelength printing will be presented alongside a new technique, multi-temperature printing, to differentiate between several antagonistic material properties (hard/soft, degradable/non-degradable, crystalline/non-crystalline) in micro- and macroscale-objects.<sup>1-3</sup>

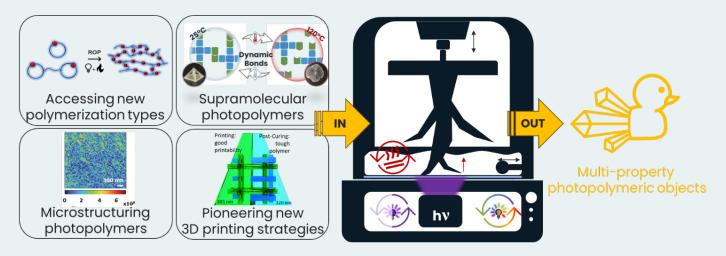


Figure: Greyscale, multi-colour and multi-temperature 3D printing strategies for micro- and macroscopic multi-property objects

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- [2] Xingyu Wu,<sup>\$,\*</sup> Katharina Ehrmann,<sup>\$,\*</sup> C.T. Gan, Benjamin Leuschel, Fred Pashley-Johnson, Christopher Barner-Kowollik\* "Two Material Properties from One Wavelength-Orthogonal Photoresin Enabled by a Monochromatic Laser Integrated Stereolithographic Apparatus (Mono LISA)", *Adv. Mat.* **2025**, e2419639, DOI:10.1002/adma.202419639
- [3] Michael Göschl,<sup>\$</sup> Dominik Laa,<sup>\$</sup> Thomas Koch, Evan Constable, Andrei Pimenov, Jürgen Stampfl, Robert Liska, Katharina Ehrmann\* "Two for one: Semi-crystalline and amorphous materials via multi-temperature 3D printing from one formulation." *Preprint, ChemRxiv.* **2025**, DOI:10.26434/chemrxiv-2025-kc7l8 10.26434/chemrxiv-2025-kc7l8

55 D2 -S10 -01

Light mediated AM / Cationic photopolymerization, photoinitiators, cationic vat photopolymerization

## STILBENE-BASED IODONIUM SALTS AS ONE-COMPONENT PHOTOINITIATORS WITH INCREASED OUANTUM YIELD OF ACID GENERATION FOR CATIONIC VPP 3D PRINTING

**Filip Petko** (1,2), Magdalena Jankowska (1), Mariusz Galek (2), Małgorzata Noworyta (1), Roman Popielarz (1), Joanna Ortyl (1,2,3)

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<sup>2</sup> Photo HiTech Ltd., Bobrzyńskiego 14, 30-348 Cracow, Poland

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New iodonium salts based on stilbene-derived chromophores with significantly improved photoinitiating properties are presented. Their high photoinitiating performance is ensured by the extended conjugated double bond system which provides major improvement in quantum yield of superacid generation, while maintaining absorption properties in UV-A and visible light [1]. The newly developed iodonium salts exhibit photoinitiating activity toward cationically polymerizable monomers such as cyclic epoxy monomers, oxetanes and glycidyl ether monomers under the irradiation by light-emitting diodes (LEDs) emitting at 365, 405 and even 430 nm, with no photosensitizing additives. Commercial one-component photoinitiators based on diaryliodonium salts are inactive under those irradiation conditions. Such high photoinitiating activity allows these salts to be used as one-component photoinitiators in cationic vat 3D printing of nanocomposites at ambient temperature.

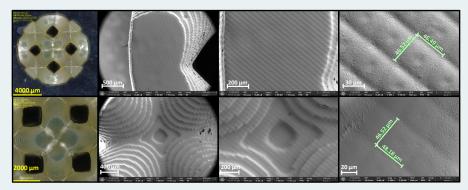


Figure: Optical microscope and SEM images of a 3D print obtained using 0.5%wt. of the developed iodonium salts.

[1] F. Petko, M. Jankowska, M. Galek, M. Noworyta, R. Popielarz, J. Ortyl, "One-Component Stilbene-Based Iodonium Photoinitiators with Increased Photoacid Quantum Yield for Cationic Vat 3D Printing", *Macromolecules*, **2024**, 57, 24, 11639–11657, DOI: 10.1021/acs.macromol.4c01692

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Research financed within the framework of the competition no. 2024/ABM/03/KPO/ project no. KPOD.07.07-IW.07-0125/24 entitled: "Title of the Undertaking: Luminescent theranostic compounds with anticancer activity, i.e., combination of photodynamic therapy and diagnostics through imaging in a single molecule and development of 3D printed topical micro-needle systems to provide precise individualized cancer therapy" from the National Plan for Reconstruction and Enhancement of Immunity, part of Investment D3.1.1 Comprehensive Development of Research in Medical and Health Sciences, a project funded by the Medical Research Authority.

56 D2 -S9 -02

Extrusion based AM / FLM process, thermodiagnostics, defects

## IR THERMODIAGNOSTICS OF FLM PROCESS

Zdeněk Veselý (1), Vladislav Lang (1), Jiří Tesař (1), Tomáš Kohlschütter (1), Jan Klepáček (1)

(1) University of West Bohemia, New Technologies – Research Centre, Pilsen, Czech Republic.

The contribution refers to the developed IR thermodiagnostics methodology and complex measurement system for FLM based 3D printing technology. Competencies of our research team [1] are in the IR technologies. We have a long term experience with IR thermodiagnostics, we are using and improving our own thermographic software with specific functions for science and research, we develop specialized IR measurement systems for diagnostics of thermal processes and thermal conditions. As a part of the OPTHERM project [2], a specialized measurement system for IR thermodiagnostics of the FLM printing process was developed.

The measurement system is composed of hardware and software parts. The hardware part includes multiple miniature IR cameras and mini computer. The software part consists of thermographic software LabIR OPTHERM, which runs on a mini computer. The developed IR thermodiagnostics methodology is used for local (small area) and global (large area) thermodiagnostics of the printing process. It enables both online temperature diagnostics of the printed component and detection of the most common types of defects during 3D printing.

The developed system can be used to optimize 3D printing process to achieve the correct temperature in the bonding zone and thus to improve the bonding of layers for higher mechanical strength of printed components. The system can be used for on-line control of the printing process, on-line detection of defects and to document the temperature history of the component printing process in the sense of documenting the quality of production.



Figure: Complex measurement system with software LabIR OPTHERM for IR thermodiagnostics of FLM 3D printing process

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57 D2 -S10 -02

Light mediated AM /

Digital light processing, soy protein, biocompatible scaffolds

## BIOCOMPATIBLE SOY PROTEIN-BASED RESINS FOR HIGH PRECISION DLP 3D PRINTING IN TIS-SUE ENGINEERING

<u>Maialen Uribarrena</u> (1), Teresa Carranza (1), Iraia Osquila (1), Ainhoa Irastorza (2), Koro de la Caba (1,3), Pedro Guerrero (1,3,4)

- (1) University of the Basque Country (Biomat group), Donostia San Sebastian, Spain.
- (2) Biogipuzkoa Health Research Institute, Tissue Engineering Group, Donostia-San Sebastián, Spain
- (3) BCMaterials, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain.
- (4) Proteinmat Materials SL, Donostia-San Sebastián, Spain.

Digital Light Processing (DLP) 3D printing enables the fabrication of highly precise structures, offering great potential for biomedical applications. In this work, 25, 40, and 50 % (w/v) soy protein isolate (SPI) was incorporated into a photocurable resin to develop biocompatible inks. These inks exhibited suitable rheological properties, maintaining viscosities below 10 Pa·s across a range of shear rates and, thus, enabling efficient 3D printing of cylindrical and rectangular scaffolds with high shape fidelity. FTIR analysis revealed changes in the intensity of the bands, suggesting interactions between SPI and the resin. Mechanical testing demonstrated compression modulus around 1 kPa, in the value range of cartilage modulus, with cohesiveness values near 1, indicating complete shape recovery after deformation. Cytocompatibility assays were performed using human fibroblasts (HS27) and confirmed cell viability, reaching values of 96 % after 72 h. These results highlight the potential of SPI-based resins as customizable inks for 3D printed scaffolds.

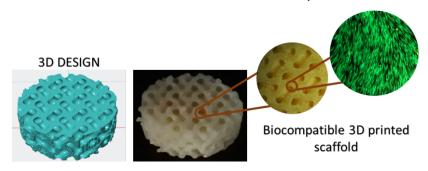


Figure: 3D design and the 3D printed scaffold with the performed live/dead assay.

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Light mediated AM /

biomaterials - polymers - synthesis

## **3D-PRINTING OF NIPU BIOMATERIALS**

## **Christine Jerome**

## **DISCLAIMER**

The abstract is not included as per author's request.

59 D2 -S10 -03

Light mediated AM

Nitroxide mediated photopolymerization, Two-photon polymerization, Surface Modification

# ADVANCES IN NITROXIDE MEDIATED PHOTOPOLYMERIZATION: TOWARD LIVING 3D MICRO AND MACRO SURFACE FUNCTIONALIZATION

### **Didier Gigmes**

Aix-Marseille University, CNRS, Institut de Chimie Radicalaire UMR7273, Marseille, France

Radical photopolymerization, particularly two-photon stereolithography (TPS), has become a key technique for fabricating complex 3D micro- and macro-structures with high spatial resolution. However, conventional free-radical photopolymerization results in "dead" polymer chains, limiting post-surface modifications. To address these drawbacks, photo-controlled reversible deactivation radical polymerization methods have emerged, enabling the creation of "living" polymer networks and further surface modification.[1] In this context, nitroxide-mediated photopolymerization (NMP2) offers a metal-free, efficient strategy with spatio-temporal control. Recently, we developed an in situ NMP2 strategy by incorporating into an acrylate resin a specifically designed photosensitive nitrone for surface reconfiguration under near-infrared light.[2] In addition, we synthesized a photosensitive alkoxyamine, capable of efficient two-photon activation and subsequent surface functionalization of microstructures.[3] In this communication, we will discuss both strategies, with a focus on the synthesis and characterization of the obtained materials.

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60 D2 -S9 -04

Light mediated AM / digital light processing, biodegradable polymers, personalized medicine

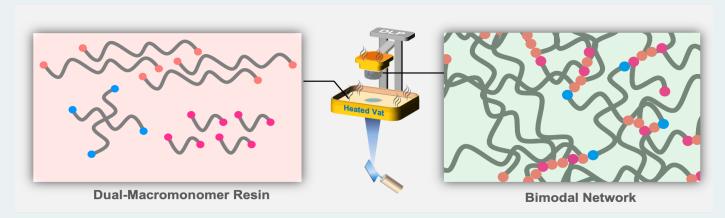
## DIGITAL LIGHT 3D PRINTING OF BIODEGRADABLE POLYMERS

## **Yinyin Bao** \* (1,2)

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- (2) Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland.

#### **Abstract**

Additive manufacturing, with its revolutionary digital fabrication methods, has brought tremendous impact on numerous fields including energy and chemical engineering, soft robotics, and biomedicine. Due to its high printing resolution, fast printing process, and flexibility in material design, vat photopolymerization 3D printing methods—especially digital light processing (DLP)—has attracted widespread interest and shown enormous potential in personalized medical devices and tissue engineering. [1,2] However, biocompatible and biodegradable materials available for these technologies that can provide excellent mechanical properties are still limited. Commonly used printing materials typically utilize oligomers and a large amount of diluents to prepare photopolymerizable resins to meet required printing parameters, and their comprehensive performance is difficult to meet practical application needs. This presentation will focus on the macromolecular design and engineering involving biodegradable photopolymers, macrophotoinitiators and resin formulations (Figure 1) in combination with heat-assisted DLP, to facilitate the application of vat photopolymerization in personalized medical implants, bioactive scaffolds, drug delivery systems and 4D printed smart devices. [3-5]



**Figure 1.** Illustration of resin formulation including dual macromonomers and macrophotoinitiator for digital light 3D printing.<sup>[3]</sup>

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61 D2 -S10 -04

Light mediated AM / Keywords: Sustainability, Additive Manufacturing, Multimaterials

## PRINTING MILK: EXPLOITING THE VERSATILITY OF MAILLARD REACTION IN LIGHT-PRINTABLE AQUEOUS DISPERSIONS FOR THE PREPARATION OF HIGH-PERFORMANCE BIOMATERIALS

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The development of sustainable resins for high-resolution additive manufacturing is often limited by the need to balance printability, mechanical performance, and material origin. In this work, we explore a biobased photocurable formulation that incorporates naturally derived components into a printable matrix. The formulation enables high-fidelity vat photopolymerization, producing solid structures in which biological constituents remain present in a form that can be selectively activated after printing.

By applying a mild thermal treatment, the printed objects undergo a progressive increase in mechanical strength, allowing the same material to express a range of mechanical responses depending on the processing conditions. Because this post-print reinforcement can be applied locally, it becomes possible to generate regions with differentiated rigidity within a single printed construct, without changing the feedstock or altering the fabrication workflow.

This approach offers a simple and scalable pathway for creating multimaterial-like behavior from a single, biobased formulation, avoiding complex chemical modifications or multi-ink systems. The resulting materials provide opportunities for applications in areas where lightweight, tunable, and environmentally conscious components are desired, including soft robotics, prototyping, and functional design.

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- [3] C. Veith, F. Diot-Néant, S. A. Miller, F. Allais, *Polym. Chem.* **2020**, *11*, 7452.
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- [5] M. Bergoglio, E. Rossegger, S. Schlögl, T. Griesser, C. Waly, F. Arbeiter, M. Sangermano, *Polymers* (*Basel*). **2024**, *16*.

62 D2 -S11 -01

**Extrusion based AM** 

1-Pellet extrusion 20- Advanced & Sustainable materials 3- Material development

## PELLET-BASED ADDITIVE MANUFACTURING: SUSTAINABILITY AND PERFORMANCE

### Ivan Sardon Barbero

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Pellet-based additive manufacturing is emerging as a key solution to foster sustainability in the industry. It enables the reuse of recycled materials, reduces production costs, and supports the principles of the circular economy. This presentation will also explore the potential of this technology to process advanced and technical materials, highlighting its versatility and high-performance capabilities.



Figure: Tumaker modular 3D printer with pellet extrusion system. The setup highlights its versatility, commitment to sustainability, and potential for research into new pellet-based materials.

Since 2016, Tumaker's pellet-based 3D printing technology has been adopted by universities and research institutions worldwide for the investigation and development of advanced and sustainable materials.

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63 D2 -S12 -01

Light mediated AM / Bioelectronics, Multi-materials, PEDOT:PSS

# SHAPING THE FUTURE OF BIOELECTRONICS: INNOVATION IN MATERIALS AND MULTI-MATERIAL 3D PRINTING

## Antonio Dominguez-Alfaro 1.2

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The bioelectronics of tomorrow envisions ambitious challenges, including tissue-integrated biohybrid implants, long-term stable brain-machine interfaces, skin-integrated electronics, and neuromorphic organic circuits designed for ultra-low power consumption. Currently, Poly 3,4-(ethylene dioxythiophene) (PEDOT) doped with polystyrene sulfonate (PSS) is considered the gold standard material in bioelectronics when interfacing with the tissue, mainly due to its mix in-electronic conduction, volumetric capacitance, 2D solution-processability and commercial availability. However, some fundamental properties remain, particularly with respect to material characteristics such as tridimensionality, bio-functionality, swelling control, charge transport, and long-term stability under electrochemical conditions.

The development of new materials to create the next generation of electroceuticals, implantable or wearable electronics requires the introduction of novel features and innovative processes, such as 3D printing, controlled biological properties (e.g., more biologically compatible dopants), and rationally designed materials with mixed conduction mechanisms.

This presentation outlines our strategy for developing bioelectronic devices, highlighting the transformative impact of material synthesis and design, manufacturing, and innovations in final integration to shape the future of bioelectronics.

- [1] A. Dominguez-Alfaro, George G. Malliaras et al. Light-Based 3D Multi-Material Printing of Micro-Structured Bio-Shaped, Conducting and Dry Adhesive Electrodes for Bioelectronics. Adv. Sci. 2024, 11, 2306424.
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- [3] A. Dominguez-Alfaro, David Mecerreyes et al. Direct ink writing of PEDOT eutectogels as substrate-free dry electrodes for electromyography. Mater. Horiz., 2023,10, 2516-2524

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64 D2 -S11 -02

Light mediated AM / Volumetric, biofabrication, machine vision

# ADVANCED TOMOGRAPHIC PRINTING: ENHANCING (BIO)FABRICATION WITH MACHINE VISION AND HIGH-THROUGHPUT TECHNOLOGIES.

Jorge Madrid-Wolff (1), Julien Sahli (1), Max Kollep (1), Paul Delrot (1)

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Tomographic volumetric printing is consolidating as a versatile tool in biofabrication and fast additive manufacturing, enabling the rapid production of cm-scale free-form structures within seconds [1]. By projecting a precise 3D light dose into photocurable materials, this method facilitates the creation of complex structures across a diverse array of materials, ranging from soft hydrogels to robust ceramics [2].

This technology is particularly interesting for applications in biology, as it is especially gentle on living cells: printing times are short (< 30 s), photoinitiator concentrations can be kept low (< 0.1 w/v%), and sheer stress is avoided. This ensures a biocompatible environment and high cellular viability (> 90%).

Moreover, our volumetric printers are compatible with multiple wavelengths across the visible spectrum, broadening the potential applications and material interactions. The expanding library of materials offers extensive opportunities to explore the relations between living organisms and their environments [3], driving forward the frontiers of biomaterials research and applications.

One exciting feature of tomographic volumetric printing is its ability to overprint around existing objects. Recently, we introduced machine-vision algorithms that automate this task, enabling users to overprint soft hydrogels around stiff meshes or produce multi-layered spheroids, for example. These algorithms open research avenues to fabricate more complex multi-material structures.

At Readily3D, we pioneer fabrication technologies that empower scientists to model (bio)materials with unprecedented speed and accuracy. In this talk we will discuss the science behind the technology and present how researchers have used them to engineer and explore the interaction between living cells and their surrounding materials.

- [1] Bernal, Paulina Nuñez, et al. "Volumetric bioprinting of complex living-tissue constructs within seconds". *Advanced Materials*, **2019**, 31.42: 1904209.
- [2] Madrid-Wolff, Jorge, et al. "A review of materials used in tomographic volumetric additive manufacturing." MRS Communications, **2023**, 13, 764-785, DOI: 10.1557/s43579-023-00447-x
- [3] Sgarminato, Viola, et al. "". Biofabrication, 2024, 16, 045034, DOI: 10.1088/1758-5090/ad6d8d

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65 D2 -S12 -02

Light mediated AM / Vat photopolymerization, sustainability, recycling

## BREAKING THE MOLD: ADVANCED ADDITIVE MANUFACTURING SOLUTIONS

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Additive manufacturing (AM), widely known as 3D printing, has become an essential and versatile platform for producing complex and customized structures. Its seamless design-to-manufacture process has
revolutionized a myriad of industries beyond rapid prototyping and personalized production. Among the various polymer-based AM technologies, vat photopolymerization (VPP) has gained increasing attention as an
advanced processing technique, offering superior surface finish, feature resolution, accuracy, and speed,
making it a key driver of innovation in high-tech manufacturing. VPP process rely on the rapid solidification
of low-viscosity liquid resins through light irradiation. This process is typically enabled by fast photopolymerization chemistries, such as free radical polymerization of (meth)acrylates or cationic polymerization of
epoxides, leading to the development of materials with excellent thermal and chemical resistance, but also
resulting in scarce light processable polymer families which generally produce highly crosslinked non-reprocessable and non-recyclable products, reinforcing a non-circular, linear economy model that raises major
environmental concerns. Besides, the requirements for low viscosity resins limits the use of high molecular
weight precursors limiting the attainable mechanical performance of printed parts.

In this talk, I will share our latest advances in the field of sustainable VPP. First, I will discuss the use of photobase generator catalysed systems to yield recyclable and reprintable thiol-isocyanate resins as a way of increasing the circularity of the VPP process [1]. Besides, I will introduce the concept of *pseudothermoplastic* printing which utilizes recently developed latex printing method to yield high performance materials with inherit recyclability due to their predominantly thermoplastic character.

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66 D2 -S12 -03

Light mediated AM / composite, nanoparticle, dynamic

## LIGHT-ASSISTED FABRICATION OF REVERSIBLE COMPOSITES

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Formulating photocurable composite resins for additive manufacturing require careful consideration of resin characteristics such as the viscosity and cure speed in combination with the processing parameters like light intensity and if involved, shear-inducing motion eg. extrusion. Additional challenges arise when covalent adaptable networks are used. Utilized for their built-in dynamic functionalities such as self-healing, triggerable flow, recycling [1], these materials, also depending on the chosen dynamic chemistry, can suffer from mechanical weakness. Previously, it was shown that through development of thiol-ene – nanocellulose elastomeric composites, significant wear resistance and hardness increases can be achieved without decreasing photopolymerization rate [2]. In the presented study, by preparing thiol-ene photopolymer coatings with dynamic chemistries, specifically cinnamates and disulfides, a base understanding of photopolymers with depolymerization potential was established. Then, such photopolymers with dynamic chemistry loaded with surface-functionalized nanosilica and more recently cellulose nanofibrils were explored for their (photo) rheological profiles, light-assisted direct ink writing, and their subsequent depolymerization performance via cellular structures.

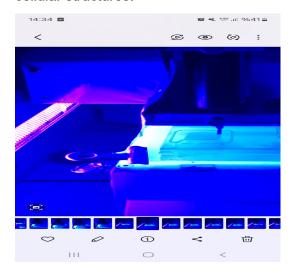


Figure: A thiol-ene – nanosilica resin with dynamic disulfide chemistry in light-assisted fabrication.

- [1] Maciej Podgorski, et al. "Toward Stimuli-Responsive Dynamic Thermosets through Continuous Development and Improvements in Covalent Adaptable Networks (CANs)", *Advanced Materials*, **2020**, 32, 1906876, DOI: 10.1002/adma.201906876
- [2] Alper Balkan, et al. "Photocurable Thiol–Ene/Nanocellulose Elastomeric Composites for Bioinspired and Fluorine-Free Superhydrophobic Surfaces", *ACS Applied Materials & Interfaces*, **2024**, 16, 61144-61156, DOI: 10.1021/acsami.4c16445

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67 D2 -S11 -03

Gel permeation chromatography, degradation studies, anti oxidants

# GEL PERMEATION CHROMATOGRAPHY: A TOOL TO MONITOR THE DEGRADATION KINETICS OF POLYMERS AND ADDITIVES

## **Subin Damodaran**(1)

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Polymers are characterized by its physical and chemical properties. These properties can be tailored by molecular weight, presence of branching, molecular structure and shape of the polymers. For polymeric materials the molar mass and molar mass distribution plays a vital role in the determination of mechanical, bulk, and solution properties. These properties govern polymer processing and the end-use performance of a given material. The shape and breadth of molar mass distribution will depend on the mechanism, kinetics and condition of the polymerization, and will dictate the end-use properties of the polymer. Polymer properties such as, hardness, tear strength, impact resistances, wear, brittleness, toughness, tackiness, etc., are important in determining the successes or failure of a given material.

Gel Permeation chromatography (GPC) can be successfully applied to most of the polymers at ambient or high temperature conditions to determine their process-property relations. In addition, the shelf life of a polymer or the changes in molar mass characteristics of a polymer while in use can be analysed and calculated with ease by using GPC.

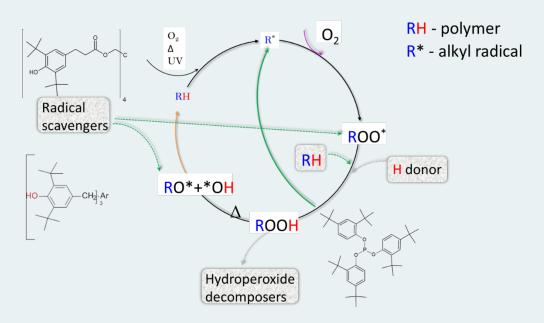


Figure: Scheme of thermo-oxidative degradation of polymers.

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68 D2 -S12 -04

Light mediated AM / polypeptides, hydrogels, DLP

## 3D PRINTING WITH POLYPEPTIDES

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- (2) Science Foundation Ireland (SFI) Centre for Research in Medical Devices (CURAM), RCSI, Dublin, D02 YN77, Ireland.
- (3) AMBER, The SFI Advanced Materials and Bioengineering Research Centre, RCSI, Dublin, D02 YN77, Ireland.

Synthetic polypeptides, derived via ring-opening polymerisation of amino acid N-carboxyanhydrides (NCAs), offer a promising bio-based feedstock for advanced 3D printing technologies. Their inherent biocompatibility and tunable properties make them particularly attractive for functional biomaterial design. Over recent years, we have demonstrated the versatility of polypeptides in both Direct Ink Writing (DIW) [1] and Digital Light Processing (DLP) [2], enabling the fabrication of complex architectures with tailored responsiveness. This presentation will provide an overview of recent advances in polypeptide-based 3D manufacturing, showcasing applications ranging from soft, printable hydrogels to stimuli-responsive 4D materials.

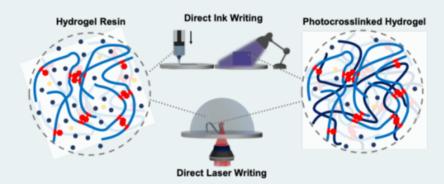


Figure: 3D printing of polypeptide hydrogels by Direct Ink Writing (DIW) [1] and Digital Laser Writing [2].

[1] Robert Murphy, Shadi Kordbacheh, Dimitrios Skoulas, Simon Ng, Kasinan Suthiwanich, Andrea M Kasko, Sally-Ann Cryan, Deirdre Fitzgerald-Hughes, Ali Khademhosseini, Amir Sheikhi, Andreas Heise "Three-dimensionally printable shear-thinning triblock copolypeptide hydrogels with antimicrobial potency", *Biomater. Sci.*, **2021**, 9, 5144-5149, DOI: 10.1039/d1bm00275a.

[2] Robert D Murphy, Colm Delaney, Srikanth Kolagatla, Larisa Florea, Craig J Hawker, Andreas Heise "Design of Statistical Copolypeptides as Multipurpose Hydrogel Resins in 3D Printing", Adv. Func. Mater., 2023, 33, 2306710, DOI: 10.1002/adfm.202306710.

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69 D2 -S11 -04

Light mediated AM / two-photon polymerization, Aligned 2-Photon Lithography, multimaterial

## REVOLUTIONIZING BIOMEDICAL FABRICATION: TWO-PHOTON POLYMERIZATION FOR MULTIMA-TERIAL 3D PRINTING

<u>Benjamin Richter</u> (1), Marc Hippler (1), Andrea Bertoncini (1), Mareike Trappen (1), Matthias Blaicher (1), Daniel Götz (1), Alexander Quick (1), Fabian Niesler (1), Michael Thiel (1)

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Multimaterial 3D printing, particularly via two-photon polymerization (2PP), revolutionizes the landscape of cell culturing, offering a bridge between traditional 2D methodologies and the need for dynamic 3D environments akin to in vivo conditions. While 2D cell culturing remains vital for high-throughput imaging, its limitations in mimicking physiological complexity underscore the necessity for 3D approaches. However, current 3D culturing techniques often struggle to replicate organic structures and are confined to simplistic shapes.

In this study, we harness the power of two-photon polymerization (2PP), employing techniques like Two-Photon Grayscale Lithography (2GL®) and Aligned 2-Photon Lithography (A2PL®) to create intricate in vitro microstructures tailored for advanced cell culturing. Our research showcases a novel workflow utilizing aligned 2PP microfabrication for 3D cell assays and perfusion within microfluidic devices. Additionally, we explore the application of 2GL® printing in generating Al-driven topographies, enhancing 2.5D cell culturing scalability and efficacy.

The versatility offered by both aligned and 2GL® printing methodologies hold immense promise across diverse fields such as biotechnology, tissue engineering, and microfluidics. By unlocking new avenues for innovation, these techniques present unprecedented opportunities for advancement within the biomedical and pharmaceutical sectors.

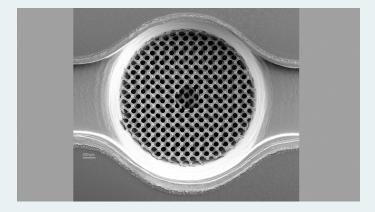


Figure: 3D Gyroid structure printed in a microfluidic chip from ibidi.

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70 D2 -S12 -05

Light mediated AM / Volumetric additive manufacturing; polymer chemistry

# ADVANCING CHEMISTRIES OF ADDITIVE MANUFACTURING: ONGOING EFFORTS AT LAWRENCE LIVERMORE NATIONAL LABORATORY

<u>Johanna Schwartz\*</u> (1), Saptarshi Mukherjee (1), Samuel Leguizamon (2), Maxim Shusteff (1), Ryan Hensleigh (1), Brian Au (1), Johanna Vandenbrande (1), Xiaoxing Xia (1), Liliana Terrel-Perez (1)

- (1) Lawrence Livermore National Laboratory, Livermore, CA, United States of America.
- (2) Sandia National Laboratories, Albuquerque, NM, United States of America.

This talk will focus on advancements in polymer-based additive manufacturing (AM) methods ongoing at Lawrence Livermore National Laboratory (LLNL), including vat photopolymerization techniques such as two photon polymerization, stereolithography, and volumetric AM as well as direct-ink-writing. Ultimately, my highly interdisciplinary teams consist of chemists and engineers working together within the Center for Engineered Materials and Manufacturing to solve real-world challenges. I will highlight my multiple ongoing projects in the field of AM, including microwave volumetric additive manufacturing, silicone printing, and utilizing AM as a tool for high throughput automated screening.

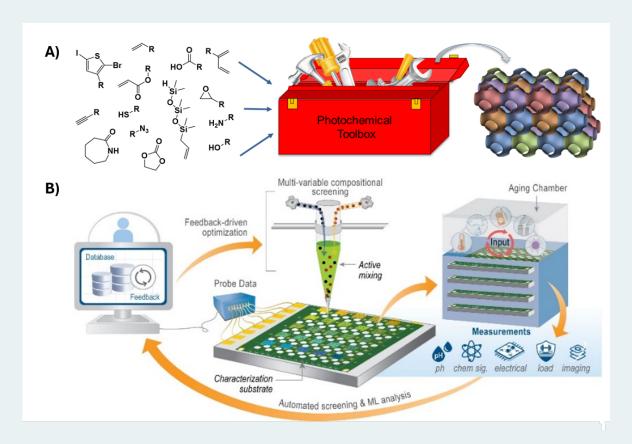


Figure: Schematic of our A) Ideal vision for expanding vat photopolymerization beyond radical acrylate chemistries. B) Studying-Polymers-On a-Chip automated screening platform.

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71 D2 -S13 -01

Light mediated AM

two-photon polymerization, nanoimprint lithography, microfluidics

# 2-PHOTON POLYMERIZATION – A VERSATILE MICROFABRICATION TECHNOLOGY FOR SCIENTIFIC CHALLENGES FROM THE NANO TO THE MACRO SCALE

### Markus Lunzer\* (1)

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2-photon polymerization (2PP) is a powerful high-resolution 3D printing technology that can produce complex parts from submicron volumetric units called voxels. As voxels are scanned in a line-by-line fashion, print time scales with volume. Faster printing can be achieved by increasing the rate of volume processed per time.

This is made possible by recent technological advances such as Adaptive Resolution, where the voxel size is dynamically adjusted to the local resolution requirements. By dividing complex parts into "coarse" and "fine" regions, whereby the bulk is fabricated with a large voxel and coarse print settings and only high-resolution segments are printed with a smaller voxel and fine print settings, a substantial reduction in print time can be achieved. As a result, complex macroscopic parts with microscopic features can be fabricated directly with 2PP within reasonable time now.

In this contribution, UpNano GmbH presents the performance capabilities of its *NanoOne* 3D printing system [1] and provides a comprehensive overview of current applications in the fields of microfluidics, mastering for polymer replication [2] as well as optoelectronics applications such as integrated photonics and biomedical applications such as organ-on-a-chip. The use cases presented are based on ongoing research activities and recent publications by the NanoOne user community.



Figure: 2-photon polymerization (2PP) enables high-resolution 3D printing of complex parts.

- [1] T. Koch, W. Zhang, T.T. Tran, Y. Wang, A. Mikitisin, J. Puchhammer, J.R. Greer, A. Ovsianikov, F. Chalupa-Gantner, M. Lunzer "Approaching Standardization: Mechanical Material Testing of Macroscopic Two-Photon Polymerized Specimens", *Adv. Mater.*, **2024**, 36: 2470275. DOI: 10.1002/adma.202470275
- [2] S. Kluck, R. Prediger, L. Hambitzer, N. Nekoonam, F. Dreher, M. Luitz, M. Lunzer, M. Worgull, M. Schneider, B. E. Rapp, F. Kotz-Helmer "Sub-Micron Replication of Fused Silica Glass and Amorphous Metals for Tool-Based Manufacturing", *Adv. Sci.*, **2024**, 11, 2405320. DOI: 10.1002/advs.202405320

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72 D2 -S14 -01

Light mediated AM / disulfide, depolymerization, closed-loop

#### CLOSED-LOOP BIOGENIC RESINS FOR SUSTAINABLE ADDITIVE MANUFACTURING

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- (2) School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK

**Abstract**: The additive manufacturing of photopolymer resins enables the rapid fabrication of bespoke 3D-printed parts. However, recycling printed parts is challenging since most commercial photopolymer resins rely on acrylates that crosslink into irreversible polymer networks upon irradiation. State-of-the-art methods to recycle and re-print 3D-printed photopolymers feature dynamic covalent bonds paired with conventional crosslinking chemistries. However, most of these are still open-loop processes since re-formulation of the recycled resin is required to print again, such as adding additional monomer and/or reactive diluents. Here, we have designed a photopolymer resin platform built exclusively from biogenic feedstock that can be 3D-printed into high-resolution parts, efficiently deconstructed to the starting resin, and subsequently re-printed in a closed-loop manner. The key distinguishing feature of our approach is the replacement of acrylates with cyclic disulfide bonds, which can undergo radical-mediated ring-opening polymerization and then thermal-assisted ring-closing depolymerization to regenerate the original resin formulation. Recent advances from our lab describing efforts to enhance mechanical performance of printed parts are also described.



Figure: Abstract graphical depiction of closed-loop 3D-printing of photopolymer resin

[1] Thiago O. Machado, Connor J. Stubbs, Viviane Chiaradia, Maher Alraddadi, Arianna Brandolese, Joshua C. Worch\*, Andrew P. Dove\* "A Renewably Sourced, Circular Photopolymer Resin for Additive Manufacturing" *Nature* **2024**, 629, 1069-1074, DOI: <a href="https://doi.org/10.1038/s41586-024-07399-9">https://doi.org/10.1038/s41586-024-07399-9</a>

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73 D2 -S13 -02

Light mediated AM / biofabrication cartilage materials

## FROM LIGHT TO LIFE: BIO INKS AS A KEY TO BIOFABRICATION FOR MULTIPLE PRINTING TECHNOLOGIES

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- (1) BIO INX BV, Zwijnaarde, Belgium
- (2) Skeletal Biology and Engineering Research Center, KU Leuven, Leuven, Belgium
- (3) Surface and Interface Engineered Materials, KU Leuven Group T Campus, Leuven, Belgium

Bioprinting has emerged as a transformative technology for both in vitro and in vivo applications, offering unprecedented precision and versatility in creating complex biological structures. This technology is capable of operating across a spectrum of resolutions, from low to high, enabling the production of structures that range from macro-scale scaffolds to intricate micro-scale designs. A crucial aspect of bioprinting is the development and utilization of bioinks that are functional, reproducible, and standardized, ensuring consistency and reliability in the printed constructs. These advancements are instrumental in various fields, including the development of sophisticated cancer models, innovative approaches to tissue regeneration, and the creation of organ-on-chip systems. By leveraging the diverse capabilities of bioprinting and ensuring high-quality bioinks, significant progress is being made in biomedical research and regenerative medicine, ultimately leading to the development of functional tissue and organ replacements, advanced drug testing systems and a deeper understanding of complex biological processes. This lecture will explore the importance of reliable and standardized bioink development for the field of biofabrication, , with a focus on their applications in tissue regeneration, organ-on-chip systems, and cancer models. To this end, some insights will be provided on the use of biofabrication for osteochondral regeneration [1,2] as well as the use of high resolution laser based biofabrication for the generation of a heart-on-a-chip to be launched to the international space station to study the effects of accelerated ageing.

- [1] **Agten H. et al.** "In vitro and in vivo evaluation of 3D Constructs engineered with human iPSC-derived chondrocytes in gelatin methacryloyl hydrogel" 2022 Biotechnology and Bioengineering, 119(10) (https://doi.org/10.1002/bit.28168)
- [2] **Agten H. et al.** "In vitro and in vivo evaluation of periosteum-derived cells and iPSC-derived chondrocytes encapsulated in Gel-MA for osteochondral tissue engineering" 2024 Frontiers in Bioengineering and Biotechnology, 12 (https://doi.org/10.3389/fbioe.2024.1386692)

74 D2 -S14 -02

Emerging AM technologies / Hot Lithography, High-Precision scalable 3D Printing Technology

## FROM VISION TO VOLUME: HOT LITHOGRAPHY FOR SCALABLE, HIGH-PRECISION INDUSTRIAL 3D PRINTING

#### **Dr. Markus Kury**

(1) Cubicure GmbH, Vienna, Austria

Persistent megatrends such as electromobility, energy technologies, and digitalization continuously drive innovation demands within all industries. At the same time, customized product solutions, miniaturization, and high product diversity are becoming more important. Especially in the field of micro-injection molding, conventional manufacturing methods are increasingly reaching their limits.

Additive Manufacturing (AM) offers a promising alternative, enabling tool-free, highly flexible production processes with extensive design freedom, rapid iteration, and high automation potential. Cubicure addresses these challenges with its innovative Hot Lithography technology, which utilizes a heated printing process. This enables the use of highly viscous photoreactive resins and expands the chemical toolbox for the development of novel, enhanced material systems. As a result, these advanced materials processed by Hot Lithography unlock new opportunities for industrial applications.

Originally based on the Caligma® printing system, this technology has been further developed for industrial applications and successfully scaled with the Cerion® system. Cerion® enables the serial production of small to medium-sized functional parts on a building platform of 1000 x 280 mm², unlocking new potential in digital volume manufacturing.

With this technology, Cubicure is setting new standards in high-performance material processing for manufacturing. The solutions presented demonstrate how digital production are redefining both prototyping and series production – with precision, efficiency, and future-proof scalability.



Figure: 3D Printing System Caligma® and Cerion ®, June 2023, ©Cubicure.

75 D2 -S14 -03

Light mediated AM / dynamic covalent chemistry, circurlar printing, photo-chemistry

#### DYNAMIC COVALENT CHEMISTRY TOWARDS SUSTAINABLE 3D ADDITIVE MANUFACTURING

#### Tao Xie (1)

(1) Zhejiang University, Hangzhou, China.

Photo-chemistry based 3D printing has the potential to become a main-stream additive manufacturing tool. Great progress has been made on fast printing methods. However, bottlenecks remain, most notably the mechanical performance and cost of the printed products. In addition, when it does become main-stream, the end-of-life treatment of the large volume printed end-products would become an issue much like plastic products made by conventional methods. Dynamic covalent chemistry design of polymer networks offers a highly attractive route towards resolving the above issues. In this talk, I will cover recent efforts in my group in this direction, with examples on chemical upcycling of waste plastics into photo-resins [1], 3D printed photo-polymers with unprecedented mechanical properties [2], and circular photo-printing [3].

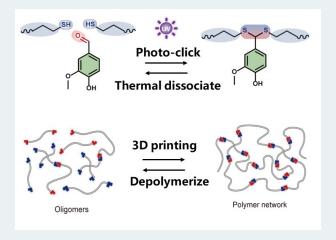


Figure: Circular 3D photo printing.

- [1] Zenghe Liu, et al "Chemical upcycling of commodity thermoset polyurethane foams towards high-performance 3D photo-printing resins", *Nature Chemistry*, **2023**, 15,1773
- [2] Zizheng Fang, et al "3D printable elastomers with exceptional strength and toughness", *Nature*, **2024**, 631, 783.
- [3] Bo Yang, et al "Circular 3D printing of high-performance photopolymers via dissociative network design", *Science*, **2025**, accepted.

76 D3 -PL

Light mediated AM semi-crystalline, composites, vat photopolymerization

### (MICRO)STRUCTURE CONTROL IN ARCHITECTED MATERIALS

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#### **DISCLAIMER**

The abstract is not included as per author's request.

77 D3 -S15 -01

Light mediated AM / Volumetric Layerless ultrafast

#### **VOLUMETRIC PRINTING: WHAT IS NEXT?**

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Laboratory of Applied Photonics Devices, Ecole Polytechnique Fédérale de Lausanne

Volumetric printing by reverse tomography commonly called by the acronym TVAM or sometimes simply VAM is a technique which consists of projecting sequences of light patterns into a rotating resin volume, producing 3D structures by the cumulative light energy deposition via resin hardening by photopolymerization [1,2]. This layerless 3D printing technology has been applied to many materials and applications from glass, ceramics, metal, polymers and hydrogels. There remains challenges to overcome such as increasing the build volume, improving feature resolution and using non-transparent composite resins. The build volume is typically of the order of a few centimeters and feature resolution is not uniform across the build volume due to diffraction. We will discuss several approaches that address these challenges. Resolution: one aspect of feature resolution is the optical voxel resolution throughout the build volume (other aspects are chemical diffusion and pattern optimization). With respect to the former, TVAM relies on optimizing projection patterns assuming light beam as rays. We have developed a TVAM pattern optimization framework using a rigorous wave propagation model [3] and showed that ray-optics start to produce artifacts when the desired features are 20 µm or under in a 10mm<sup>3</sup> build volume. Thus below 20 µm feature size, wave propagation and optimization must be used. Build volume /resolution: the etendue of the light source determines the feature resolution. The best resolution is when the etendue is the minimum, meaning the light source has a single spatial mode (SM). A laser can achieve this. In practice, SM laser optical power is low (few tens of milliwatts in the blue violet region). This, in turn limits the build volume for TVAM to few millimeters to maintain a short print time (< 60 seconds). By using phase modulation instead of amplitude modulation, the effective light efficiency of the pattern projection has been shown to be 70 times higher [4,5] and with beam shaping, the optimal resolution can now be extended to the centimeter scale.

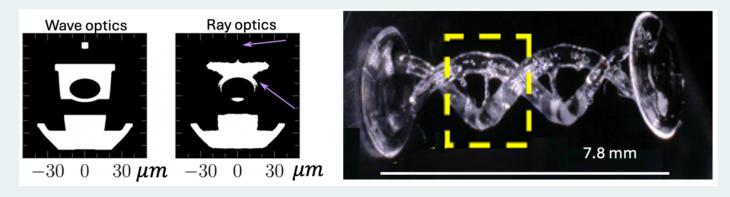


Figure: (left) wave optical model is required for < 20 um feature size (right) phase coding provide optimal resolution across the build volume

- [1] Kelly, B. E., Bhattasharya I, Heidari H., Shusteff M, Taylor H. "Volumetric additive manufacturing via tomographic reconstruction". *Science* **363**, 1075–1079 (2019). DOI: 10.1126/science.aau7114
- [2] Loterie D., Delrot P., and Moser C., "High-resolution tomographic volumetric additive manufacturing", *Nature Communications*, Vol. 11, 2020. https://doi.org/10.1038/s41467-020-14630-
- [3] Weschsler F., Gigli C., Madrid-Wolff J., Moser C., "Wave optical model for tomographic volumetric additive manufacturing", *Optics Express*, 32, 8,14705-14712 (2024). doi: 10.1364/OE.521322.
- [4] Álvarez-Castaño M., Madsen A. G., Madrid-Wolff J, Sgarminato V., Boniface A., Glückstad J., Moser C., *Holographic tomographic volumetric additive manufacturing*, Nature Communications 16, 2551(2025).
- [5] Álvarez-Castaño M., Pu Ye, Moser C High Light-Efficiency Holographic Tomographic Volumetric Additive Manufacturing using a MEMS-based Phase-only Light Modulator, https://arxiv.org/abs/2506.02578

78 D3 -S16 -01

Emerging AM technologies /

liquid crystal elastomers, direct laser writing, soft micro-robots

### DIRECT LASER WRITTEN MICRO-MIRROR ARRAYS ENABLE 90° INCIDENCE ANGLE ACTUATION IN LIGHT RESPONSIVE SOFT MICRO-ROBOTS

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Light Robots, Faculty of Engineering and Natural Sciences, Tampere University, P.O. Box 541 Tampere, Finland.

Liquid crystal elastomers (LCEs) have emerged as promising dynamic materials for soft robotics due to their capacity for reversible and programmable shape transformations under external stimuli [1, 2]. Conventional light-driven actuation of LCEs typically relies on laser illumination to induce photothermal effects, triggering molecular reorientation and material deformation. While normal-incidence (near zero angle of incidence) laser actuation theoretically offers the highest efficiency, maintaining consistent normal incidence during operation is impractical, especially in dynamic microrobotic systems. In practical applications, side-incident laser illumination is often employed; however, reflection at the LCE surface reduce energy transfer efficiency, leading to suboptimal actuation performance. To address this challenge, we propose a novel approach that integrates direct laser writing (DLW) [3] fabricated micron-scale waveguide arrays onto the LCE surface (Figure 1). These waveguide arrays significantly enhance light coupling into the material, ensuring efficient and precise actuation even at 90 degrees incident angle.

This work highlights the transformative potential of DLW-fabricated micron waveguide arrays in advancing light-driven LCE actuators for soft robotics. By enhancing LCE integration into robotic systems, our method significantly increases the flexibility and adaptability of LCE-based actuators, allowing them to operate effectively under diverse optical conditions.

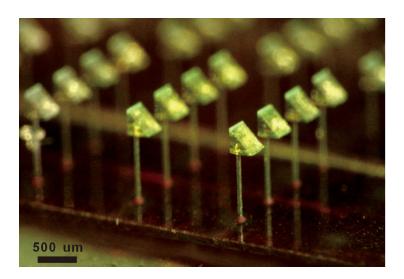


Figure 1: Optical image of micron-scale waveguide arrays on LCE surface, May 2025.

- [1] K. M. Herbert, H. E. Fowler, J. M. McCracken, K. R. Schlafmann, J. A. Koch, T. J. White, Synthesis and alignment of liquid crystalline elastomers, *Nat. Rev. Mater.* **2021,** 7, 23-38, DOI: 10.1038/s41578-021-00359-z
- [2] T. J. White, D. J. Broer, Programmable and adaptive mechanics with liquid crystal polymer networks and elastomers, *Nat. Mater.* **2015**, 14, 1087-1098, DOI: 10.1038/nmat4433
- [3] H. Zeng, P. Wasylczyk, C. Parmeggiani, D. Martella, M. Burresi, D. S. Wiersma, Light-Fueled Microscopic Walkers, *Adv. Mater.* **2015**, 27, 3883-3887, DOI: 10.1002/adma.201501446

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Emerging AM technologies /

Tomographic volumetric printing, (meth)acrylate photopolymerization, oxygen inhibiton

## ENHANCING BUILD VOLUME AND PRECISION IN TOMOGRAPHIC VOLUMETRIC ADDITIVE MANUFACTURING THROUGH ADVANCED POLYMER CHEMISTRY

Yujie Zhang (1), Katherine Houlahan (1), Daniel Webber (1), Antony Orth (1), Nicolas Milliken (1), Kathleen L. Sampson (1), Thomas Lacelle (1), Hao Li (1), Hendrich de Haan (2), Liliana Gaburici (1), Chantal Paquet (1)

- (1) National Research Council of Canada, Ottawa, Ontario, Canada
- (2) Ontario Tech University, Oshawa, Ontario, Canada

Tomographic Volumetric Additive Manufacturing (TVAM) offers a transformative approach to 3D printing by enabling the rapid fabrication of complex, high-resolution structures in a single step. Unlike traditional layer-by-layer techniques, TVAM reconstructs 3D objects by projecting a sequence of light patterns into a rotating vial of photoresin; the print forms volumetrically when the accumulated light dose exceeds the gelation threshold.

A key challenge in TVAM is the need to use low concentrations of photoinitiators to achieve sufficient light penetration throughout the print volume. This constraint prolongs gelation time and makes the system highly susceptible to oxygen inhibition—a significant limitation due to oxygen's rapid diffusion and its potency as a radical quencher.[1] The resulting heterogeneous polymerization compromises print fidelity, particularly in fine features, and limits scalability.

This study investigates polymer chemistry strategies to address these limitations. By formulating photoresins with enhanced reactivity, identifying optimal print conditions (e.g., photoinitiator concentration and light intensity), and incorporating additives to mitigate oxygen inhibition, we achieve faster gelation, reduced oxygen inhibition time, and more uniform polymerization throughout the print volume. These advances enable faster print speeds, higher resolution, and the production of larger-volume prints (16-fold increase in print volume) without compromising quality.

Overall, our findings highlight the critical role of tailored polymer chemistry in advancing TVAM, opening new possibilities for high-precision, scalable 3D printing across diverse application areas.

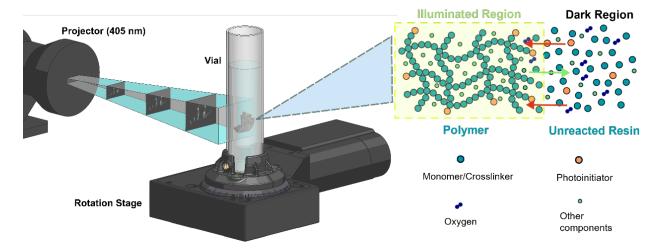


Figure: Tomographic volumetric printing with advanced polymer chemistry

[1] Yujie Zhang *et al.* "Impact of Oxygen Inhibition on (Meth)acrylate Photopolymerization in Tomographic Volumetric Printing", *Advanced Manufacturing*, **2025**, Under Review. <a href="https://ssrn.com/abstract=5157227">https://ssrn.com/abstract=5157227</a>

80 D3 -S16 -02

biomaterials, regenerative medicine, degradation

# DESIGNING FOR DEGRADATION: THE NEXT FRONTIER OF 3D PRINTING RESORBABLE MEDICAL DEVICES

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Although work in resorbable polymers has been extensive, few materials have been utilized solely in FDA-approved orthopedic hardware and scaffolds. Materials explored along this path include polylactides, poly(ε-caprolactone) (PCL), and polycarbonates. Polylactides, including PLGA, have been found to resorb in 1-2 months (too early) and typically undergo rapid bulk degradation leading to a localized acidosis and inflammatory response. PCL is known to degrade very slowly, sometimes over years, thereby preventing tissue remodeling and vascularization. Most of these polymers rely on crystallinity for toughness and result in brittle materials that fracture at low strains or deformations. Additive manufacturing (AM), especially VAT photopolymerization, is one way to fabricate crosslinked networks. The range of bone defect types, fracture sites, and cases of multiple fractures makes AM uniquely situated for the fabrication of resorbable scaffolds for bone defect repair. However, more recent fumarate-based copolyesters crosslinked with ester containing thiols [1] and ceramic composite fillers have greatly expanded both the mechanical properties and degradability of the resulting resins. [2] Clinical success of 3D printed composite scaffolds will depend on fully degradable polymer networks that possess mechanical properties suitable for fixation and controlled degradation properties. However, until now, fully resorbable, 3D printable polymers suitable for load sharing and load bearing orthopaedic applications [3] did not exist.

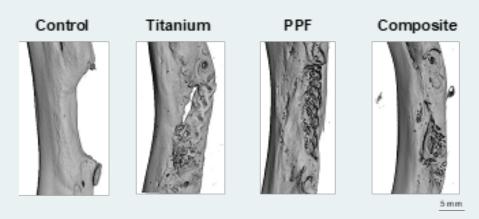


Figure: Micro-computed tomography of rabbit radii explanted at 12 weeks. Representative volume renderings of control defects and defects filled with titanium, PPF, and composite gyroids.

[1] A Krillova, T Yeazel, K Gall\*, ML Becker\* "Thiol-based Three-Dimensional Printing of Fully Degradable Poly(propylene fumarate) Star Polymers" *ACS Applied Materials and Interfaces* **2022**, *14*(*34*), 38436-38447. **DOI:** <u>10.1021/acsami.2c06553</u>

[2] T Yeazel, A Kirillova, K Gall\*, ML Becker\* "Influence of Post-3D Printing Processing Conditions on Poly(propylene fumarate) Star Polymer Hydroxyapatite Nanocomposite Properties" *RSC Applied Polymers* **2023**, *1*, 73-81. **DOI**: 10.1039/D3LP00013C

[3] EK Augustine, A Camarena, TR Yeazel, L Kang, G Wimmer<sup>†</sup>, NC Stinson, J Fernandez-Moure\*, ML Becker\*, "Resorbable 3D Printed Osteosynthetic Plates for Rib Fracture Repair" *Advanced Healthcare Materials*, **2025**, *in press*.

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ROS-responsive polymers, hydrogels, biomedical applications

### ROS-RESPONSIVE 3D POLYMER SCAFFOLDS VIA LIGHT PRINTING TECHNIQUES FOR BIOMEDICAL APPLICATIONS

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- (1) Institute of Polymer Science and Technology (ICTP-CSIC), Madrid, Spain.
- (2) POLYMAT, University of the Basque Country UPV/EHU, San Sebastián, Spain.
- (3) Instituto de Investigaciones en Tecnologías Energéticas y Materiales Avanzados (IITEMA), Universidad Nacional de Río Cuarto (UNRC), Rio Cuarto, Argentine.
- (4) Ikerbasque, Basque Foundation for Science, Bilbao, Spain.

The additive manufacturing of stimuli-responsive polymers has gained increasing attention for the development of customized 3D/4D printed scaffolds that respond to biological stimuli for personalized medicine purposes. Among different biological stimuli, reactive oxygen species (ROS) have emerged as powerful cell-signaling agents in disease but also in physiology. ROS effect can vary from beneficial cell survival to non-desirable oxidative stress when they are overproduced, thus causing inflammation, cancer, and age-related diseases.[1] Here, we will present different strategies to modulate the ROS production through the design of 3D/4D tailor-made polymer scaffolds via digital light printing (DLP). In one approach, we synthesized aqueous soluble redox monomers from oligomers of ethylene glycol sulfur diacrylate, which presented photopolymerizable properties. They were processed by DLP 3D printing leading to ROS-responsive thioether-based hydrogels with response to ROS. These 3D printed scaffolds were used as 5-Fluorouracil carriers to inhibit the growth of melanoma cancer cells.[2] Considering that overproduction of ROS in tumor/inflamed areas is generally linked to pH changes becoming slightly acidic, we also developed 3D printable hydrogels with response not only to ROS but also to temperature and pH for the treatment of anti-inflammatory pathologies. [3] On the other hand, we designed ROS responsive hydrogels through the use of semiconducting polymer nanoparticles (SPNs), which acted as both visible-light photoinitiators and photosensitizers in 3D printable acrylic hydrogels, for photodynamic therapies against mouse glioma cancer cells and S. aureus bacteria.[4]

- [1] Miryam Criado-Gonzalez, David Mecerreyes "Thioether-based ROS responsive polymers for biomedical applications", *J. Mater. Chem. B*, **2022**, 10, 7206-7221, DOI: 10.1039/D2TB00615D
- [2] Maria Regato Herbella et al., "ROS-responsive 4D printable acrylic thioether-based hydrogels for smart drug release", *Chem. Mater.*, **2024**, 36, 3, 1262-1272, DOI: 10.1021/acs.chemmater.3c02264
- [3] Maria Regato Herbella et al., "Multiresponsive 4D Printable Hydrogels with Anti-Inflammatory Properties", *ACS Macro Lett.*, **2024**, 13, 9, 1119-1126, DOI: 10.1021/acsmacrolett.4c00404
- [4] Rocío Natera Abalos, et al., "Poly(3-hexylthiophene) nanoparticles as visible-light photoinitiators and photosensitizers in 3D printable acrylic hydrogels for photodynamic therapies", *Mater. Horiz.*, **2025**, Advanced article, DOI: 10.1039/D4MH01802H

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82 D3 -S16 -03

Emerging AM technologies / Liquid Crystal Elastomers, 4D Printing, Soft Robotics

# ADDITIVE MANUFACTURING OF LCES: PROGRAMMING ACTUATION, ENABLING MOTILITY, AND ADVANCING AUTONOMY IN SOFT ROBOTICS

#### Carlos Sánchez-Somolinos\* (1,2)

- (1) Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, Zaragoza, 50009, Spain.
- (2) Centro de Investigación Biomédica en Red de Bioingeniería, Biomateriales y Nanomedicina, Instituto de Salud Carlos III, Zaragoza, 50018, Spain.

Structuring smart materials in three dimensions has opened new avenues for soft robotics, enabling complex actuation and diverse functionalities. Liquid crystalline elastomers (LCEs) are particularly promising in this domain due to their ability to anisotropically deform in response to stimuli such as heat, light, or humidity. Additive manufacturing of LCEs allows precise control over molecular alignment, enabling programmable, reproducible, and scalable shape transformations. This lecture will highlight recent developments from the Advanced Manufacturing Laboratory, including the creation of multiresponsive systems, biomimetic and self-sustained movements, and multimodal actuation—essential steps toward more autonomous soft robotic devices.

Acknowledgments: The described research is part of the projects STORM-BOTS and PRIME. STORM-BOTS has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 956150 (STORM-BOTS). PRIME has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement no. 829010 (PRIME). Funding has also been received from Spanish "Ministerio de Ciencia, Innovación y Universidades (MCIU)" through AEI/FEDER(UE) PID2020-118485RB-I00 project, Gobierno de Aragón project PROY\_E28\_24, FEDER (EU), Fondo Social Europeo (DGA E15\_20R) and by CIBER-Consorcio Centro de Investigación Biomédica en Red (CB16/01/00263), Instituto de Salud Carlos III.

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83 D3 -S17 -01

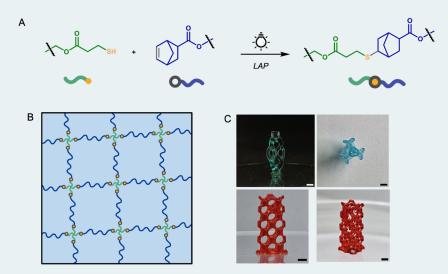
Light mediated AM / hydrogels; tissue engineering; volumetric printing

#### LIGHT-PROMOTED VOLUMETRIC PRINTING OF TOUGH HYDROGELS

Mahsa Ebrahimi (1,2), Mariana Arreguin Campos (1,2), Ulrike Arickx (1), Lorenzo Moroni (2), Matthew B. Baker\* (2), Louis M. Pitet\* (1)

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- (2) Department of Instructive Biomaterials Engineering and Department of Complex Tissue Regeneration, MERLN Institute for Technology Inspired Regenerative Medicine, Maastricht University, Universiteitssingel 40, Maastricht 6229 ET, The Netherlands.

Tissue engineering offers a promising approach to addressing several common degenerative diseases. However, major gaps still exist when it comes to mimicking the compositional complexity and mechanical integrity of several native tissues. Articular cartilage stands out as exhibiting remarkable strength and resilience. We have formulated a synthetically accessible modular system that leads to relatively uniform network configurations [1]. The outcome is relatively high toughness and mechanical strength that is modulated via the molar mass of the building blocks [2]. Furthermore, we utilize photo-curable crosslinking chemistry (thiol-norbornene) that is very rapid. This combination allowed us to employ volumetric printing to construct complex custom shapes. The printed objects are mechanically robust despite containing upwards of 80% water and having relatively thin scaffold diameters (< 150  $\mu$ m). This approach provides a promising avenue by which customizable and tough hydrogel materials can be rapidly fabricated for potential applications in regenerative medicine.



**Figure:** A: Thiol-norbornene crosslinking reaction; B: Cartoon representation of a uniform hydrogel network; C: several examples of printed constructs using 3D volumetric printing.

- [1] Ebrahimi, M.; Arreguín-Campos, M.; Dookhith, A. Z.; Lynd, N. A.; Sanoja, G. E.; Aldana, A. A.; Baker, M. B.; Pitet, L. M. "Tailoring network topology in mechanically robust hydrogels for 3D printing and injection" ACS Appl. Mater. Interfaces 2024, 16, 25353-25365. https://doi.org/10.1021/acsami.4c03209
- [2] Arreguín-Campos, M.; Ebrahimi, M.; Dookhith, A. Z.; Lynd, N. A.; Sanoja, G. E.; Aldana, A. A.; Baker, M. B.; Pitet, L. M. "Architectural differences in photo polymerized PEG-based thiol-acrylate hydrogels enable enhanced mechanical properties and 3D printability" *Eur. Polym. J.* **2024**, *212*, 113070. <a href="https://doi.org/10.1016/j.eurpoly-mj.2024.113070">https://doi.org/10.1016/j.eurpoly-mj.2024.113070</a>

84 D3 -S18 -01

4D printing, DLP, UCST hydrogels

## 4D PRINTING OF UCST-BASED HYDROGELS FOR PROGRAMMABLE SHAPE MORPHING USING DLP

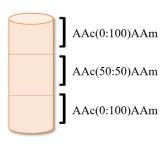
Fato NIANG (1), Vincent LAPINTE (1), Sébastien BLANQUER \* (1)

(1) ICGM, Université de Montpellier, ENSCM, CNRS, Montpellier, France

4D printed temperature-responsive hydrogels have garnered significant attention due to their broad range of applications, including soft robotics, tissue engineering, and drug delivery [1]. However, UCST systems remain much less explored than their LCST counterparts but they are essential for specific applications, such as those requiring water retention at high temperatures or expressing volumetric expansion by arising the temperature, highlighting the need of UCST systems as efficient as LCST ones. Studies have shown that highly hydrophilic monomers, such as acrylic acid, can produce UCST systems when copolymerized with monomers capable of strong hydrogen bonds [2].

Building on this premise, our research focuses on the 4D printing of hydrogels composed of acrylic acid (AAc) and acrylamide (AAm), responsive to both temperature and pH. These hydrogels undergo anisotropic shape transformations driven by swelling rate differences, achieved by precisely controlling resin composition during the printing process carried out by Digital Light Processing (DLP)

Our findings demonstrate highly predictable and programmable systems with excellent mechanical properties, very good resolution and remarkable deformation amplitudes. Additionally, 3D printing allows precise control over response kinetics by incorporating pores of varying sizes into the designs. We also successfully tackled the challenge of achieving multi-materials using DLP without adhesion issues, marking a significant advancement. Finally, our study reveals an unprecedented UCST behavior for poly(acrylic acid) upon photo-crosslinking. This breakthrough represents a game-changer, unlocking new possibilities for creating 4D LICST materials, even when the linear polymer lacks this property.





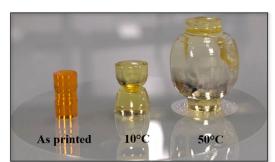


Figure: 3D design of the printed object (left); Picture of the hydrogels after printing, at swelling equilibrium at 10 °C and at 50°C (right).

[1] Hua, L.; Xie, M.; Jian, Y.; Wu, B.; Chen, C.; Zhao, C. Multiple-Responsive and Amphibious Hydrogel Actuator Based on Asymmetric UCST-Type Volume Phase Transition. *ACS Appl. Mater. Interfaces* **2019**, *11* (46), 43641–43648, DOI: 10.1021/acsami.9b17159

[2] Nan, Y.; Zhao, C.; Beaudoin, G.; Zhu, X. X. Synergistic Approaches in the Design and Applications of UCST Polymers. *Macromolecular Rapid Communications* **2023**, 2300261, DOI: 10.1002/marc.202300261

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85 D3 -S17 -02

Light mediated AM / TVAM, computational optics, overprinting

## OVERPRINTING APPLICATIONS WITH TOMOGRAPHIC VOLUMETRIC ADDITIVE MANUFACTURING USING DR.TVAM

Felix Wechsler (1), Viola Sgarminato (1), Baptiste Nicolet (2), Riccardo Rizzo (1), Christophe Moser (1)

- (1) Laboratory of Applied Photonics Devices, École Polytechnique Fédéral Lausanne (EPFL), Lausanne, Switzerland
- (2) NVIDIA, Switzerland

Tomographic volumetric additive manufacturing (TVAM) [1,2] allows optical based 3D polymerization of centimeter scale objects by projecting 2D patterns on a rotating single photon absorptive medium. It can be applied to different materials ranging from acrylates to biomaterials or ceramics [3].

One key problem in TVAM is the calculation of the required 2D patterns which need to be projected to obtain a successful print. Recently, we introduced a versatile open-source optical simulation package called Dr. TVAM [4, 5]. Based on a powerful and highly optimized ray tracing framework [6], we can simulate a variety of different optical conditions in TVAM. For example, it is possible to print directly in square shaped vials by calculating the refracted optical path of the 2D patterns while propagating through the surface of the vials. Also, we can rigorously optimize patterns under optical scattering conditions (such as bio materials with scattering cells). The entire framework is compatible with automatic differentiation, which allows its users to use gradient-based optimization in order to generate patterns that satisfy various objective functions, so as to enforce certain desired properties in the final prints.

In this study we further optimize Dr.TVAM and showcase its capabilities in printing over existing elements which impact the optical light propagation. As one application we printed complex perfusable microfluidic channels connecting pre-existing, light-occluding inlets in square shaped vials using a biocompatible hydrogel system. We also explore printing optical elements onto existing elements such as LEDs.

- [1]: Kelly, Brett E., et al. "Volumetric additive manufacturing via tomographic reconstruction." *Science* 363.6431 (2019): 1075-1079.
- [2]: Bernal, Paulina Nuñez, et al. "Volumetric bioprinting of complex living tissue constructs within seconds." *Advanced materials* 31.42 (2019): 1904209.
- [3]: Madrid-Wolff, Jorge, et al. "A review of materials used in tomographic volumetric additive manufacturing." MRS communications 13.5 (2023): 764-785.
- [4]: Nicolet, Baptiste, et al. "Inverse Rendering for Tomographic Volumetric Additive Manufacturing." *ACM Transactions on Graphics (TOG)* 43.6 (2024): 1-17.
- [5]: https://github.com/rgl-epfl/drtvam
- [6]: Nimier-David, Merlin, et al. "Mitsuba 2: A retargetable forward and inverse renderer." ACM Transactions on Graphics (ToG) 38.6 (2019): 1-17.

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86 D3 -S18 -02

photopolymerization; mechanism; excited states

## PRIMARY PHOTOCHEMICAL PROCESSES INVOLVED IN 3D PRINTING BY VAT PHOTOPOLYMERIZATION

Xavier Allonas, Ariana Villarroel-Marquez, Céline Croutxé-Barghorn, Christian Ley, Emile Goldbach

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Photopolymerization reaction is developed and studied for a long time and has led to important industrial achievements. Although that many photoinitiating systems have been proposed over the years and that the photopolymerization mechanism has been understood since a long time, one can quite often observe a real difficulty to link the primary processes occurring in the excited states and the actual properties of the materials created. This paper aims to give some examples on how the photochemical processes control the properties of the photopolymers obtained through vat photopolymerization [1-2]. In this paper, it is shown that the photopolymerization of a photosensitive resin containing various concentrations of photoinitiator and photoabsorber allows the prediction of the depth of penetration Dp [3-5]. Real-time FTIR kinetics of photopolymerization allows the evaluation of the critical energy Ecexp. More interestingly, the in-depth conversion can be predicted from conversion-time curve over a multi-layer printed object. As shown by measurement performed by confocal Raman microscopy, the z-anisotropy in conversion can be predicted from RT-FTIR kinetics curves. Similarly, the effect of overcure can be taken into account, showing the interest of this approach.:

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- [2] Emile Goldbach, Xavier Allonas, Lucile Halbardier, Christian Ley, Céline Croutxé-Barghorn, "RAFT-mediated thermoplastic material by photopolymerization: controlling liquid-solid transition for vat photopolymerization in 3D DLP printing", *Eur. Pol. J.* **2023**, 197, 112335. DOI: 10.1016/j.eurpolymj.2023.112335
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87 D3 -S17 -03

**Emerging AM technologies** 

Volumetric additive manufacturing (VAM), Polymer chemistry, Emerging Technology

## EXPANDING THE SCOPE OF MATERIALS ACCESSIBLE TO VOLUMETRIC ADDITIVE MANUFACTURING (VAM)

<u>Johanna Vandenbrande</u> (1), Ryan Hensleigh (1), Ethan Rosenberg (1), Martin De Beer (1), Beck Walton (1), Dominique Porcincula (1), Erika Fong (1), Aftab Bhanvadia (1), Hazel Galvan (1), James Kelly (1), Joe Tringe (1), Emer Baluyot (1), Maxim Shusteff (1), Saptarshi Mukherjee (1) and Johanna Schwartz (1) Lawrence Livermore National Lab, Livermore, CA, USA.

Volumetric additive manufacturing (VAM) is an innovative optical-based 3D printing technique that can produce objects in minutes. [1-3] This method significantly accelerates the production of custom 3D objects on demand and expands the range of printable materials compared to conventional additive manufacturing techniques. However, implementing VAM with photocatalytic systems that involve irreversible ligand dissociation, such as photohydrosilylation of silicones, poses significant challenges. The activated catalysts continue reacting even after illumination ceases, resulting in reduced resolution control. To address these limitations, the developed two strategies, zero-dose optimization and the inclusion of catalyst poisons to successfully printed 3D silicone fluidic devices and 3D objects. Additionally, incorporating fumed silica nanoparticles to act as the glass former into a clear UV-active organic resin has demonstrated the development of gradient refractive index (GRIN) lenses with smooth index gradients as well as colored and dichroic glass geometries. [4] Separately, the scope of VAM printing methods is widened through the exploration of microwave-VAM (MVAM), which employs microwave radiation to thermally cure binders. [5] This technique enables the creation of 3D objects in resins previously not accessible through optical VAM methods.

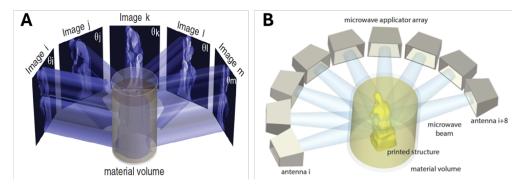


Figure: Comparison of optical VAM (A) that utilizes partnered illumination from many directions to deliver a computed 3D exposure dose into a responsive material to (B) MVAM that uses preposition of beams from antenna array focus energy to arbitrary locations, enabling complex patterning.

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88 D3 -S18 -03

Two-photon polymerization, Single-photon absorption, High-speed high-resolution 3D printing

#### ACCELERATING TWO-PHOTON POLYMERIZATION VIA SINGLE-PHOTON ACTIVATION

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Photopolymerization-based additive manufacturing enables high-speed fabrication of complex 3D structures but is constrained by a tradeoff between resolution and printing speed. Single-photon absorption (1PA) ensures rapid polymerization but is limited in resolution, while two-photon absorption (2PA) provides sub-micrometer precision at the cost of slower throughput.

We introduce a synergistic dual-mode excitation method that leverages the complementary strengths of both mechanisms by employing 1PA via a CW blue laser to pre-sensitize a photocurable resin, followed by 2PA using a tightly focused femtosecond (fs) laser beam to provide the required energy reaching the polymerization threshold for solidifying the resin. This sequential dual-excitation approach alters the voxel growth kinetics, reducing the polymerization threshold and accelerating the voxel growth. We develop a diffusion-free theoretical model that elucidates the pre-sensitization dynamics, where oxygen depletion and sub-threshold latent polymerization induced by 1PA pre-sensitize the resin for more efficient 2PA. Experimental validation confirms that this mechanism enables a 29% reduction in fs laser power and a two-fold decrease in exposure time compared with polymerization performed only by 2PA. Furthermore, the method improves axial voxel confinement by 63%. The theoretical framework not only explains the observed enhancements but also offers predictive power for optimizing printing parameters in high-viscosity resins. This dual-excitation strategy provides a scalable approach toward high-resolution, high-throughput 3D microfabrication.

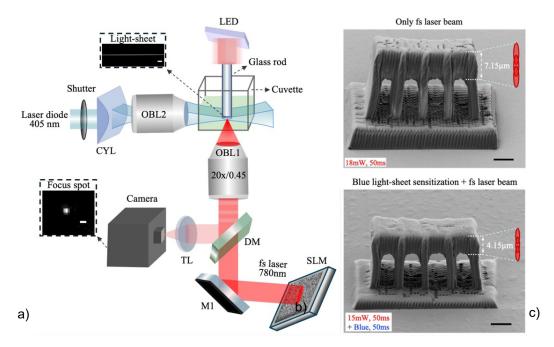


Figure: a) Experimental setup of blue light-sheet-assisted 2PP, b) SEM images of the printed bridge by only 2PP and (c) by blue light-sheet-assisted 2PP. The scale bars are 5  $\mu$ m.

89 D3 -S17 -04

Emerging AM technologies

3D electronics, volumetric printing, photoresins

### MATERIALS AND METHODS FOR GENERATING 3D ELECTRONICS WITH VOLUMETRIC ADDITIVE MANUFACTURING

#### **Chantal Paquet**

Security and Disruptive Technologies Research Center, National Research Council of Canada

Volumetric additive manufacturing (VAM) is a newly developed polymer 3D printing technique that uses tomographic projection to print all-at-once enabling objects to form orders of magnitude faster than traditional vat polymerization 3D printing methods. This technique also has the unique ability to print over top of an existing structure, a method we term overprinting. We propose to use this printing platform in an unconventional way – to 3D overprint a pattern of a functional polymer overtop of an existing object and subsequently metallized the newly printed pattern to produces 3D printed conductors. This presentation will introduce volumetric additive manufacturing, highlight challenges of printing with VAM and the development of photoresins and printing requirements needed to generate high resolution 3D electronics.

90 D3 -S18 -04

High performance polymer, DLP, biomedical device

#### APPROACHES TO PRINT HIGH PERFORMANCE POLYMER BY DLP

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- (2) 3DMedlab, Marignane, France

High-performance polymers such as poly(trifluoroethylene), poly(olefin)s, and poly(ether ketone) offer excellent chemical resistance and mechanical robustness, making them attractive candidates for demanding applications, particularly in the biomedical field [1]. However, their inherent processing limitations—particularly in additive manufacturing techniques such as digital light processing (DLP) [2]—have significantly restricted their use in fabricating complex, custom-made architectures and hindered rapid production.

To overcome these challenges, we have developed a smart and reproducible strategy to print 3D structures using these types of polymers. Our approach relies on a photo-curable formulation consisting of dispersed polymer particles with a hydrosoluble binder matrix. This enables straightforward processing *via* DLP 3D printing, yielding to composite materials with custom-made architecture. Afterward, through a series of post-processing steps, we successfully produced a high-performance polymer with tailored flexibility and structural integrity, as demonstrated in Figure 1 on a fully PTFE-printed object.

Such printed materials exhibit promising mechanical and chemical properties, and the method paves the way for the production of a wide range of high-performance, biostable, and biocompatible devices. Notably, this technique is particularly well-suited for vascular repair and other advanced biomedical applications where structural integrity, complex architecture, and functionality are critical.

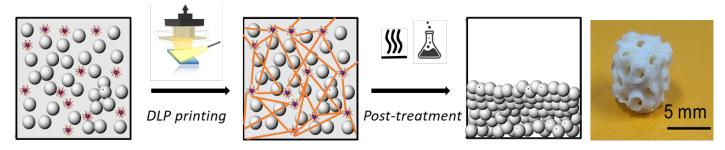


Figure 1: Processing approach from PTFE aqueous dispersion to pure PTFE constructs by DLP.

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91 D3 -S17 -05

two-photon lithography, macromolecular design, structure-property relationships

#### MACROMOLECULAR DESIGN OF INKS FOR 3D MICROPRINTING

#### Samantha Catt (1), Eva Blasco (1)

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Two-photon 3D laser printing (2PLP) is a leading technique for fabricating intricate microscale structures with high precision. As technology advances, there is growing interest in developing versatile inks capable of producing functional or responsive materials. Traditionally, 2PLP inks are based on multifunctional small molecules or polymers with a distribution of crosslinkable groups, limiting our understanding of how ink properties influence print behavior and final material performance. This study explores a rational approach to ink design using defined macromolecular structures. First, pre-polymer inks with tailored comonomer compositions are developed, to vary properties like glass transition temperature and molecular weight [1]. Second, a sequence-defined synthesis method is introduced to assess how monomer order impacts printing, marking the first use of sequence-defined oligomers in 2PLP. The findings demonstrate that molecular structure significantly affects both printability and the characteristics of the printed materials, such as photoactive-group conversion and mechanical properties. This precision in molecular design enables clearer structure—property relationships, supporting the development of tuneable, high-performance functional materials.

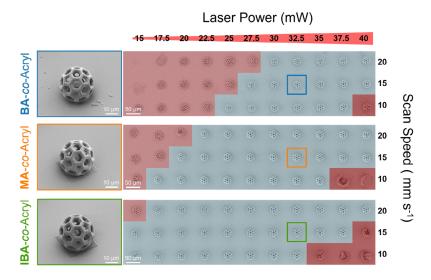


Figure: SEM images demonstrating the varied printing range of three 2PLP inks over differing laser powers and scan speeds.

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92 D3 -S18 -05

Extrusion based AM /

additive manufacturing; biofabrication; stem cells

### SUSTAINABILITY OF ADDITIVE MANUFACTURING TECHNOLOGIES TO CREATE SMART SCAF-FOLDS FOR REGENERATIVE MEDICINE

Lorenzo Moroni\* (1)

#### **DISCLAIMER**

The abstract is not included as per author's request.

93 D3 -S19 -01

Extrusion based AM / iquid crystal elastomers, 4D print, Soft robots

#### 4D PRINTED ADAPTIVE SOFT ROBOTS OF LIQUID CRYSTAL ELASTOMERS

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In the family of smart materials, liquid crystal elastomers (LCEs) stand out as ideal candidates for mimicking the muscular functionality of soft robots. This is attributed to their unique combination of the entropic elasticity inherent in polymeric elastomers and the anisotropy of mesogens, which together enable reversible shape-changing behavior and programmability [1,2]. The high processability of LCEs allows for the fabrication of customized structures through advanced techniques such as 4D printing. Furthermore, the deformation of LCEs can be precisely controlled by manipulating the alignment of mesogens [3-5]. These properties make LCEs highly suitable for applications requiring dynamic and adaptive mechanical responses, such as bio-inspired soft robotics.

In this report, we present a novel segmental soft crawling robot that possesses the capability to dynamically adjust its posture and generate adaptive locomotion modes. Multi-material 4D printing plays a pivotal role in the development of this robot. It facilitates the fabrication of the segmental architecture comprising alternating soft LCE-MWCNTs and rigid acrylic resin, and enables high-curvature bending in each segment by inducing a gradient alignment of mesogens through an ingenious exterior nozzle tip shearing approach. Moreover, the implementation of a light-fueled strategy enables the independent and precise control of each segment within the segmental architecture. As a result, the robot achieves localized or overall curvature changes (approximately 0.62~1.49 cm<sup>-1</sup>) to realize multiple postures. This enables adaptive and well-controlled locomotion of the robot, including controllable bidirectional crawling, transitions between crawling and rolling modes, as well as self-righting behavior, demonstrating its capability for continuous exploration in complex terrains.

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94 D3 -S20 -01

Light mediated AM / ROMP, photolithography, DIW

# 3D PHOTOROMP: USING LIGHT TO CONTROL RING-OPENING METATHESIS POLYMERIZATIONS FOR 3D PRINTING

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- (2) University of Illinois at Urbana-Champaign, Urbana, Illinois, USA.

Photoactivated catalysts have been extensively investigated for the initiation of ring-opening metathesis polymerization. However, much less work has been done on using light to enable active control of ROMP. Our group is investigating multiple approaches to use light to control both reaction rates and polymer composition. In this talk we will share our research into approaches to controlling ring-opening metathesis polymerizations with light and their applications in 3D printing. With catalyst-based photocontrol we demonstrate control over the front velocity and direction of propagation of a frontal ring-opening metathesis polymerization (FROMP). Frontal reactions continue propagation after initiation through a self-sustaining thermal front, and the speed and direction of a propagating front cannot be easily controlled. Using photochemistries to regulate catalyst activity we have demonstrated both acceleration and deceleration of FROMP and can control the direction and shape of FROMP propagation in a sheet of resin. An alternative approach is monomer-based photocontrol, which utilizes photoisomerizable monomers to control the composition and thermomechanical properties of ROMP copolymers. We will present initial results on two different methods of monomer-based photocontrol and demonstrate application in grayscale photolithography and 3D printing. Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

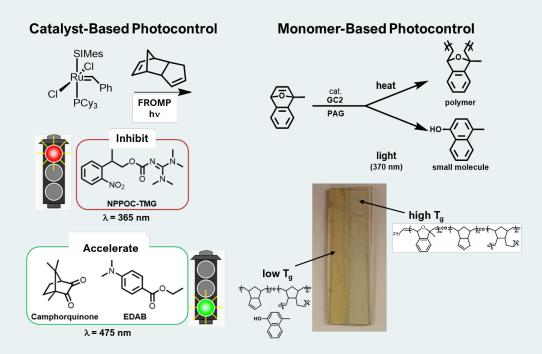


Figure: Routes towards photocontrol of ROMP and FROMP for additive manufacturing.

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95 D3 -S19 -02

Emerging AM technologies / Two photon polymerization, ultrathin films, soft microdevices

### From Tattoo Electronics to 3D Microdevices: Soft Microsystems via 2-Photon Lithography Virgilio Mattoli (1)

(1) Istituto Italiano di Tecnologia, Center for Materials Interfaces, Pontedera (PI), Italy

Soft, ultra-thin electronics based on free-standing polymer films offer a powerful platform for integrating electronic functionality onto complex, non-planar surfaces such as human skin. Fabricated using solution-processable materials and printing techniques, these "tattoo electronics" enable imperceptible healthcare monitoring and active, skin-conformal interfaces [1,2]. Moving beyond planar systems, the integration of two-photon lithography (2PL) opens up new possibilities for three-dimensional design, enabling the direct fabrication of intricate microstructures with sub-micron resolution onto freestanding ultrathin substrates. This approach merges the precision of high-resolution additive manufacturing with the versatility needed for advanced micro-mechanical, photonic, and biomedical applications [2,3]. In this talk, we present recent advancements achieved within the EU-funded 5D NanoPrinting and IV-Lab projects [5], focusing on the development of conformal sensors and devices through the combined use of ultrathin film technology, direct inkjet printing of functional materials, and two-photon polymerization, also showcasing techniques such as self-shadowing and 3D lift-off lithography for the realization of metallic interconnections on complex substrates. Additionally, we discuss scalable strategies for the transfer of 2PL-fabricated components onto a variety of surfaces, enabling flexible and modular system integration across multiple application domains. Together, these developments represent a significant step toward fully integrated soft Electro-Mechanical Systems (MEMS) that unite the mechanical adaptability of tattoo electronics with the architectural complexity and functional sophistication of 3D microdevices.

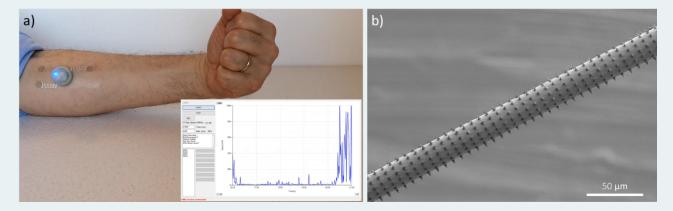


Figure: a) Ultrathin tattoo electrodes for detection of EMG signals and wireless transmission [2]; b) Microstructures integrated on small diameter wire by nanometric-thin film wrapping [3]

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- [5] <a href="https://5dnanoprinting.eu">https://5dnanoprinting.eu</a>; <a href="https://iv-lab.eu/">https://iv-lab.eu/</a>

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active flow sculpting, microfluidics, acoustofluidics

#### ACTIVE FLOW SCULPTING FOR THE NEXT GENERATION OF 3D PRINTING NOZZLES

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<sup>1</sup>Technical University of Munich, Munich, Germany. <sup>2</sup>Rose-Hulman Institute of Technology, IN, USA. <sup>3</sup>Chonnam National University, Gwangju, South Korea.

Introduction: Additive manufacturing has transformed material science by enabling 3D printing of tunable structures for applications like micro-robotics, sensors, and tissue engineering [1]. However, conventional extrusion-based printing uses fixed nozzle shapes, which limits control over the extruded material compositions and printed geometries. Recent methods offer some composition and flow control but rely on bulky, complex systems [2]. Passive techniques like co-axial nozzles, Dean vortices, and hydrodynamic focusing lack dynamic modulation [3–4]. Here, we present Active Flow Sculpting (ActiSculpt), a method for spatiotemporal modulation of multi-layered laminar streams using on-demand acoustic streaming, enabling dynamic flow structuring. We developed a software to predict the cross-sectional flow patterns by using a comprehensively enhanced acoustic streaming model that accurately depicts the experimental conditions. We achieved a five-fold increase in the moment of inertia (Mol) of the sculpted cross-sectional flow profile, which translates into a wide range of bending and torsional strengths of a cured fiber.

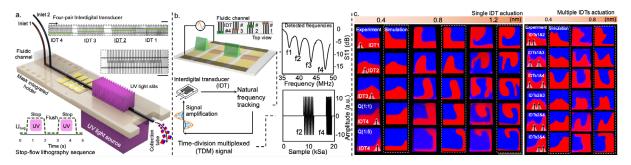
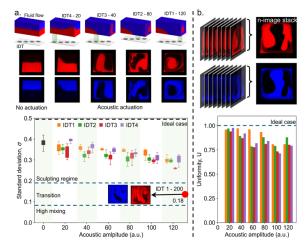


Fig. 1. (a) ActiSculpt setup, (b) On-demand acoustic actuation, (c) Flow modulation by on-demand control of IDTs.



**Fig. 2**. (a) Sculpting with minimal diffusive mixing (b) uniformity of sculpted shapes by IDTs 1-4.

Results and discussion: Distinct sculpted flow shapes are achieved in a precisely controllable manner by selectively varying the input power to IDTs 1–4. The sculpted shapes are characterized using a diffusion parameter based on standard deviation, with values remaining above the mixing threshold even at higher power levels (Fig. 2a). The sculpted shape uniformity is assessed by comparing results across different cycles. The uniformity exceeds 75% (up to ~95%) for different actuations by IDTs 1-4, confirming the robustness of our method (Fig. 2b). We measured the MoI of the sculpted shapes to vary by 5-folds using a single ActiSculpt platform (not shown), which highlights versatility of our method.

**Conclusion:** The ActiSculpt platform offers highly flexible and unique capabilities to actively manipulate multi-layered flows on-demand, which will unveil new possibilities in the field of microfluidic flow control, 3D printing and additive manufacturing.

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97 D3 -S19 -03

**Emerging AM technologies** 

FLOW SCULPTING; ANISOTROPIC MICROPARTICLES; MULTI-MATERIAL FIBERS

#### 3D HYDRODYNAMIC FLOW LITHOGRAPHY

<u>Yiying Zou</u> (1), Mehmet Akif Sahin (1), Muhammad Zia Ullah Khan (1), Muhammad Usman Akhtar (1), Ghulam Destgeer \* (1)

(1) Technical University of Munich, Munich, Germany

The ability to customize microparticles in size, shape, and composition is essential for advanced applications in various fields. However, existing fabrication techniques often face limitations in terms of the diversity in particle structure, complexity of device manufacturing, or production throughput. We present a 3D hydrodynamic flow lithography method for continuous production of multi-material, anisotropic microparticles and fibers with engineered shapes and tunable sizes. Our method integrates sequential 3D hydrodynamic flow sculpting (3D HFS) and stop-flow lithography (SFL) within a oxygen-permeable PDMS-based 3D microfluidic device, to sculpt the shape of the flow and then periodically turn them into solid particles. By strategically playing with three key 3D HFS parameters—inlet arrangement, main channel topology, and outlet channel geometry—we demonstrate productive control over flow shaping, enabling the generation of over 10 distinct flow structures, as validated by computational fluid dynamics simulations and experimental particle production (SFL, ~104 particles/hour). Crucially, our method leverages 3D-printed molds and soft lithography technology to obtain the 3D PDMS channels, which enbles precise positioning of the inlet ports with respect to the main channel, distinct main channel topology for flow sculpting, various cross-sectional shapes of the outlet channel, and clogging-free curing of fiber or particles. This platform offers a versatile, scalable, and high-throughput solution for engineering anisotropic microparticles, opening new possibilities in drug delivery, directed self-assembly, biosensing, microbots, and tissue engineering, etc.

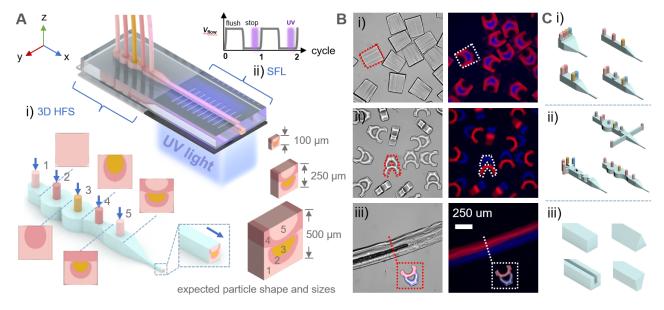


Figure: 3D hydrodynamic flow lithography. (A) Microfluidic device and numerical simulation model for corresponding flow profile prediction. (B) microscope images of the produced anisotropic microparticles and fiber. (C) Various designs of 3D HFS microchannel.

98 D3 -S20 -03

Emerging AM technologies / multiaxis printer design

**ADDON MANUFACTURING:** A multi-axis, multi process additive manufacturing system to print on top of existing surfaces.

Fergal Coulter (1), André Studart (1)

(1) Complex Materials Group, Department of Materials, ETH Zürich, Switzerland

Here we present a modular open hardware and software design for a 7 axis printing system featuring various laser based measurement devices. The machine can 3D Scan and digitally reconstruct then print upon most non-reflective substrate surfaces, irrespective of their curvature.

By combining different deposition techniques such as atomizing spray, microjet, cold-paste or melt extrusion, the versatile system is capable of depositing a range of material classes in a fashion akin to over-moulding.

The talk will discuss various techniques to scan surfaces depending on whether the substrate geometry is known a-priori or not. Strategies are revealed to calculate the print toolpaths ensuring the deposition nozzle is always perpendicular to the curved substrates. Finally, the hardware decisions and limitations are disclosed.

Use cases for such a machine are manyfold, but in this instance, we focus on bespoke implantable medical devices – in particular printing custom aortic heart valves with integrated ascending aorta. The multi-material nature of such a device requires various elastic moduli and anisotropic compliance, with sub-millimeter membranes and fibers running seamlessly over its entire length.



Figure: Printing silicone on a curved substrate using a 6 axis process

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99 D3 -S19 -04

two-photon polymerization; reconfigurable & programmable materials; liquid crystal elastomers

#### RECONFIGURABLE AND PROGRAMMABLE MATERIALS FOR LIGHT-INDUCED 3D & 4D PRINTING

Keynaz Kamranikia (1,2), Sébastien Dominici (1,2), Mehdi Belqat (1,2), Xingyu Wu (1,2), Quentin Bauerlin (1,2), Karine Mougin (1,2), **Arnaud Spangenberg** (1,2)

- (1) Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France.
- (2) Université de Strasbourg, France.

4D printing concept appears in 2013 with the idea to facilitate the assembling of macroscopic objects [1]. The fourth dimension refers not only to the ability for material objects to change form after they are produced, but also to their ability to change function after they are printed [2-4]. At the microscale, 3D direct laser writing (3D DLW) based on multiphoton polymerization has become the gold standard for submicrometer additive manufacturing. Various stimuli-responsive materials have been employed to manufacture advanced microactuators. In particular, liquid crystal elastomers (LCEs) have attracted considerable attention due to their reversible, large shape-morphing and their fast response towards temperature or light stimuli. However, their processability by 3D DLW is not easy and the resulting objects rarely exhibit controlled and predictable deformation. In order to increase the complexity of deformation and thus to fulfil the requirements of nanorobotics, new programming strategies must be implemented. Besides, most of the printed objects present fixed properties. The possibility to reconfigure their properties on demand would definitively be a key parameter for many applications.

In this talk, we propose alternative strategies to reconfigure or program the shape and the surface properties of 3D printed micro-object. Firstly, the employ of controlled radical polymerization to confer to the object a living character will be introduced. Secondly, a new approach to perform the alignment of LCEs in a precise manner will be discussed. By playing both on the orientation strategy and the fabrication parameters, different deformations (curling, bending, twisting...) can be programmed starting from a single CAD model. A collection of building block is first demonstrated, then assembly of these building block is achieved, leading to 3D micro-objects presenting sophisticated behaviour. This work opens up new prospects for moving from a programmable material to a functional 3D-printed device.

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100 D3 -S20 -04

multiphoton 3D laser printing, soft materials, 3D microprinting

## SUPRAMOLECULAR INK DESIGN APPROACH FOR MULTIPHOTON 3D LASER PRINTING OF SOFT MATERIALS

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Since its technological realization in the 1980s 3D printing has undergone tremendous progress, visible in its manifold applications in various fields in academia as well as industry nowadays. Especially for the manufacturing of precise, high-quality structures at the microscale, multiphoton 3D laser printing (MPLP) has been established as the method of choice [1]. Exploiting the process of multiphoton absorption, 3D microstructures with submicrometer features can be easily manufactured by programmed scanning of a tightly focused near-infrared laser. Besides technological progress, the printing material library for MPLP expanded drastically in recent decades, especially for materials in the stiffer mechanical regime. Importantly, ink design for MPLP becomes rather sophisticated when softer materials with lower stiffness are desired. The reason for this is the necessity of high amounts of multifunctional crosslinker moieties in MPLP inks to have the necessary density of photopolymerizable groups to enable efficient 3D microprinting of complex microarchitectures. Consequently, resulting printed materials often have high crosslinking densities and feature rather stiff mechanical properties, rendering them impractical for use in many applications for example in life sciences, where softer materials are highly sought. However, softer materials compatible with MPLP often suffer in their microprinting performance and structural quality especially when complex 3D geometries are targeted.

Here, we present a new supramolecular ink design approach to achieve soft smart materials *via* MPLP. Our method exploits supramolecular chemical principles to mimic the function of crosslinker moieties, enabling the creation of complex 3D microstructures with bulk Young's moduli as low as 260 kPa in aqueous environments. This approach not only simplifies ink preparation but is also highly versatile, allowing for the precise 3D microprinting of both hydrophilic and hydrophobic materials, as well as smart materials. Collectively, the superior 3D printability, ease of ink preparation, and high adaptability of our supramolecular design make it an ideal strategy for material science and engineering, particularly for the development of functional 3D materials that can be precisely fabricated at the microscale for applications across a broad range of disciplines.

[1] P. Mainik, C. A. Spiegel, E. Blasco, "Recent Advances in Multi-Photon 3D Laser Printing: Active Materials and Applications", *Adv. Mater.*, **2024**, 36, 2310100.

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101 D3 -S19 -05

SLS or Powder Bed Fusion AM/

Laser remelting, Additive Manufacturing, Titanium alloy

## LAYER-WISE IN-SITU REMELTING IN LASER POWDER BED FUSION OF TI6AL4V: MICROSTRUCTURAL AND MECHANICAL IMPLICATIONS

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Laser remelting presents a promising approach to enhance the mechanical properties and reduce defects in additively manufactured components [1] [2]. This study explores the impact of layer-wise laser remelting on the microstructure and hardness of Ti6Al4VI fabricated using Laser Powder Bed Fusion (LPBF) on an EOS M100 system. A series of samples were produced with selected process parameters, followed by the application of controlled remelting strategies. Microstructural characterization was carried out using Scanning Electron Microscopy (SEM) and Electron Backscatter Diffraction (EBSD), while hardness testing was conducted to evaluate mechanical performance. Preliminary findings indicate that remelting influences grain morphology and crystallographic texture, highlighting its potential to refine the microstructure and enhance consistency of parts fabricated under suboptimal processing conditions.

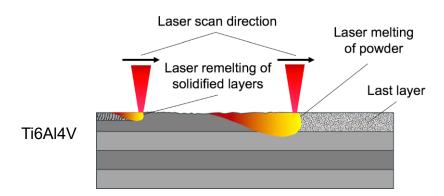


Fig: Schematic representation of the working principle of laser surface remelting

[1] Chen, X., Qiu, C, "In-situ development of a sandwich microstructure with enhanced ductility by laser reheating of a laser melted titanium alloy", Scientific Reports, **2020**. 10, 15870 10.1038/s41598-020-72627-x.

[2] J. Karimi, C. Suryanarayana, I. Okulov, K.G. Prashanth, "Selective laser melting of Ti6Al4V: Effect of laser re-melting", Materials Science and Engineering: A, **2021**, Volume 805,140558 10.1016/j. msea.2020.140558.

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102 D3 -S20 -05

Extrusion based AM

Microfibrillation, inmiscible blends, rheology

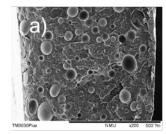
#### IN-SITU MICROFIBRILLATED PP/PET COMPOSITES BY 3D PRINTING

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Morphological control of immiscible systems allows the physical and mechanical properties of these systems to be tailored to the specific requirements of each application. Recently, microfibrillar composites (MFCs), commonly referred to as microfibrillar composites (MFCs), have attracted particular interest as they allow fibrillar morphologies to be obtained *in-situ*, providing uniaxially reinforced products with improved mechanical performance due to the high level of anisotropy. In recent years, new processing technologies, based on additive manufacturing, have provided the opportunity to obtain CFMs with full control of the microfibrillar morphology of these systems.

This work explores the potential of 3D printing to obtain *in-situ* CFMs based on polypropylene (PP) and poly(ethylene terephthalate) (PET) blends. Specifically, the effect of the printing velocity has been evaluated, since it plays a key role in the acquisition of fibril morphology (Figure 1), together with the viscosity ratio and elasticity ratio of matrix and dispersed phase. i A comprehensive conventional and advanced rheological study has provided a better understanding of the morphology of the MFCs, and the magnitude and evolution of isotropisation.



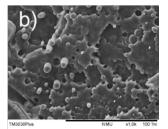


Figure 1: SEM images of the PP/PET 70/30 sample, without compatibiliser, obtained by: a) compression moulding; b) 3D-printing, 50 mm/s.

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103 D3 -S19 -06

Extrusion based AM / rheology, dense pastes, quality

#### LINKING MATERIAL PROPERTIES AND PROCESSING IN 3D PRINTING DENSE PASTES

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While progress has been made in rapidly customizing the shape of material goods through additive manufacturing processes, customizing the properties of the materials and responding to disruptions in the supply chain and new regulations is still a slow development process. A major factor slowing materials customization is understanding the interactions between components in complex mixtures used to make functional products and, especially, how those interactions impact manufacturability. Our research integrates materials, rheology and processing to enable manufacturing innovation practices that include the materials needed for manufacturability early in a product design process. Here we focus on materials with high particle loadings, which are of particular interest when the particle provides the desired functionality and the polymer acts to bind them together into a shape. As new continuous processing technologies, such as 3D printing, become more prevalent, low binder content has introduced challenges, particularly due to the high viscosities encountered in dense pastes. Understanding how the formulation elements, including particle and binder properties, impact the rheological and solidification properties and how those translate to processing will enable rapid formulation design and robust processes. We focus on direct ink write additive manufacturing and examine the rheology and processability of dense pastes (>60 vol% particles) and show how the nature of the binder, the particle size distributions and the processing parameters influence the quality of the final solid part. This work allows us to understand how to link formulation properties to processing to design dense pastes for improved, 3D printed materials.

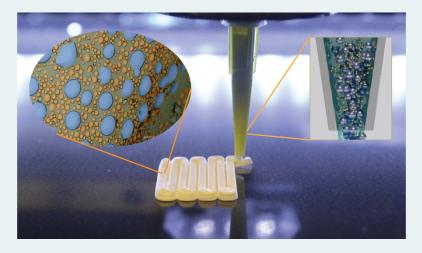


Figure: Additive manufacturing dense pastes

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104 D3 -S20 -06

Light mediated AM / Vat photopolymerization, multimaterial, dual-wavelength

### MULTIMATERIAL ACTINIC SPATIAL CONTROL (MASC) ADDITIVE MANUFACTURING OF ORGAN-IC-INORGANIC MULTIMATERIAL PARTS

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Multimaterial additive manufacturing attracts and inspires multidisciplinary approaches for combining disparate materials into single parts. Approaches span a range of chemical "bottom-up" techniques, engineering "top-down" technologies, and hybridized manufacturing strategies. With an emphasis on the underlying chemistry of vat-based additive manufacturing, we will discuss our most recent efforts toward incorporating combinations of organic and inorganic materials into the same printed part [1]. Our approach involves a technique we refer to as Multimaterial Actinic Spatial Control (MASC) and leverages chemical orthogonality and selectivity that can be spatially controlled via different wavelengths of light [2,3]. In this way, the use of multiwavelength projection systems in vat-based additive manufacturing enables access to multimaterial parts that ultimately contain highly disparate organic (soft, flexible, insulating) and metallic (stiff, ductile, conductive) domains with full three-dimensional control over their placement [4].

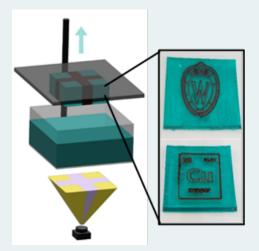


Figure: Generalized concept of metal-MASC.

- [1] "Additive Manufacturing of Metal-Incorporated Resin Objects" Andrew J. Boydston, Evan M. Sherbrook. U.S. patent 12,138,853B2 issued November 12, 2024.
- [2] Johanna J. Schwartz, Andrew J. Boydston "Multimaterial Actinic Spatial Control 3D and 4D Printing" *Nat. Commun.* **2019**, 10, 791.
- [3] Kyle C. H. Chin, Grant Ovsepyan, Andrew J. Boydston "Multi-Color Dual Wavelength Vat Photopolymerization 3D Printing via Spatially Controlled Acidity" *Nat. Commun.* **2024**, 15, 3867.

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105 D3 -S19 -07

Extrusion based AM / Nanostructure, self-assembly, hierarchy

#### DIRECTED SELF-ASSEMBLY OF NANOSTRUCTURED POLYMERS VIA 3D PRINTING

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Nature creates remarkable materials by controlling the hierarchical assembly of molecules. Inspired by natural systems, we combine molecular design and materials characterization with directed assembly via extrusion-based 3D printing to program the structure and function of polymer-based materials across length scales. First, I will describe how in both liquid crystalline polymers[1] and block copolymers[2] we can control the extent of nanostructure alignment and functional anisotropy via the nonequilibrium processing the material undergoes during and following 3DP. By tailoring flow history and microstructural layout, we are able to encode 'multiple properties' in structures composed of a single material. We also explore our ability to move beyond alignment to the selection of nanostructure itself through flow, and to tailor microstructure 'on-the-fly' by coupling reactive extrusion with phase separation.

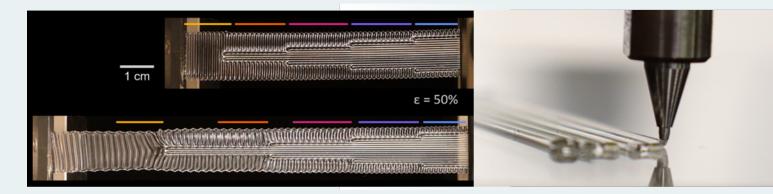


Figure 1: Graded soft elastomers via 3D printing directed self-assembly

[1] R. Telles, A. Kotikian, G. Freychet, M. Zhernenkov, P. Wasik, B. Yavitt, R. Pindak, E.C. Davidson\*\*, J.A. Lewis\*\*, "Spatially programmed alignment and actuation in printed liquid crystal elastomers," *PNAS*, **2025**, DOI: 10.1073/pnas.241496012

[2] A.S. Fergerson, B.H. Gorse, S.M. Maguire, E.C. Ostermann, E.C. Davidson, "Reprocessable and mechanically tailored soft architectures through 3D printing of elastomeric block copolymers," *Advanced Functional Materials*, **2024**, DOI: 10.1002/adfm.202411812

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106 D4 -PL

Light mediated AM / Sustainability, Mechanochemistry, Metamaterials

#### ADDITIVE MANUFACTURING OF PROTEIN-BASED MECHANICAL METAMATERIALS

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Bio-sourced and biodegradable polymers for additive manufacturing could enable the rapid fabrication of parts for a broad spectrum of applications ranging from healthcare to aerospace. However, a limited number of these materials are suitable for vat photopolymerization processes. Herein, we report a process to fabricate protein-based constructs using commercially available vat photopolymerization printers. We have utilized bovine serum albumin (BSA) as a model single-chain nanoparticle that can be chemically derivatized with acrylate and methacrylate functionalities.[1-3] Aqueous resins were formulated from these materials to produce complex 3D geometrical constructs with a resolution comparable to commercial resins. Interestingly, we show that BSA can serve as mechanoactive elements that enable strain strengthening of the material. I will also present other globular proteins that we have also 3D printed to create high-performance bioplastics.

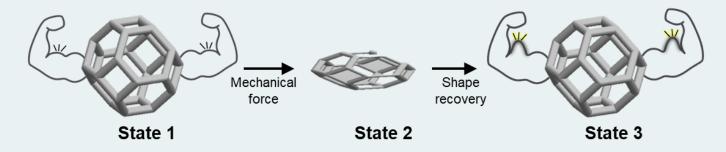


Figure: 3D Additive Manufacturing Conference Logo, October 2024.

[1] Naroa Sadaba, et al. "Strain learning in protein-based mechanical metamaterials" *Proc. Natl. Acad. Sci. U.S.A.*, **2024**, *121*, e2407929121, DOI: 10.1073/pnas.2407929121

[2] S. Cem Millik, et al. "3D-Printed Protein-Based Bioplastics with Tunable Mechanical Properties Using Glycerol or Hyperbranched Poly(Glycerol)s as Plasticizers." *Biomacromolecules*, **2025**, *26*, 1725, DOI: 10.1021/acs.biomac.4c01497

[3] S. Yu, et al. "4D Printed Protein-AuNR Nanocomposites with Photothermal Shape Recovery". *Adv. Funct. Mater.* **2023**, 2311209, DOI: 10.1002/adfm.202311209

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107 D4 -S21 -01

gradient printing, sensor, actuator

#### 3D-PRINTED FUNCTIONALLY GRADED MATTERS

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3D gradient printing is a type of fabrication technique that builds three-dimensional objects with gradually changing properties. Yet, computer-aided design tools have not been set up to generate such desired structural gradients, lacking the possibility of controlling the material's directional dependence on the generation of form. In light of these limitations, a breakthrough strategy towards designing very smooth gradients during the high resolution stereolithography 3D printing is reported. Our chemomechanical programming allows the design of a family of multi-responsive hydrogel-based actuators with fast, reversible, repeatable and multimodal bending actuation in response to any immediate environmental change from a single printed structure [1]. Likewise, programming electromechanical gradients within ionically conductive hydrogels address the challenge of building novel self-powered iontronic touch sensors with tactile feedback for recognition applications [2].

- [1] Odent J., Vanderstappen S., Toncheva A., Pichon E., Wallin Th.J., Wang K., Shepherd R. F., Dubois Ph., Raquez J.-M., "Hierarchical Chemomechanical Encoding of Multi-Responsive Hydrogel Actuators via 3D Printing", *Journal of Materials Chemistry A*, **2019**, 7, 15395-15403, DOI: 10.1039/C9TA03547H
- [2] Odent J., Baleine N., Biard V., Dobashi Y., Vancaeyzeele C., Nguyen G., Madden J., Plesse C, Raquez J.-M., "3D-printed stacked ionic assemblies for iontronic touch sensors", *Advanced Functional Materials*, **2022**, 33, 2210485, DOI: 10.1002/adfm.202210485

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108 D4 -S22 -01

Light mediated AM / digital light processing, liquid crystal elastomer, actuation

## DIGITAL LIGHT PROCESSING 4D PRINTING OF LIQUID CRYSTAL ELASTOMERS: OVERCOMING LIMITATIONS IN MESOGEN ALIGNMENT

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4D printing of soft actuators using smart materials offers great potential for creating flexible and adaptable structures in various applications such as artificial muscles, medical devices, and soft robotics. Among these materials, liquid crystal elastomers (LCEs) are especially attractive due to their ability to undergo large, rapid, and reversible shape changes in response to external stimuli like heat or light [1]. To 4D print LCEs, direct ink writing (DIW) has become a widely used technique, offering effective mesogen alignment through shear during extrusion. However, DIW is limited to simple or flat geometries, and printing more complex 3D shapes often requires additional support materials or embedded strategies. In contrast, digital light processing (DLP) enables high-resolution printing of complex structures but lacks inherent alignment control, resulting in LCEs that cannot perform actuation [2]. To address this limitation, we present two straightforward methods for inducing mesogen alignment in DLP-printed LCEs, based either on magnetic field alignment of the resin [3] or mechanical alignment of the printed material. By adjusting the phase transition temperature and optimizing the crosslinking strategy, we fabricate LCEs with tunable actuation temperatures (50-90 °C) and actuation strains (20-50%), along with multiple actuation modes (extension, bending, twisting). Their potential is demonstrated through the fabrication of complex reversible shape-changing DLP-printed LCE structures showing several programmable actuation modes.

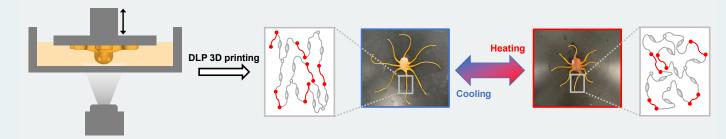


Figure 1: DLP 4D Printing of a Reversible Shape-Changing LCE Octopus

- [1] Zhecun Guan, Ling Wang, Jinhye Bae "Advances in 4D Printing of Liquid Crystalline Elastomers: Materials, Techniques, and Applications", *Materials Horizons*, **2022**, 9, 1825-1849, DOI: 10.1039/D2M-H00232A
- [2] Katie M. Herbert, Hayden E. Fowler, Joselle M. McCracken, Kyle R. Schlafmann, Jeremy A. Koch, Timothy J. White "Synthesis and Alignment of Liquid Crystalline Elastomers", *Nature Reviews Materials*, **2022**, 7, 23-38, DOI: 10.1038/s41578-021-00359-z
- [3] Rakine Mouhoubi, Vincent Lapinte, Sébastien Blanquer, "Programmable Liquid Crystal Elastomers Via Magnetic Field Assisted Oligomerization", *Advanced Functional Materials*, **2025**, 24, 244400, DOI: 10.1002/adfm.202424400.

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109 D4 -S21 -02

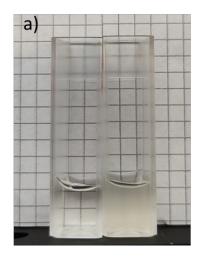
Light mediated AM / bioprinting; light scattering; hydrogel

### OVERCOMING SCATTERING IN TOMOGRAPHIC VOLUMETRIC BIOPRINTING USING COMPUTA-TIONAL LIGHT OPTIMIZATION

**Qianyi Zhang**, Felix Wechsler, Viola Sgarminato, Christophe Moser\*

Laboratory of Applied Photonics Devices, School of Engineering, Institute of Electrical and Micro Engineering, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Tomographic volumetric additive manufacturing (VAM) has emerged as a transformative 3D printing technology for rapidly fabricating complex geometries. It offers significant advantages for bioprinting due to its short process time (a few tens of seconds). However, the presence of high cell densities (5 ~10 million cells mL-1) in bioinks introduces substantial light scattering, which degrades printing resolution (from ~100 microns to millimeter scale) and fidelity, hindering the fabrication of biologically relevant microstructures such as vascular channels and cavities. To address this challenge, we utilize a computational patterning framework leveraging physically based differentiable rendering [1] to optimize light delivery in scattering environments. This method iteratively refines tomographic projections by simulating light-matter interactions in cell-laden hydrogels, enabling precise compensation for scattering effects. Experimental results demonstrate that our approach achieves 200 µm diameter channels at 1 million cell mL-1 and 500 µm diameter channels at 10 million cell mL-1. Furthermore, we integrate this computational method with refractive index matching strategies, reducing scattering artifacts by minimizing optical heterogeneity between cells and the hydrogel matrix. The compatibility of these dual strategies—algorithmic scattering compensation and refractive index engineering—enables unprecedented print fidelity in turbid bioinks. This advancement expands the scope of tomographic VAM for engineering functional tissues with intricate microarchitectures.



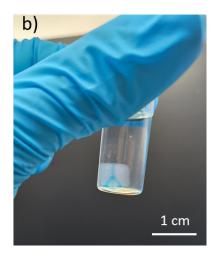


Figure: Printing in cell-laden hydrogels with scattering correction. a) Example of a hydrogel without and with human fibroblast cells (5 million cells mL<sup>-1</sup>). b) Tomographic volumetric bioprinting of hollow channels (500 µm diameter) with hydrogels containing 5 million cells mL<sup>-1</sup>.

[1] Baptiste Nicolet, Felix Wechsler, Jorge Madrid-Wolff, Christophe Moser, and Wenzel Jakob. "Inverse Rendering for Tomographic Volumetric Additive Manufacturing", ACM Trans. Graph., **2024**, 43, 6, Article 228, DOI: 10.1145/3687924

110 D4 -S22 -02

Extrusion based AM / Architecture, Polymers, Sustainability

## EXPLORING SUSTAINABLE, HIGH-PERFORMANCE THERMOPLASTIC MATERIALS FOR ARCHI-TECTURAL AND CONSTRUCTION APPLICATIONS THROUGH ROBOTIC LARGE-FORMAT ADDITIVE MANUFACTURING

Fabio Caltanissetta (1), Luca Morelli (1), Giulia Filippone (1), Giovanni Avallone (1)

(1) Caracol AM, Paderno Dugnano, Italy.

Over recent years, interest in robotic Large Format Additive Manufacturing (LFAM) has grown across industries due to its ability to produce high-performance, lightweight, and topologically optimized components, overcoming volume limitations faced by traditional additive methods [1]. The architectural sector, in particular, sees great potential for 3D printing to revolutionize building design, construction, and sustainability by enabling complex, customized structures that push traditional boundaries, reducing material waste, and speeding up construction timelines through on-site or prefabricated printing. Thermoplastics, valued for their versatility, durability, and ease of processing, are especially promising for architectural applications, offering sustainable, reusable options for lightweight structures. However, challenges remain in developing material formulations that meet rigorous technical and architectural standards related to product certification. This study aims to identify sustainable materials and design principles that are suitable for this purpose and, at the same time reduce environmental impact —targeting up to an 80% reduction in CO2 emissions and the possibility of recycling the material at the end of the life cycle. This work aims to provide an industrial perspective on the problem, examining the economic implications and addressing the challenges associated with the material supply chain.



Figure: Examples of 3D printing structures for architectural applications realized in LFAM.

[1] Van Woensel, R. N. P., van Oirschot, T., Burgmans, M. J. H., Mohammadi, M., & Hermans, K. "Printing architecture: An overview of existing and promising additive manufacturing methods and their application in the building industry.", *The International Journal of the Constructed Environment*, **2018**, 9(1), 57-81.

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111 D4 -S21 -03

Light mediated AM

nanocomposites; functional composites; surface modification

## SURFACE-MODIFICATION OF INORGANIC NANOFILLERS FOR PHOTOPOLYMERIZATION-BASED 3D PRINTING OF HIGH-PERFORMANCE FUNCTIONAL POLYMER NANOCOMPOSITES

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Additive manufacturing (AM), particularly vat photopolymerization (VP), has emerged as a powerful technology for fabricating complex, high-resolution components with broad applicability across medical, automotive, and aerospace sectors. VP offers key advantages over traditional methods, including design flexibility, rapid prototyping, and efficient material usage. Its ability to process liquid photopolymer resins with high spatial resolution makes it especially attractive for the production of functional materials with tailored mechanical, optical, and electrical properties.

A critical advancement in VP is the integration of nanomaterials into photocurable resins to fabricate multifunctional nanocomposites. However, achieving uniform dispersion and strong matrix-filler interactions remains challenging due to the inherent incompatibility between inorganic nanomaterials and organic resin matrices. Surface modification strategies are therefore essential, and must be tailored to the nanomaterial's chemistry and the intended functional enhancement—whether mechanical reinforcement, conductivity, or piezoelectric response.

This study explores the surface functionalization of two nanomaterials—tetragonal barium titanate nanoparticles (BTO NPs) and graphene oxide (GO)—to enhance their compatibility with VP resins and the performance of the resulting nanocomposites.

BTO NPs were modified with dopamine dodecylamine (DDA) to yield hydrophobic BTO-DDA particles, while GO was functionalized via grafting with a sustainable and photocurable polyester, poly(butylene itaconate-co-adipate) (PBIA), to improve resin dispersibility and interfacial adhesion. Nanocomposites containing BTO-DDA exhibited piezoelectric coefficients up to 50 pC/N at 3.0 wt.% loading, while maintaining the mechanical integrity of the host polymer, achieving nearly one-third of the performance of bulk BTO. [1]

Similarly, GO@PBIA nanocomposites demonstrated substantial mechanical enhancements, with up to 57% increase in elastic modulus and 100% increase in tensile strength at very low filler loadings (0.05 wt.%), outperforming those prepared with unmodified GO. Optical and morphological analyses confirmed homogeneous filler dispersion, while electrical measurements showed that GO retained its conductivity after PBIA grafting. [2]

These results underscore the potential of surface-engineered nanofillers to produce high-performance VP-printed nanocomposites with multifunctional properties, paving the way for their application in advanced structural and electronic components.

[1] Mirko Maturi, Lorenzo Migliorini, Sara M. Villa, Tommaso Santaniello, Natalia Fernandez-Delgado, Sergio I. Molina, Paolo Milani\*, Alberto Sanz de León\*, and Mauro Comes Franchini\*, "3D-Printing of Highly Piezoelectric Barium Titanate Polymer Nanocomposites with Surface-Modified Nanoparticles at Low Loadings", *Advanced Functional Materials*, **2025**, 2407077. DOI: 10.1002/adfm.202407077

[2] Mirko Maturi\*, Simone Maturi, Alberto Sanz de León, Lorenzo Migliorini, Maria de la Mata, Tiziana Benelli, Loris Giorgini, Paolo Milani, Mauro Comes Franchini and Sergio I.Molina, "Enhanced Properties of 3D-Printed Graphene Oxide Nanocomposites through Itaconic Acid Polyester Grafting", *ACS Applied Polymer Materials*, **2025**, 7, 7, 4371–4382. DOI: 10.1021/acsapm.5c00014

112 D4 -S22 -03

Light mediated AM

Photobase Generators, Vat Photopolymerization, Polythiourethanes

## NEW GENERATION OF TETRAPHENYLBORATE-BASED PHOTOBASE GENERATORS FOR ADDITIVE MANUFACTURING

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(1) POLYMAT and Department of Polymers and Advanced Materials: Physics, Chemistry and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, Donostia-San Sebastián, 20018, Spain.

Photobase generators (PBGs) are photosensitive compounds that trigger a polymerization reaction by generating organic bases upon light irradiation. PBGs are generally used to "photo-promote" base catalyzed reactions with high spatial and temporal control, which makes them suitable for 3D printing applications. However, few studies have been made on the use of PBGs for DLP, as usually the efficiency of these types of photocatalyst is lower than the generally used radical photoinitiators, as well as limited polymerization kinetics of some anionic polymerizations. Besides, some type of PBGs only show activity at low wavelengths (high energy) UV light, a photosensitizer is needed to enable their activity in more benign wavelengths as well as the ones available on DLP type of printers. This lowers the polymerization rates, as first the energy transfer from the photosensitizer to the PBG must occur. Additionally, they show a limited stability, which complicates their application in 3D printing.[1]

Consequently, in this work an anthraquinone-based unimolecular PBG is developed and implemented in a polythiourethane system with the aim of avoiding the use of photosensitizer together with increasing the polymerization rate and stability of the resin for its application in vat photopolymerization.

[1] Xabier Lopez de Pariza, Oihane Varela, Samantha O. Catt, Timothy E. Long, Eva Blasco, Haritz Sardon "Recyclable photoresins for light-mediated additive manufacturing towards Loop 3D printing", *Nat Commun.* **2023**. 14. 5504. DOI: 10.1038/s41467-023-41267-w

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113 D4 -S21 -04

Extrusion based AM

Protein-polysaccharide, scaffolds, shape memory

## 3D PRINTED PROTEIN SCAFFOLDS INCORPORATED WITH FIBROUS BIOPOLYMERS FOR TISSUE ENGINEERING

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3D printing of natural biomaterials opens up new possibilities in regenerative medicine by allowing the creation of customized structures. In this work, scaffolds were developed using gelatin and soy protein isolate, and collagen, bacterial cellulose or  $\beta$ -chitin were incorporated into the inks to tailor and analyze the physicochemical, morphological and mechanical properties as well as the biocompatibility of the scaffolds printed with an extrusion 3D printer in order to evaluate their potential as cartilage substitutes.

The tested formulations based on a fibrillar protein (collagen) or fibrillar polysaccharides (bacterial cellulose or  $\beta$ -chitin) showed a rheological behavior suitable for 3D printing at a temperature of 30 °C. The 3D printed scaffolds accurately reproduced the designed geometry and exhibited high shape fidelity. The physical protein-protein and protein-polysaccharide interactions were analyzed by FTIR spectroscopy. The intensity of the FTIR bands associated with amide I, II and C-O confirmed the strong physical interaction between the protein and the polysaccharide. Additionally, scaffolds presented a homogeneous and compact structure, as confirmed by SEM. All the compositions showed a swelling capacity higher than 400 % at 37°C, presenting a good shape memory in repetitive compression tests at deformations of 10%.

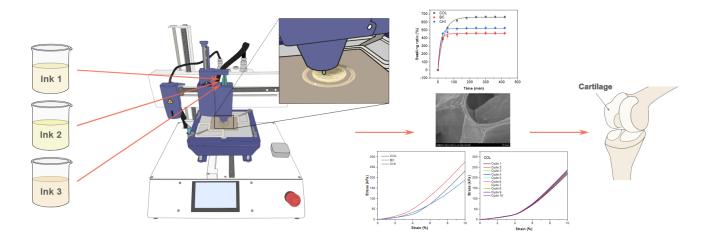


Figure: 3D printing of scaffolds for cartilage regeneration.

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Extrusion based AM / bioprinting; biosensing; functional materials

### MONITORING DISEASE IN 3D PRINTED CELL MODELS

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The shift from 2D to 3D cell cultures constitutes a key development in translating in vitro research to clinical applications. Unlike 2D systems, 3D models more closely mimic in vivo microenvironments, providing improved insight into cell behavior, disease progression, and drug response. This advancement, however, demands sensing technologies tailored for complex 3D structures. A promising solution to this challenge lies in integrating sensors directly into the materials used to construct 3D cell models, particularly through 3D printing [1]. By incorporating sensors into (bio)inks, more realistic models that not only mimic in vivo conditions but also enable real-time monitoring of biological processes can be created [2]. In this work, we present various 3D models developed from biopolymers, synthetic polymers, and decellularized extracellular matrix-based hydrogels, integrated with plasmonic nanoparticles (NPs) or conjugated polymers for in vitro sensing. Bare gold NPs are employed to detect cell-secreted metabolites via Surface Enhanced Raman Spectroscopy (SERS), while conjugated polymers allow for colorimetric and fluorescence imaging. We employed different material compositions, model configurations, and sensor combinations to enable the sensing and monitoring of diverse biological processes within 3D environments.

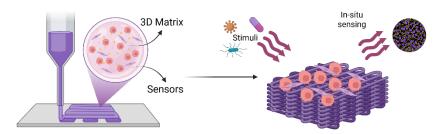


Figure: Scheme of the design of 3D printed scaffolds for in situ sensing of biological processes.

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115 D4 -S22 -05

Photodynamic chemistry, Dibenzazepine, degradability

#### PHOTODYNAMIC DIBENZAZEPINE CHEMISTRY FOR 3D PRINTING

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Light-induced three-dimensional printing (L3DP) is an additive manufacturing technique that enables precise and rapid fabrication of complex structures through photochemical reactions, offering significant advantages such as high spatial resolution, accuracy and surface finishing ability. Nevertheless, the development of functional and sustainable photoinks still requires meticulous effort and remains an ongoing scientific challenge [1]. Photoinks should not be designed solely for durability and mechanical strength but also incorporate functionality, degradability and re-processability to comply with contemporary necessities. Photo Dynamic Covalent Bonds (PDCBs) emerge as a revolutionary solution to fulfill these requirements by harnessing light energy to achieve reversible transformations. PDCB especially utilizes [2+2] cycloaddition reactions where photodimerization occurs between two alkenes to form a cyclobutane ring [2]. However, the presence of alkenes is not only necessity but also an extended system of conjugation is required in the molecules to permit the photochemical cycloaddition reaction [3]. Dibenzazepine (DBA) is a conjugated aromatic compound commonly recognized for its biological activity; however, it is also capable of undergoing [2+2] cycloaddition reactions and reversible transformation [4].

This study aims to introduce of DBA photodynamic group to crosslinked materials in order to obtain functional, degradable and re-processable 3D materials. Initially, DBA derivatives featuring diverse functional groups were synthesized to examine the influence on their dimerization and subsequent cleavage behaviors. Accordingly, acrylate-functionalized DBA monomer and allyl-functionalized DBA dimer were utilized in the presence of multifunctional thiol compounds to generate crosslinked materials. Moreover, main chain polymers modified with diacrylate groups were synthesized by reacting a hydroxyl-functionalized DBA dimer and bifunctional isocyanate derivatives to access long chain degradable crosslinkers.

**Acknowledgements**. E.A would like to acknowledge the financial support of the European Union under the name of Marie Skłodowska-Curie Actions (MSCA).

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**Emerging AM technologies** 

Melt-electrowriting, Cardiac tissue engineering, Polycaprolactone

Multifunctional Conductive Polymer-Hydrogel Scaffolds for Cardiac Tissue Engineering via Melt Electrowriting and Electrospinning

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Cardiovascular diseases, notably myocardial infarction (MI), remained a leading cause of global mortality [1]. In response, we pioneered the development of multifunctional cardiac patches using a biofabrication platform that integrated Melt Electrowriting (MEW) and Solution Electrospinning (SE). This approach enabled the design of hierarchical 3D scaffolds combining micro- and nanoscale fiber architectures that replicated both the mechanical and biochemical characteristics of the native cardiac extracellular matrix. Our core work focused on formulating a composite polymer-hydrogel patch based on polycaprolactone and fibrin hydrogel, engineered for enhanced elasticity and electrical performance. We addressed key limitations of polycaprolactone—notably hydrophobicity and mechanical fatigue—by tuning scaffold geometry, incorporating copolymers, and introducing gold nanorod-doped conductive hydrogels. Additional surface modifications with polypyrrole via in situ polymerization further improved scaffold conductivity. To mimic the native biochemical milieu, we functionalized the scaffolds with bioactive peptides (e.g., RGD) using electrospinning and chemical surface modifications. We validated the biohybrid constructs through a series of in vitro assays to assess mechanical integrity and cellular compatibility. By integrating material innovation with precision biofabrication, we addressed critical challenges in cardiac scaffold design.

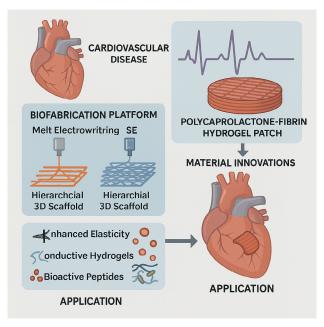


Figure: Schematic illustration of the proposed research plan.

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Poly(4-hydroxybutyrate), photopolymerization, cardiac

## BIOCOMPATIBLE AND BIODEGRADABLE POLY(4-HYDROXYBUTYRATE)-BASED PHOTOCURABLE RESINS FOR VAT PHOTOPOLYMERIZATION 3D PRINTING

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3D Printing technologies and materials are critically important for frontline biomedical applications such as medical devices or tissue engineering. Despite the immense versatility of Vat Photopolymerization 3D printing technology, the limited availability of resins that combine both biocompatibility and biodegradability properties limits its biomedical applications. PHAs are fully biobased, biocompatible and biodegradable thermoplastic polyesters that have recently attracted increasing attention. Among them, poly(4-hydroxybutyrate) (P4HB) stands out for its superior properties and FDA approval.<sup>1</sup>

In this work, new P4HB-based photocurable resins have been developed for Vat Photopolymerization 3D-printing techniques, through Ring Opening Polymerization (ROP) of  $\gamma$ -butyrolactone ( $\gamma$ -BL)<sup>2</sup> and subsequent end-capping with photoreactive acrylate groups. The synthesis of a photocurable diluent based on 4-hydroxybutyrate (4HB) is also carried, to formulate UV-curing inks suitable for Digital Light Processing (DLP) printing. Biodegradability and biocompatibility assessment in vitro of the newly developed photocurable formulations using human cardiomyocytes derived from induced pluripotent stem cells (hiPSC-CM), supports their potential applicability in cardiac-related applications including the design of temporary scaffolds.

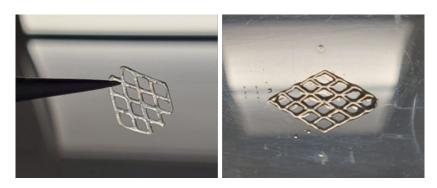


Figure: Rhombic scaffolds obtained by 3D printing of P4HB-based resin.

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Extrusion based AM

Material for energy, DIW, functional material

# ABSTRACT FOR YOUNG RESEARCHERS SYMPOSIUM 3D PRINTING OF LI-IONS BATTERIES VIA SOL GEL DEPOSITION

#### **BLANC Nahel**

Electrification of our modes of transportation and machinery is closely linked to a greener future, making battery research a key field of investment and innovation.

While significant progress has been made in the development of improved active materials with lower cost and reduced environmental impact, other aspects still require in-depth investigation.

One challenge hindering the widespread adoption of electrification is the limited availability of standard battery formats (cylindrical, pouch, prismatic), which are not always optimized for specific applications. 3D printing offers a promising approach to overcome this limitation by enabling the design of batteries tailored to the particular requirements of a device or system. In addition, it allows for increased complexity and customization in battery architectures, which can enhance cycling performance.

While many AM techniques were researched like FDM[1], SLA and DLP or injekt printing[2], one emerged as more promising for multimaterial use: Direct Ink Writting (DIW).

In this study, we propose a methacrylate based system, wich serves both as a binder and matrix material to print elctrodes with DIW. We also investigate the influence of different process parameters on the electrochemical performance of printed electrodes.

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Light mediated AM / Allyl Cellulose; Vat polymerization; Sustainability

### ALLYL CELLULOSE (AC) AS A SUSTAINABLE FEEDSTOCK FOR THE 3D-PRINTING OF ALL-CELLU-LOSE HYDROGELS

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The growing demand for sustainable and biocompatible materials in additive manufacturing(AM) has increased the interest for the use of renewable raw materials in 3D (bio)printing.[1] Due to its to its abundance, biodegradability, and excellent thermal and mechanical properties, cellulose has emerged as material of choice.[2] However, due to its inherent crystallinity and prevalent hydrogen bonding, developing cellulose-based feedstocks has been a challenge.

Allyl cellulose (AC) is a promising candidate for the preparation of renewable feedstocks due to its solubility in water, chemical tunability and mechanical properties.[3] The physicochemical properties of the photopolymerizable AC derivatives, such as rheological behaviour, thermal stability and printability, were investigated, demonstrating compatibility with different 3D printing techniques, particularly extrusion-based and vat photopolymerization processes.[4]

The results showed that AC precursors can be used alone or in combination with other natural polymers to produce dimensionally stable, free-standing 3D objects with good resolution and shape fidelity. Furthermore, the printed materials were found to be cytocompatible towards a fibroblast cell line. These promising results point to new applications of cellulose hydrogels in additive manufacturing, impacting areas such as bioinks, drug delivery systems, tissue engineering and soft robotics.

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High performance polymer, thermal conductivity, PEKK, PEI

### ENHANCING HEAT DISSIPATION IN ADDITIVELY MANUFACTURED HIGH-PERFORMANCE POLY-MERS USING THERMALLY CONDUCTIVE REINFORCEMENTS

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Additive manufacturing, specifically fused filament fabrication (FFF), is widely adopted in aerospace and automotive industries due to its potential for weight reduction and complex designs. Replacing metals with high-performance thermoplastics and their composites significantly improves fuel efficiency, corrosion resistance, and flexibility. However, the inherently low thermal conductivity (TC) of polymers poses challenges for effective heat dissipation. Incorporating thermally conductive fillers such as carbon fibers (CF) can enhance the thermal conductivity of these polymers. This study focuses on improving the thermal conductivity of high-performance polymers such as polyetherimide (PEI) and polyetherketoneketone (PEKK) through the addition of CF. Additionally, the effects of various 3D printing parameters on thermal conductivity were systematically analysed. Through detailed characterization and analysis, optimal 3D printing conditions were established. Although the addition of CF enhanced thermal diffusion and led to faster cooling rates, it also resulted in increased porosity within printed samples. This higher porosity subsequently lowered the measured thermal conductivity relative to theoretical predictions. The findings demonstrate significant potential for using CF-reinforced polymers in heat dissipation applications, underscoring the importance of optimizing 3D printing parameters to balance improved thermal performance with reduced porosity.

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Extrusion based AM

Protein, Deep Eutectic Solvent, cellulose

## DEVELOPMENT OF PROTEIN-BASED SOLUTIONS FOR 3D PRINTED SCAFFOLDS AS CARTILAGE SUBSTITUTES

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- (3) Proteinmat Materials SL, Donostia-San Sebastián, Spain.

The use of natural biomaterials offers new strategies in tissue engineering to develop porous structures through 3D printing. In this work, the formulation of a protein-based gel was optimized using different contents of cellulose obtained from red algae (10, 15 and 20 wt % based on protein content) to improve the mechanical properties of the resulting 3D printed scaffolds. A deep eutectic solvent (DES), constituted of chorine chloride and citric acid, was employed to dissolve cellulose and provide the scaffolds with ionic conductivity. The gels showed shear-thinning behavior at 30 °C, favoring extrusion-based 3D printing. Moreover, 3D printed scaffolds exhibited solid-like behavior and reproduced the designed geometry, showing high shape fidelity. The mechanical performance of the scaffolds was assessed by compression, 3-point bending and tensile measurements, which showed a good strain recovery capacity, with elastic modulus values between 1.3 and 1.9 MPa, suitable for the scaffold application as a cartilage substitute. Results showed that the scaffolds with 15 wt % cellulose improved mechanical properties as well as swelling (150 %) at 37 °C and, thus, this formulation was selected for biocompatibility assessment, which showed cell viability values above 95 %, demonstrating the potential of the scaffolds developed as cartilage substitutes.

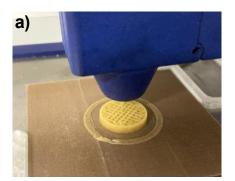




Figure: 3D printing process of a) cylindrical and b) rectangular scaffolds.

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2-Photon Printing, Conducting Polymers, Polymers

## MICRO-SIZED MIXED CONDUCTING HYDROGELS VIA 2-PHOTON LITHOGRAPHY FOR ORGANIC ELECTROCHEMICAL TRANSISTORS AND CELL INTERACTIONS

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The mixed transport of electrons and ions in polymeric systems gives rise to numerous applications, ranging from energy storage to bioelectronics[1]. Conducting scaffolds composed of conducting polymers can enhance interactions with cells for biosensing and stimulation[2,3]. Furthermore, application as organic electrochemical transistor (OECT) on the micro-scale will be studied. The conducting material in these scaffolds can be the base material itself or an additive that infers conducting properties to an insulator[4,5].

We employ 2-photon lithography to generate semi-interpenetrated hydrogel network structures with sub-mi-cron resolution. Conductivity is achieved through implementation of in-house synthesized self-doped conducting polymers based on Poly(3,4-ethylenedioxythiophene) (PEDOT-S) into 2-photon printable N-i-sopropylacrylamide inks. To validate our material, the formation of the conductive double network is characterized using conductivity measurements, electrochemical impedance (EIS), FTIR analysis, and light microscopy. Moreover, long-term stability and cell compatibility is tested.

By tailoring conductive 3D hydrogel scaffolds, we will be able to optimize the way we interface with single cells, cell populations, or tissues. The generation of an semi-interpenetrating network of organic polymers with mixed conductance behaviour within 3D structured hydrogels provides a first step towards enhancing interaction with living systems.

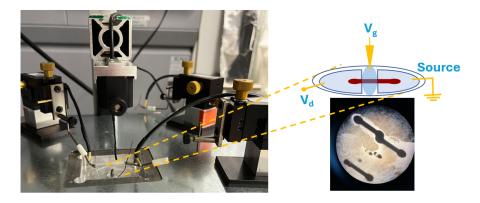


Figure: Concept of PEDOT-S containing micro-structured hydrogels for use in Organic Electrochemical Transistors.

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two-photon lithography, protein printing, tunable mechanical properties

#### MULTIPHOTON NANOLITHOGRAPHY WITH PROTEINS

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Over the past decade, additive manufacturing has gained attention for applications ranging from biomedical engineering to aerospace. In tissue engineering, a key challenge remains the precise 3D structuring of biocompatible, biodegradable, and bioactive materials at the nanoscale. Natural biomaterials are generally limited to 2D structuring with micrometer resolution [1,2], while synthetic polymers allow sub-100 nm features but often lack biocompatibility or mechanical suitability [3].

Here, we present functional protein- and amino acid-based photoresists tailored for 3D multiphoton lithography (MPL) with tunable mechanical properties. Methacrylated proteins (streptavidin, BSA, collagen) were combined with PEG-diacrylate or methacrylated hyaluronic acid and riboflavin as a biocompatible photoinitiator. Amino acid-based phosphorodiamidates (e.g., valine- or alanine-derived) offered further tunability. We evaluated resin combinations for 2D/3D printability, feature resolution, and mechanical and functional properties using AFM and single-molecule fluorescence microscopy. Structures with Young's moduli ranging from 20 kPa to 100 MPa and sub-diffraction-limited features (down to ~80 nm lateral and ~280 nm axial size) were fabricated. Remarkably, amino acid-based materials showed up to tenfold modulus shifts between dry and wet states with minimal swelling. Structured streptavidin retained bioactivity after printing, enabling up to 10<sup>6</sup> biotin bindings per 1 µm³ and demonstrating suitability for applications in immunoassays and extracellular vesicle delivery.

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Light mediated AM / Dental Materials; Fracture Toughness; Block Copolymers

#### DEVELOPMENT OF FRACTURE TOUGH 3D PRINTED DENTAL MATERIALS

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The additive manufacturing of dental protheses using 3D printing requires the generation of products exhibiting excellent mechanical properties and a high fracture toughness. Since the applicability of common monofunctional (meth)acrylate monomers in 3D printing is limited due to their low reactivity and high volatility, the currently commercially available 3D printing resins predominantly consist of mixtures of difunctional (meth) acrylate monomers, which upon curing result in highly crosslinked, brittle materials that are not suitable for the 3D printing of high impact denture bases.

Materials with a moderate crosslinking density and thus superior mechanical properties can be obtained from resins comprising a combination of mono- and multifunctional monomers. Additionally, the fracture toughness of the resulting cured materials can be significantly improved by the addition of toughening agents, *e.g.* block copolymers [1]. We have evaluated the performance of a variety of mono- and multifunctional (meth)acrylate monomers, as well as the influence of different toughening PCL-*b*-PDMS-*b*-PCL triblock copolymers on the flexural strength, flexural modulus, and fracture toughness, and we will present the results which we obtained for 3D printed dental formulations based on these materials.

Figure: Structure of the ABA triblock copolymer toughening agent.

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Light mediated AM / VAT 3D printing Battery

#### ADDITIVE MANUFACTURING OF LIFEPO4 USING VAT PHOTOPOLYMERIZATION

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Miniaturization of electronic devices as well as the advent of new technologies such as the Internet of Things, have prompted the energy storage market to comply with the recent requirements mandated by these technologies. Given the limitations of the current energy storage production line, being mostly dominated by the slurry casting method, battery performance, especially lithium ion battery, as well as its functionality has already reached its threshold. This is often due to limitation on ionic diffusion, which consequentially influence their power density and loading. Therefore, reaching both high energy and power density with a high loading electrode has been a challenge.

With the introduction of 3D electrode architectures [1], attempts have been made to surpass the limitations of the current commercial batteries by nano-engineering of electrode [2]. However, these methods often do not comply with the large-scale production currently adopted by the market. Additive manufacturing or 3D printing of batteries, has enabled myriads of possibilities for architectural design of electrode which give rise to higher utilization of active materials inside the bulk of electrode as well as improving ionic diffusions in the electrode [3].

In this research, for the first time, we have attempted the SLA production of LFP electrode active materials. The inks were optimized for both high resolution and electrochemical performance. The performance of the electrode was compared using cellular architecture with different surface area in both green and sintered state.

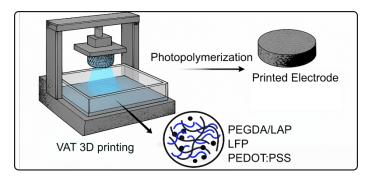


Figure: VAT 3D printing of battery electrode

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Light mediated AM / DLP, PEDOT, Bioelectronics

#### MULTIFUNCTIONAL AND 3D PRINTABLE PEDOT-BASED MATERIALS FOR BIOELECTRONICS

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The emerging area of bioelectronics is demanding a new generation of 3D printable organic materials with mixed ionic and electronic conductivity, soft mechanical properties, biocompatibility and multifunctionality. [1,2] This work shows different approaches for the design of 3D printable electroactive materials for a wide variety of bioelectronic applications. In the first place, photopolymerizable (under UV light) and conductive inks based on PEDOT:PSS, the most successful polymer in the field, are formulated to be employed for additive manufacturing of 3D hydrogels by Digital Light Processing (DLP) technique, showing high versatility, high resolution characteristics and great potential as flexible wearable electronic materials for electrophysiological recordings. Secondly, a less-damaged method for the photopolymerization of the inks developed in the first part is explored. For that purpose, a new photoinitiator system based on PEDOT:PSS/Rf/TEA is developed for fast visible light photopolymerization of water soluble acrylic monomers. As a result, conducting PHEA/ PEDOT scaffolds with 500 µm hole size are synthetized for tissue engineering applications. Finally, the multifunctionality of the developed electroactive hydrogels is studied. For that reason, hydrogels based on PNIPAM thermo-responsive polymer and conductive PEDOT:PSS are successfully processed, leading to 4D PNIPAM/PEDOT multifunctional hydrogels with drug delivery capabilities and thermo-responsiveness. In addition, these hydrogels can be integrated in an organic electrochemical transistor (OECT) in order to develop a multifunctional bioelectronic device, showing the great ability of these materials in the field of bioelectronics.

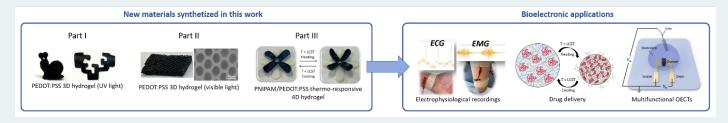


Figure: Work outline.

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Light mediated AM / RAFT, itaconate, polypeptide

## RAFT-MEDIATED 3D PRINTING OF POLYLACTONE/ITACONATES WITH POLYPEPTIDE SURFACE FUNCTIONALISATION

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Reversible addition-fragmentation chain transfer (RAFT) polymerisation has received interest in vat 3D printing for fabricating functional materials [1]. Most research focuses on architectural control and post-printing functionalisation by leveraging the RAFT agent within the printed structure. However, this technique remains predominantly relying on (meth)acrylates monomers, which are typically derived from fossil sources [2]. In this work, we developed an itaconic acid-functionalized 4-arm-polyester as a crosslinker for RAFT polymerisation of two renewable itaconate monomers: dimethyl-itaconate and dibutyl-itaconate. These monomers were successfully polymerized using 2-hydroxyethyl-acrylate (HEA) as a co-monomer via RAFT, demonstrating good control over the degree of polymerisation and conversion. Additionally, the incorporation of the RAFT agent enables the monomers to be 3D printed with high resolution, eliminating the need for additives. Our printable resins contain up to 50% of renewable content, representing a significant advancement in promoting more sustainable RAFT 3D printing while also expanding the range of monomers compatible with this technique. The printed structures are water swellable and pH-responsive due to the presence of HEA and itaconic acid. Taking advantage of the active RAFT groups, in-situ surface functionalisation of the 3D printed structures with methacrylated poly-L-lysine was demonstrated adding to the surface antimicrobial properties while preserving the mechanical strength of the itaconate network.

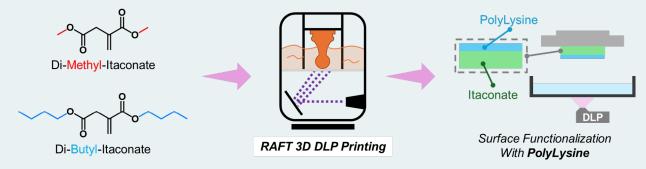


Figure: 3D DLP printing of itaconate-base resins and surface functionalization

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**Emerging AM technologies** 

Dermatitis – 3D-printing – Drug-delivery

### SMART HYDROGEL PATCHES: A 3D-PRINTED SOLUTION FOR CONTROLLED DERMATITIS TREAT-MENT

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Dermatitis encompasses a group of chronic inflammatory skin disorders marked by redness, itching, and irritation, often requiring prolonged topical treatment. It affects a significant portion of the population and can severely impact quality of life. Conventional therapies often suffer from low patient compliance and limited control over drug release [1,2].

In this study, 3D-printed transdermal patches based on sodium alginate and waterborne polyurethane (WBPU), loaded with cortisone, were developed to provide a localized, sustained-release platform for improved dermatitis treatment. Inks were prepared using alginates of different viscosities (low, medium, high) and varying Alginate/WBPU ratios, following Olmos-Juste et al. [3] with slight modifications. Sodium alginate was dispersed in WBPU (1, 3, and 5 wt%), homogenized, and then cortisone was added.

Rheological properties were analyzed to assess printability and shape fidelity, focusing on viscoelasticity, shear-thinning, and recovery. Suitable inks were printed into patches with distinct geometries using a modified Voladora 3D printer (Tumaker, S.L., Spain). Samples were cross-linked in CaCl<sub>2</sub> solution and dried. Mechanical tests assessed tensile strength and flexibility. Morphology was analyzed to evaluate structure and surface quality, and swelling behavior was studied to understand fluid uptake and its influence on release.

In vitro release studies under simulated skin conditions were conducted to evaluate cortisone diffusion kinetics. This work highlights the potential of combining rheology-informed formulation design with 3D printing to create personalized dermal drug delivery systems targeting chronic inflammatory skin conditions.

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two-photon photopolymerization, microfabrication, photoinitiators

### NEW RADICAL PHOTOINITIATORS AND THEIR APPLICATION IN THE PRODUCTION OF THREE-DI-MENSIONAL POLYMERIC MATERIALS OF THE MICRO-NEEDLE TYPE BY TWO-PHOTON PHOTOPO-LYMERIZATION PRINTING TECHNOLOG

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Two-photon photopolymerization is one of the methods for producing nano- and microscale 3D objects. Its principle of operation is based on the absorption of not one but two photons at the same time by the photoinitiators 'molecule in the light-curing composition, which leads to the initiation of the polymerization process. [1] This work presents a study of new radical photoinitiators for 3D printing using two-photon photopolymerization technology. Several micrometer-sized 3D objects such as micro-needles were printed using two lasers: a 1064 nm laser and a 532 nm laser as light sources. The images shown taken with a scanning electron microscope (SEM), show the precision of the printing and the excellent resolution of the new resins for 3D printing.

Research financed within the framework of the competition no. 2024/ABM/03/KPO/ project no. KPOD.07.07-IW.07-0125/24 entitled: "Title of the Undertaking: Luminescent theranostic compounds with anticancer activity, i.e., combination of photodynamic therapy and diagnostics through imaging in a single molecule and development of 3D printed topical micro-needle systems to provide precise individualized cancer therapy" from the National Plan for Reconstruction and Enhancement of Immunity, part of Investment D3.1.1 Comprehensive Development of Research in Medical and Health Sciences, a project funded by the Medical Research Authority.

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Extrusion based AM

Lattice structures, Tissue engineering scaffolds, mechanical properties

#### MECHANICAL LOAD-BEARING CAPABILITY STUDY OF BONE-MIMICKING 3D-PRINTED IMPLANTS

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There are 206 bones in the human body. An estimated 1.78 million fractures occur annually, and this number is expected to surge with global population growth [1]. There is a strong need to develop robust implants that can resist different loads experienced by our body, especially sudden impact loads [2]. The rise of additive manufacturing has opened pathways for exploring intricate designs and hence a possibility towards restoring the ecosystem of the damaged bone by mimicking its microstructures [3]. In the current study, tissue engineering scaffolds that mimic the trabecular structure of bone were designed with different configurations and porosities. These scaffolds were manufactured using filament based additive manufacturing technique and with polylactic acid as feedstock. The mechanical performance of these scaffolds was evaluated under quasi-static compression and dynamic compression. The results show that the strength of the scaffolds decreased with increase in porosity under both loads. However, the difference between quasi-static and impact strengths was not significant for the 65% porous scaffold. Considering the uncertainty of real-life impact scenarios, such as falls and accidents, porosity level under 65% is considered safer.



Figure: Trabecular bone-mimicking implant with stochastic open pore architecture.

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Extrusion based AM / Composite, functional, sintering

## HIGHLY FILLED COMPOSITES EXTRUSION: FAST TRACK TO INDUSTRIAL 3D PRINTING PRODUCTION

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Thermoplastic extrusion-based 3D printing is rapidly evolving from a prototyping tool into a viable solution for end-use industrial production. A major driver of this shift is the advancement of materials—particularly highly filled and reinforced composites—which offer functional properties far beyond those of standard thermoplastics (1).

To process these materials effectively, the traditional Fused Filament Fabrication (FFF) method is complemented by Fused Granulate Fabrication (FGF) (2). This pellet-based approach allows for higher throughput, lower material costs, and compatibility with a wider range of industrial-grade composites. A particularly promising innovation emerges when these extrusion technologies are combined with debinding and sintering steps to enable the production of fully dense, high-performance parts.

To explore the full potential of these technologies, their applications across key industrial sectors will be examined—from the additive manufacturing of high-performance permanent magnets to precision tooling and the fabrication of complex industrial heat exchangers. The study will also focus on material compounding strategies needed to achieve filler loadings above 90% by weight, including the use of advanced polymer matrices and functional additives for stable extrusion. In parallel, it will address the hardware requirements for handling such demanding materials, with an emphasis on process control, external monitoring systems, and calibration protocols that ensure consistent, high-quality results – porosity < 1%. Finally, essential post-processing workflows will be presented, highlighting how green parts are transformed into fully functional end-use components (density ≥ 7.6 g/cm³).

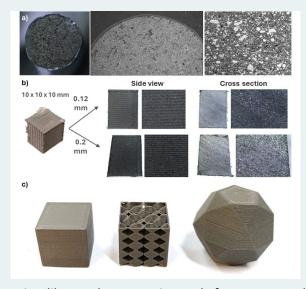


Figure: Example of 3D-printed parts with complex geometry made from a composite containing 90% w.t. stainless steel. a) filament optimization, b) process control, c) final parts.

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photopolymerization, photoinitiators, DLP 3D printing

### LIGHT-DRIVEN PRECISION: NOVEL PHOTOINITIATORS ENABLING HIGH-RESOLUTION 3D PRINT-ING OF ZIRCONIA SCAFFOLDS FOR BONE TISSUE ENGINEERING

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- (4) Photo HiTech Ltd., Cracow, Poland.

The regeneration and reconstruction of bone tissue remain significant challenges in modern medicine, particularly in the context of complex or large bone defects caused by trauma, congenital disorders, tumors, or degenerative diseases. Additive manufacturing (AM), commonly known as 3D printing, has emerged as a transformative technology in biomedical applications due to its ability to fabricate complex, patient-specific structures with high precision and controlled porosity. In the context of bone tissue engineering, AM enables the creation of scaffolds that mimic the natural architecture of bone, thereby promoting vascularization, nutrient exchange, and osteointegration. The selection of appropriate materials for these scaffolds is critical to ensure mechanical stability, biocompatibility, and long-term performance. [1]

The integration of additive manufacturing (AM) technologies into biomedical engineering has revolutionized approaches to bone tissue reconstruction. Among the materials considered for 3D printing of bone substitutes, zirconia (ZrO<sub>2</sub>) stands out due to its high mechanical strength, excellent wear and corrosion resistance, and proven biocompatibility. Unlike traditional metal implants, zirconia-based scaffolds offer favorable aesthetic and biological properties, making them suitable for both load-bearing and non-load-bearing orthopedic applications. [1]

In this study, zirconium dioxide (ZrO<sub>2</sub>) was utilized as the primary ceramic material for scaffold fabrication due to its exceptional mechanical properties and biocompatibility. To enable the application of light-based additive manufacturing technique, a stable ceramic slurry was prepared, incorporating ZrO<sub>2</sub> particles within a photocurable resin matrix. A key aspect of this formulation involved the use of newly synthesized photoinitiator compounds, specifically designed to optimize polymerization efficiency under visible light exposure. These novel photoinitiators were tailored to ensure adequate curing depth. Their chemical structure was selected to enhance light absorption and initiate free-radical polymerization effectively within the highly scattering ceramic medium. This innovative approach enabled the successful printing of complex zirconia-based structures with high resolution and structural integrity, representing a significant advancement in the field of ceramic additive manufacturing for biomedical applications.

#### **Acknowledgments**

The present research work was funded by the LIDER NCBiR project contract number LIDER13/0081/2022 "Innovative porous ceramic materials printed in the DLP technique with the use of high-performance photochemical initiators dedicated to integration with bone tissue".

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Extrusion based AM

Large format additive manufacturing, cork, composites

## CORK COMPOSITES FOR LARGE-FORMAT ADDITIVE MANUFACTURING: SUSTAINABLE DESIGN AND PROCESSING

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Cork is a lightweight natural material with a unique open-cell structure that offers excellent thermal and acoustic insulation, primarily used for wine stoppers and construction panels. However, the production of these products generates significant waste (up to 30 wt.% of the raw cork) which is often incinerated, which has sparked growing interest in the valorization of cork waste for industrial applications. One promising alternative is its use as a filler in polymer composites to reduce both weight and environmental impact. However, cork's low density often requires larger volumes of fossil-derived polymers to maintain processability, limiting the overall sustainability of the composites. Although cork-filled filaments with 20 wt.% cork are already available for extrusion-based additive manufacturing processes, higher filler loadings (up to 50 wt.%) have only been achieved through conventional methods like injection molding, highlighting a need for further progress in additive manufacturing.[1]

In this context, the project FUTURECORK explores the use of recycled cork to develop composites for large-format additive manufacturing (LFAM) using fused granular fabrication (FGF). We successfully synthesized and printed composites containing and analyzed the effect of cork dispersion within the polymer matrix on the processability and mechanical performance of the materials. Our results show that cork composites can be effectively processed in LFAM up to 30 wt.% cork, even for large particle sizes (around 1 mm size), and maintain satisfactory mechanical properties. Sustainability analyses indicate that incorporating 30 wt.% cork can reduce the carbon footprint of the final product by up to 25%, primarily due to a lower usage of the polymer matrix. Finally, we performed a biomimetic parametric design approach to develop interior design objects, demonstrating how bio-based materials can be combined with digital design to create functional, sustainable, and visually appealing products. These findings underscore the potential of cork waste as a viable, eco-friendly filler in additive manufacturing, paving the way for more sustainable materials in large-format applications. [2]

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Extrusion based AM / FDM, warping, PBS

### BLENDING POLY(BUTYLENE SUCCINATE) WITH POLYLACTIDE AND POLY(BUTYLENE ADIPATE-CO-TEREPHTHALATE) FOR 3D PRINTING APPLICATIONS

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Poly(butylene succinate) (PBS) is a prominent biodegradable polyester; however, its high degree of crystallinity (Xc) hinders its processability in 3D printing, often leading to distortions such as warping and shrinkage, which are typical challenges when printing semicrystalline polymers. In this work, we engineered ternary blends incorporating PBS, poly(butylene adipate-co-terephthalate) (PBAT), and poly(L-lactide) (PLLA) in various proportions to optimize printability. The thermal, morphological, and mechanical properties of the blends were systematically investigated both before and after extrusion-based additive manufacturing. Techniques including differential scanning calorimetry, polarized light microscopy, scanning electron microscopy, and synchrotron radiation X-ray analysis were employed for in-depth characterization. The results demonstrated that the blends could be successfully printed, even with high PBS content, achieving a low warping behavior that facilitates 3D printing. The observed performance was closely linked to the interplay between composition and phase morphology, enabling the design of PBS-rich systems with tailored properties. This study contributes valuable insights toward the formulation of biodegradable polymer blends suitable for high-performance 3D printing applications.

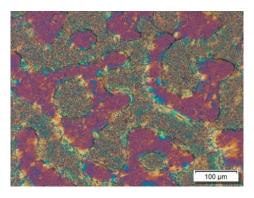


Figure: PLOM micrograph showing the morphology of a PBS, PLA and PBAT ternary blend

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Multiphoton lithography, microfluidic chip, immunotherapy

#### IMMUNE NICHE-ON-A-CHIP ENABLED BY IN SITU HIGH-RESOLUTION 3D PRINTING

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#### Introduction

While conventional T cell therapies have limited efficacy against solid tumors, T memory stem cells (TSCM) offer improved efficacy [1]. We hypothesize that recapitulating key immune niche features in vitro enhances TSCM expansion. Here, we introduce a strategy utilizing multiphoton lithography (MPL) to create immune-mimetic scaffolds integrated into microfluidic chips.

#### Methods

The microscaffolds were fabricated with the commercial MPL system NanoOne (UpNano GmbH) using a custom-developed low fluorescent photopolymer (UpFlow, UpNano GmbH). Stromal cells were isolated from the inguinal lymph nodes C57BL/6 mice and dendritic cells were isolated from the bone marrow of C57BL/6 mice. T cells were isolated from the spleen of OT1 mice.

#### **Results and Discussion**

Acrylate-based resins designed for MPL were developed to support confocal imaging and enable the in-chip printing of complex microscaffolds. The resin with the best performance was used to fabricate lattice structures with pore sizes ranging from 50 to 150 µm. Five coatings were tested to improve fibroblast retention and proliferation. Dopamine and fibronectin were found to be the most effective and was used to coat scaffolds printed directly within a microfluidic chip. Stromal, dendritic, and T cells were successfully cultured on the microscaffolds. Flow cytometry data revealed that T cells cultured in the artificial immune niche exhibited a higher population of TSCM compared to traditional methods using IL2 and IL7/15.

#### **Conclusions**

A tailored material was engineered and functionalized to support stromal cell adhesion and scaffold fabrication within microfluidic chips. Tri-culture of stromal, dendritic, and T cells recreated a lymph node-like niche, increasing TSCM yield over standard methods.

[1] Luca Gattinoni et al. "A human memory T cell subset with stem cell–like properties", *Nat Med*, **2011**, 17, 1290-1297, DOI: 10.1038/nm.2446

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Extrusion based AM

medical devices, medical 3d printing, biomedical materials

## A FRAMEWORK FOR VALIDATING 3D PRINTING MATERIALS FOR CUSTOM-MADE MEDICAL DEVICES: PLA CASE STUDY

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In the growing field of medical 3D printing, regulatory compliance and material validation are critical for enabling the creation of patient-specific medical devices by both commercial manufacturers and hospitals [1]. Manufacturers are responsible for the safety of the products and for navigating the extensive regulatory land-scape affecting healthcare-related products. In particular, the European Medical Device Regulation and the Quality Management System standard ISO 13485 [2] have to be considered when producing custom-made medical devices such as biomodels and surgical guides.

Herein, we propose a comprehensive validation framework for evaluating medical 3D printing materials based on relevant ISO industry standards. This set of tests evaluates essential parameters applicable to medical device manufacturing, including dimensional accuracy, printability, chemical and physical properties, mechanical properties and biocompatibility, before and after sterilization.

This work demonstrates the practical application of the framework through a case study involving polylactic acid (PLA), a material widely used for creating anatomical models intended for intraoperative reference and surgical planning [3]. The results confirm PLA's potential utility and suitability when validated comprehensively using a structured approach. This framework provides a practical solution for manufacturers and health-care institutions to systematically validate 3D printing materials, enhancing quality assurance practices and compliance, ultimately leading to improved patient safety and clinical outcomes.

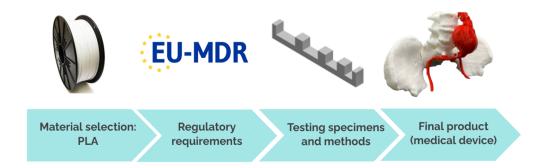


Figure: Validation process for a 3D printing material used in medical device manufacturing.

[1] Kveller, C. et al. First experiences of a hospital-based 3D printing facility – an analytical observational study. *BMC Health Serv Res 24*, **2024**, 28 DOI: 10.1186/s12913-023-10511-w

[2] Nicole Wake et al. "Chapter 7 - Quality Assurance of 3D Printed Anatomic Models." 3D Printing for the Radiologist **2022**, 89-98, DOI: 10.1016/B978-0-323-77573-1.00003-8

[3] Magdalena Żukowska et al." Additive Manufacturing of 3D Anatomical Models—Review of Processes, Materials and Applications" *Materials*, **2023**, *16*(2), 880, DOI: 10.3390/ma16020880

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4D printing, Smart materials, tissue models

### DESIGN OF 4D CARDIOVASCULAR TISSUE MODELS: DYNAMIC CARDIAC PATCH

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#### **DISCLAIMER**

The abstract is not included as per author's request.

Hydrogel microparticle systems, DNA hydrogels, 3D cell culture

## FORMATION AND CHARACTERIZATION OF DURABLE SIZE- AND STIFFNESS-CONTROLLED DNA MICROBEADS FOR 3D CELL CULTURE APPLICATIONS

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Hydrogel microparticles (HMPs) are valuable tools in 3D cell culture for the modulation and study of cellular behavior, yet many polymer-based HMPs lack tunable and modular control over material properties [1]. Short-comings which DNA can help to overcome [2]. Here, we present DNA-based hydrogel microbeads [3] assembled from DNA nanostar precursors, which offer precise control over stiffness, viscoelasticity, and functionalization. The DNA microbeads are formed via droplet-templated encapsulation of nanostars and linkers, producing stable, cell-sized ( $10-60~\mu m$ ) hydrogels with tunable mechanical properties ranging from 30 Pa to 6 kPa. By varying the DNA-nanostar design, we modulate microbead viscoelasticity. Functionalization with collagen-derived peptides (cyclic-RGD) via click chemistry promotes their uptake into fibroblast spheroids. Within the spheroids, the microbeads are retained for multiple days and exhibit stiffness-dependent deformation, indicating active cellular interaction. This study introduces the first DNA-based HMPs with customizable mechanical and biochemical properties, offering a versatile and biocompatible platform for advancing 3D cell culture and tissue engineering applications.

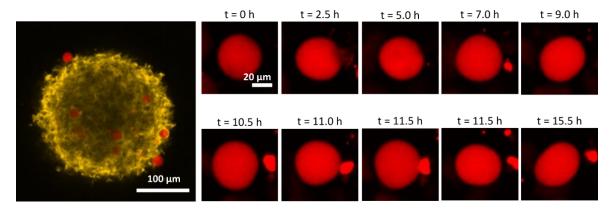


Figure: Following the incorporation of cyclic-RGD, the DNA microbeads (red) are taken up into fibroblast spheroids (yellow) and are remodeled over time.

- [1] Andrew C. Daly "Granular Hydrogels in Biofabrication: Recent Advances and Future Perspectives", *Adv. Healthcare Mater.*, **2024**, 13, 2301388, DOI: 10.1002/adhm.202301388
- [2] Zhang Y. et al., "Smart and Functionalized Development of Nucleic Acid-Based Hydrogels: Assembly Strategies, Recent Advances, and Challenges", *Adv. Sci.*, **2021**, 8, 2100216, DOI: 10.1002/advs.202100216
- [3] Afting C. & Walther T., et al., "DNA microbeads for spatio-temporally controlled morphogen release within organoids", *Nat. Nanotechnol.*, **2024**, 19, 1849–1857, DOI: 10.1038/s41565-024-01779-y

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Extrusion based AM

Micropattern, mechanical properties, cell growth

### GRADIENT BASED RANDOMIZATION OF SCAFFOLD MICROPATTERNS FOR MECHANICAL PROP-ERTY CONTROL AND CELL GROWTH ENHANCEMENT IN 3D BIOPRINTED MODELS

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Bioprinted scaffolds provide versatile platforms for tissue engineering offering environments tailored for cell culture and growth. While highly randomized micropatterns enhance cellular proliferation and adaptability [1], they pose some challenges in maintaining controlled mechanical properties [2]. In this study, we introduce a configurable micropattern based on a discretized grid structure, where each point undergoes random directional distortion with a controlled magnitude, enabling areas of both high and low randomization within the same scaffold. This approach aims to balance cellular accommodation with structural integrity, optimizing conditions for cell viability while ensuring mechanical reliability. We propose a systematic evaluation of 6 different bioprinted scaffold models (b,c,d,f,g,h) with varying degrees and distributions of micropattern distortions printed using extrusion based bioprinting. These models have been mechanically tested and a comparative analysis within a simulated environment has been performed to assess their suitability for tissue engineering application based on their mechanical properties compared to a scaffold with null disturbance (a) and a completely randomized one (e). This study seeks to validate the hypothesis that a hybrid randomization approach could reach a comfortable environment for cell growth while retaining tunable mechanical properties.

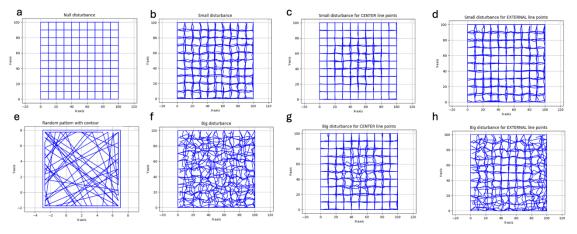


Figure: Each of the eight different micropatterns used in the study.

- [2] Liu, Y., Wan, Y., Li, C., Guan, G., Wang, F., Gao, J., & Wang, L. Gradient scaffolds in bone-soft tissue interface engineering: Structural characteristics, fabrication techniques, and emerging trends, *Journal of Orthopaedic Translation*, 2025, *50*, 333-353, https://doi.org/10.1016/j.jot.2024.10.015.
- [1] Mukasheva, F., Adilova, L., Dyussenbinov, A., Yernaimanova, B., Abilev, M., & Akilbekova. Optimizing scaffold pore size for tissue engineering: insights across various tissue types. *Frontiers in Bioengineering and Biotechnology*, 2024, 12, 1444986, <a href="https://doi.org/10.3389/fbioe.2024.1444986">https://doi.org/10.3389/fbioe.2024.1444986</a>

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Photoreactor, reproducibility, modular

## STANDARDIZING LIGHT: A MODULAR PHOTOREACTOR FOR CONTROLLED, REPRODUCIBLE AND HIGH-THROUGHPUT PHOTOCHEMICAL REACTIONS

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Despite the growing relevance of photochemical processes for applications such as synthetic chemistry, coatings, and additive manufacturing, the field still lacks economically accessible and standardized equipment for conducting reproducible batch photochemistry. Indeed, key photonic parameters—such as light intensity, photon flux, and irradiation dose—are often uncontrolled, making experimental replication difficult and thus hampering fast and efficient progress. Our work provides a solution through a 3D printed, cost-effective design in the form of a concentric modular photoreactor (CMP).[1]

The system ensures excellent reproducibility (<1% errors in conversions *via* NMR in exemplar photopolymerization reactions) due to its innovative architecture. Its modular construction supports various reaction vessel types and permits a wide range of wavelengths, enabling versatile, low-cost, high throughput and standardized experimentation. Thus, this innovation provides a reliable and accessible set-up for reaction screening, kinetic analysis, and reproducible photochemical transformations across disciplines.

[1] Leiza, A., Jarrell, S., Lopez de Pariza, X, Sardon, H., Vidal, F. Patent submitted (EP25382925.3.). 2025

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biofabrication, microarchitected hydrogels

## SUBTRACTIVE TWO-PHOTON MICROPRINTING OF ARCHITECTED HYDROGELS TO GUIDE CELL NETWORK FORMATION

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#### **DISCLAIMER**

The abstract is not included as per author's request.

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