Thiol-ene materials promote volumetric 3D printing

Researchers from Lawrence Livermore National Laboratory (LLNL) in California have developed a new class of polymer materials for volumetric additive manufacturing (VAM) that can produce objects nearly instantly with bulk-equivalent mechanical properties. This potentially expands the versatility of volumetric three-dimensional (3D) printing. This work was recently published in *Advanced Materials* (doi:https://doi.org/10.1002/adma.202003376).

VAM is an emerging 3D printing strategy that can swiftly produce complex 3D objects through a single photocuring operation. This strategy greatly overcomes the drawbacks of layer-by-layer-based 3D printing fabrication, including long production times, rough surfaces, unstable mechanical properties, and constraints on viscosity and reactivity.

Previously, the researchers from LLNL combined three molecular building blocks to develop a versatile VAM-printed photoresin based on thiol-ene chemistry (i.e., organic reaction between thiols and alkenes to form thioethers), which accesses a broad range of mechanical, thermal, and optical performances. "Thiol-ene materials are attracting research interest because they have a well-ordered polymer network, allowing a wide variety of mechanical performance from stiff and strong to soft and stretchy," says Maxim Shusteff, the work's principal investigator. By adjusting the relative monomer composition within thiol-ene resins, the modulus and toughness of printed objects can be varied by over two orders of magnitude (0.12–421 MPa, 0.50–36 mJ m^{-3}), and the ultimate strain changed by over one order of magnitude, from 36.1% to 293%. VAM-printed objects have versatile and tailorable mechanical properties for many fields, such as the manufacturing industry and biomedical engineering.

A critical issue solved in this work is that thiol-ene cross-linking chemistry does not have the threshold response needed for VAM to work because the oxygen inhibition in radical initiated thiol-ene reactions is negligible, the team leader says. For this, a chemical inhibitor (2,2,6,6-tetramethyl-1-piperidinyloxy or TEMPO) is introduced to create the required nonlinear threshold behavior. Further, by modulating the content of initiator and inhibitor, the reaction kinetics can be greatly controlled.

In this VAM system, a 3D distribution of light energy is delivered to the resin vat by superimposing exposures from multiple angles and directions, termed as computed axial lithography. Through reconstruction by a 3D CAD model and calculating absorbed optical dose distribution by computed tomography, complex geometries can be easily and swiftly fabricated by VAM printing. "We showed a quantitative ability to design the resin response to absorbed optical energy by measuring the gelation threshold and incorporating it during our build," Shusteff tells *MRS Bulletin*.

In addition, this work established the first comprehensive framework for quantitative spatial-temporal control over volumetric energy distribution. This demonstration creates a common reference for controllable 3D fabrication and for comparing resin systems, making VAM possible with new groups of materials.

"We are looking toward tackling materials that are even more challenging for 3D printing such as silicones," Shusteff says. For the next step, he says, "We are also advancing computational simulations of polymer formation at different scales—molecular, intermediate, and particle scale. These help us make better design decisions and better understand the properties of our materials."

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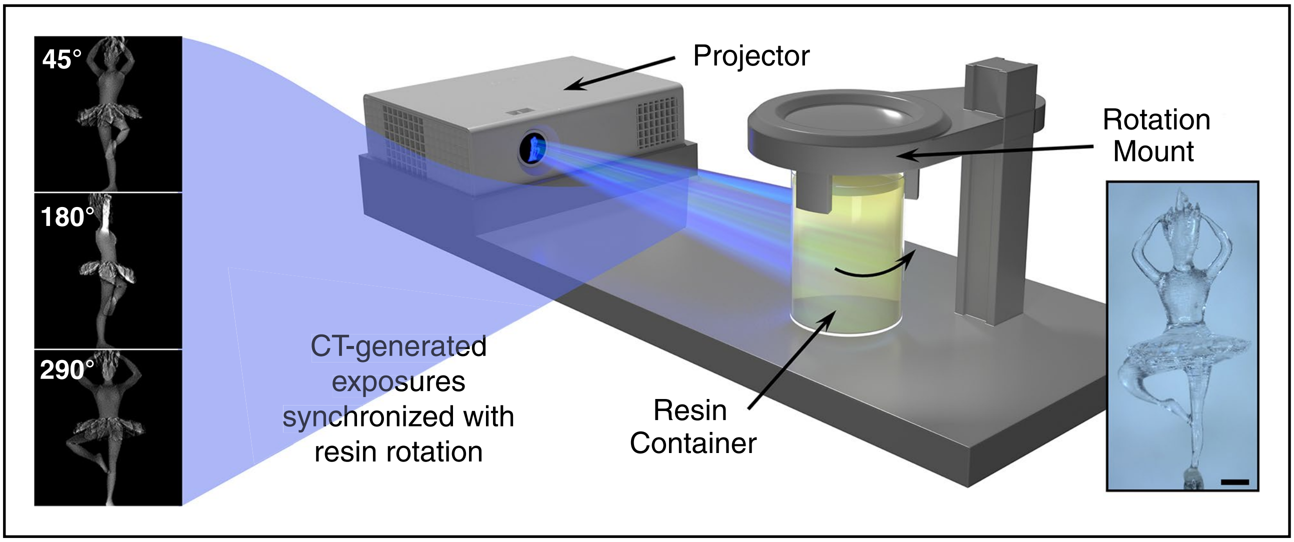

Schematic of volumetric additive manufacturing hardware configuration. The insets at left present example projections from different angles, resulting in the 3D structure shown in the right inset. Scale bar: 2 mm. CT is computed tomography. Credit: Maxim Shusteff.