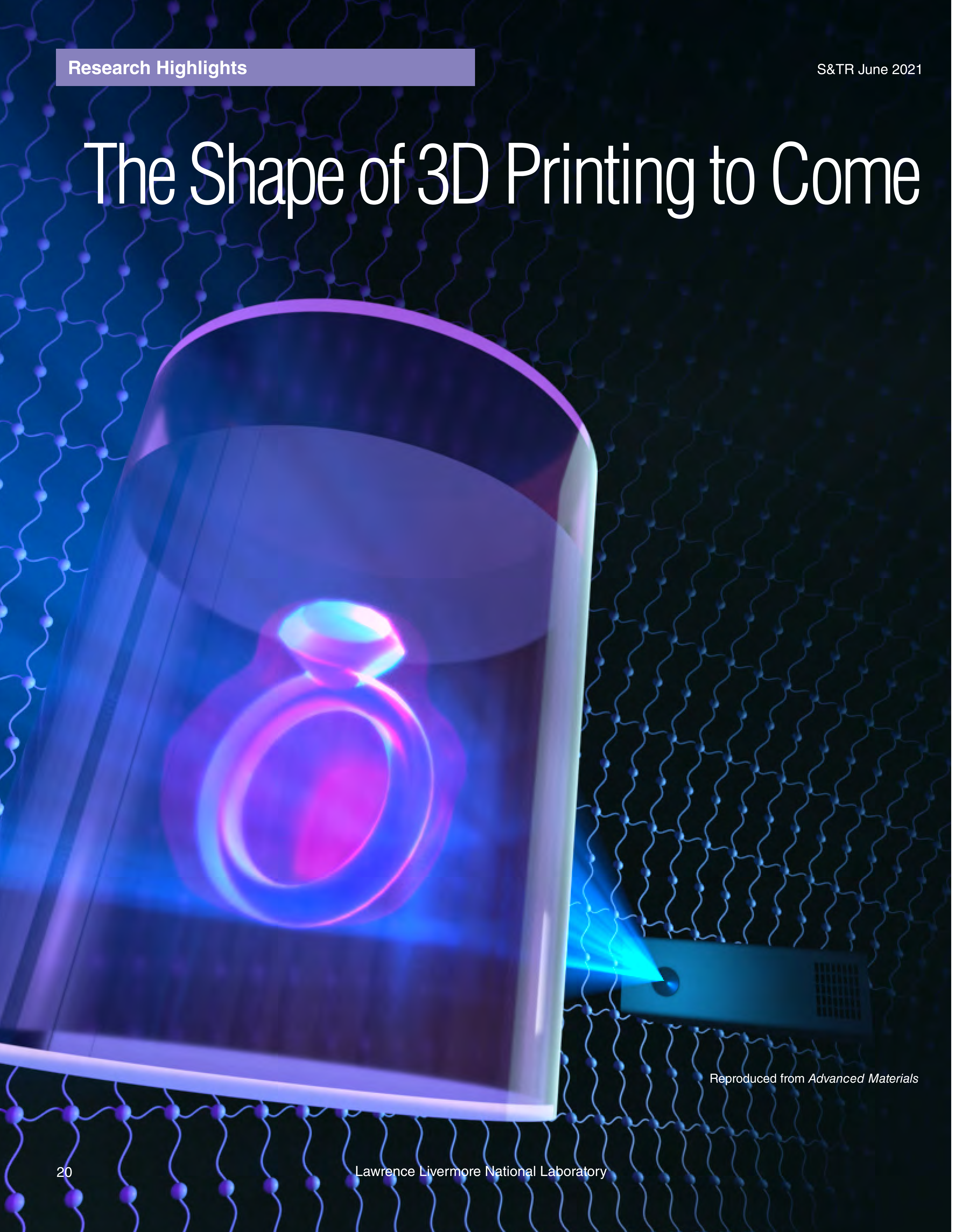
The Shape of 3D Printing to Come



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ADDITIVE manufacturing has improved the strength and reliability of parts for the aerospace and automotive industries and the ease of tailoring prosthetic parts for the medical field. Yet on-demand three-dimensional (3D) printing, for the everyday consumer has remained out of reach due to limited material options and poor product quality. New research at Lawrence Livermore, however, has broadened the range of materials available for 3D printing. "The promise of 3D printing has long been touted, but low-quality materials have held back widespread implementation," says Maxim Shusteff, principal investigator for the research effort. "Making more material classes available for 3D printing is a big step."

Unlike acrylate resins that yield brittle, fragile objects, Livermore researchers have demonstrated that tough and tunable thiol-ene resins achieve the material properties required to 3D print reliable biomaterials as well as functional materials—materials with innate, controllable properties for applications in electronics, among other uses. Further, the research team successfully printed 3D structures in thiol-ene resin using Computed Axial Lithography (CAL), an additive manufacturing technology co-developed with the University of California, Berkeley. The team's efforts also uncovered reference points for controlled 3D fabrication that can be applied to printing with other high-performance polymers, informing next-generation 3D printing.

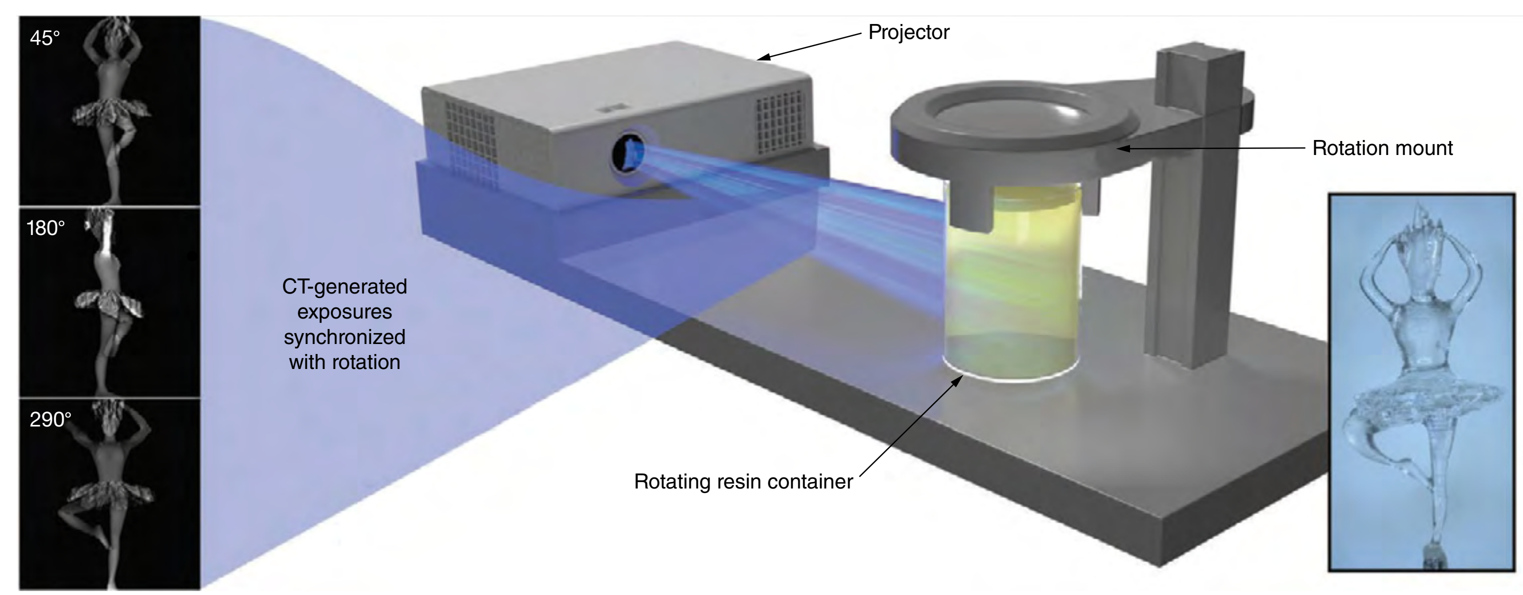
Volume Versus Layers

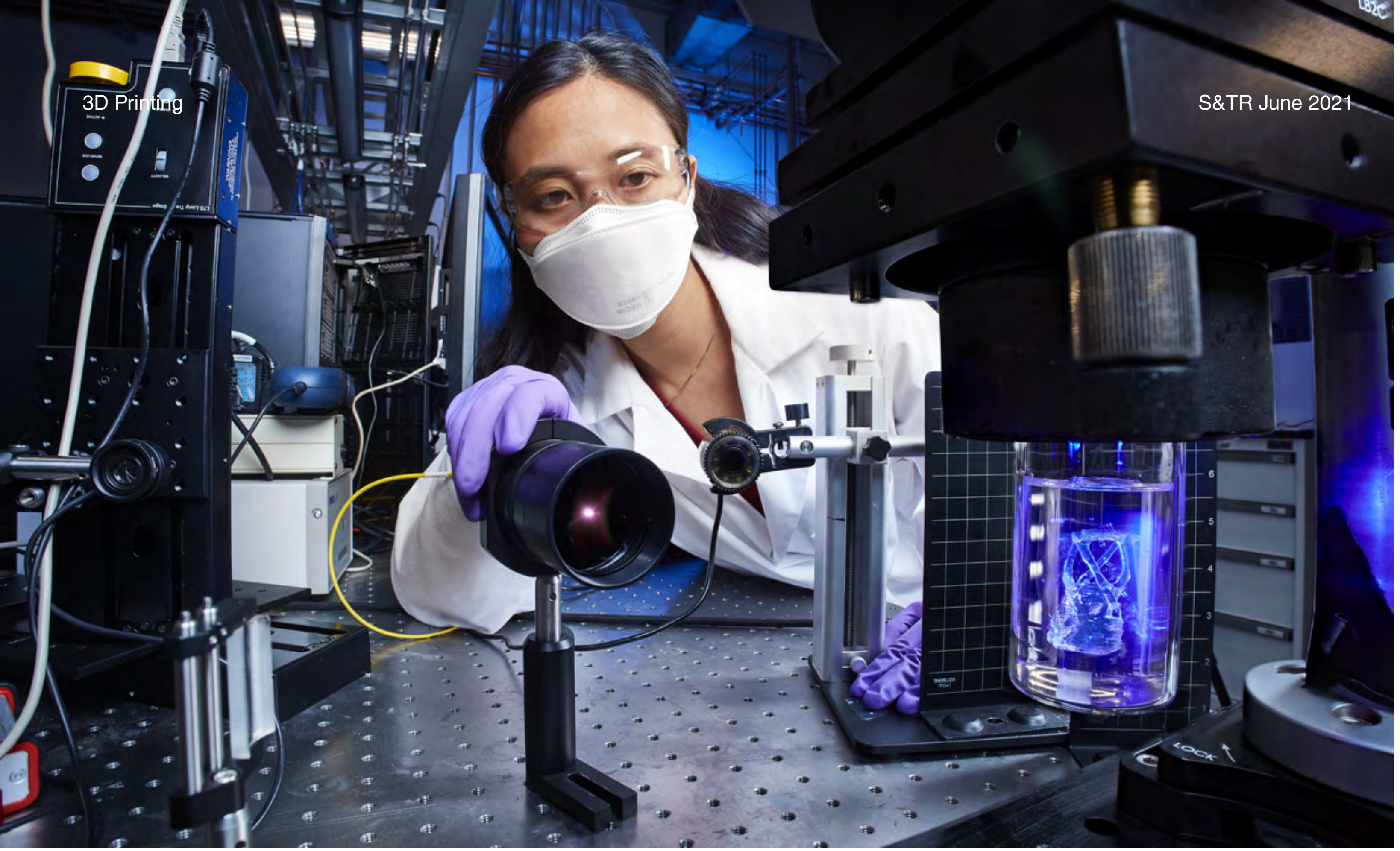
CAL produces objects by delivering 3D-patterned light energy from multiple angles into a spinning vial of photosensitive resin. The resin has an energy threshold below which the material will not polymerize (cure). As the vial spins, the light creates a 3D energy pattern within the resin to cure the liquid into a solid at designated points. The uncured resin is drained, leaving behind a printed object in a matter of seconds, significantly faster than layer-by-layer assembly, which can take from 30 minutes up to days. The uncured material can also be re-used, reducing material waste. (See *S&TR,* March 2018, pp. 13–15.)

Compared to traditional, layer-by-layer additive manufacturing, CAL is a volumetric additive manufacturing (VAM) technology that operates more like a glass blower transforming molten material into a vase than a carpenter building a container board by board. As a result, the one-step process creates a smoother finished product.

CAL uses standard parts for a lower operating cost than earlier VAM technologies. The ability to control the projected image into a print feedstock and the rotation of the resin vial enables faster production of complex and curved shapes. CAL can overprint as well, meaning a polymer object can be printed over an existing object. In an early example, the team printed a handle for a metal screwdriver. More recently, the researchers printed hollow channels for conveying liquids within an object's inlets and outlets. Given these advantages, in combination with the research team's recent material discoveries, CAL can enable faster 3D printing of higher quality parts than those made from commercially available 3D printable materials, removing barriers to 3D printing at scale.

Rather than printing objects layer by layer, the Computed Axial Lithography (CAL) projects beams of 3D-patterned light into a vial of photosensitive resin. As the vial spins, the light cures the resin into the desired shape with a smoother surface than other additive manufacturing techniques. (Illustration by Jacob Long.)





Livermore scientist Erika Fong demonstrates how CAL creates a three-dimensional, solid part within a container of resin. (Photo by Garry McLeod.)

A Different Chemistry

Additive manufacturing techniques that apply material layer by layer require fast-acting chemical reactions to solidify the part as it prints. Acrylates, which undergo rapid-chain growth reaction kinetics during curing, meet this need and have been the standard choice for 3D printing. Yet, acrylates yield tough, brittle printed parts. Shusteff's team understood that a material with a better-ordered molecular structure than the structure of acrylates, if successfully used in 3D printing, would yield a more durable product able to withstand greater mechanical loads.

The team's research identified thiol-ene-based polymers, a class of materials with controllable (tunable) properties. Supported by a Laboratory Directed Research and Development project in advanced photopolymer materials development, Shusteff, his Livermore colleagues, and academic collaborators from the University of Colorado developed thiol-ene resins with the kinetics needed for VAM technologies such as CAL. Unlike oxygen inhibition that contributes to fast curing in acrylate, thiol-ene photopolymerization reactions see negligible oxygen inhibition. Therefore, the team incorporated an inhibitor, 2,2,6,6-tetromethyl-1-piperidinyloxy, also known as "TEMPO," to generate the required threshold behavior. From that point, the team formulated resins from specific combinations of monomers to create a tunable mechanical response.

Mechanical testing of the resin samples revealed a range of qualities from inflexible to rubbery, tough to soft. "We needed to build in curing kinetics with a threshold response for this new set of chemicals to be successful in VAM," explains materials engineer Caitlyn Cook. "The result is a much more versatile material that can be hard, tough, elastic, or everything in between for use in functional materials and biomaterials."

The Right Dose

The next step was designing the dose of light CAL delivers in the thiol-ene resin to successfully print a 3D structure, establishing a reference for other resin systems yielding high-performance printed engineering polymers. Studying how the resin behaves at different light dosages aligns the experimental data with computational models that apply predicted photochemical behavior to predict the success of building more 3D-printed structures. "We created a common reference scale for controlled 3D fabrication that we can use to understand which polymers react to light and how the reactions impact different material properties," says Livermore researcher Erika Fong. "Greater knowledge of material properties combined with our understanding of how to tailor the energy dose make us confident we can successfully 3D print with other chemistries, even chemicals on the market today."

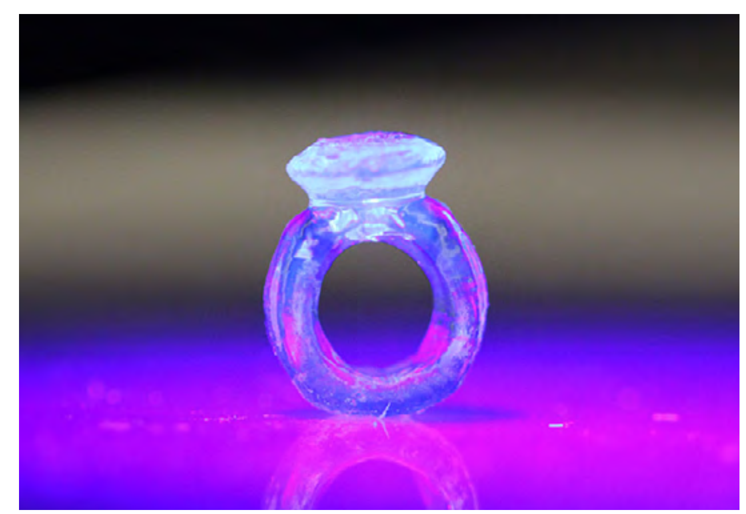
Shusteff adds that the approach of studying absorbed energy dose in resin can be applied for more accurate predictions of resin curing in layer-by-layer printing as well. The absorbed energy dose paints a picture of printing parameters such as light intensity, exposure time, photoinitiator absorbance, and light penetration depth—all relevant factors for 3D printing techniques using photosensitive polymers, even layer-by-layer additive manufacturing technologies. Next, the team plans to apply their research to the silicone materials class used for contact lens material and weather-tolerant caulking, a material group Shusteff describes as "notoriously difficult to adapt to 3D printing."

Scaling for Industry

Enabling a greater range of materials in faster, single-step VAM technologies makes a technology such as CAL even more promising. "Industry partners see CAL's speed as game changing, particularly for bio-related applications," says Shusteff. "Speeds greater than those offered by traditional techniques are needed to maintain the viability of biomaterial cells."

In the near term, the team is working with Livermore's Innovation and Partnerships Office (IPO) to demonstrate CAL's value in rapid prototyping. "The Laboratory has built a very strong intellectual property portfolio in 3D printing that attracts collaborative research partners and licensing interest," says Genaro Mempin, a business development executive in IPO. "But industry demands proof. So, we've demonstrated this technology at Livermore's Advanced Manufacturing Laboratory."

The Advanced Manufacturing Laboratory, located outside the Livermore gate, helps accelerate strategic partnerships by presenting how innovations can meet specific operational needs. The facility helps partners speed material evaluation and characterization by offering state-of-the art 3D printing equipment and analytical instruments too expensive for most companies to purchase for their own use.



Livermore researchers can quickly 3D print stronger, more flexible objects from thiol-ene resins using CAL, a volumetric additive manufacturing (VAM) technology. (Photo by Maxim Shusteff.)

Materials engineer Caitlyn Cook tests how fast a material reacts to light in VAM technologies to characterize the kinetics and apply her findings to other materials considered for 3D printing. (Photo by Garry McLeod.)

So far, Shusteff's team has printed small parts. Mempin can see CAL's potential for car parts, household goods, toys—anything where plastic is used—with the long-term goal of placing an affordable 3D printer in retail stores, even dental offices. Shusteff adds, "Tissue printing and bioprinting are still to be proven, but we can see the possibilities more clearly. Currently, the choice of materials with the right properties for bioprinting—generally polymer hydrogels—is much narrower than for other applications, but the VAM framework is yielding insights into designing new and better biocompatible hydrogels."

Recent material developments include successful printing of silicon photopolymers to increase functionality in VAM-printed parts. The team has printed in glass and a glass-precursor material. Livermore's research points the way to more possibilities in 3D printing. Says Cook, "Laser-based systems and new VAM approaches will continue to enhance print resolution and improve overall part performance, moving industry closer to on-demand, 3D-printed parts for consumers."

—Suzanne Storar

Key Words: 3D printing, additive manufacturing, Advanced Manufacturing Laboratory, Computed Axial Lithography (CAL), Laboratory Directed Research and Development program, photopolymerization, resins, thiol-ene-based polymers, volumetric additive manufacturing (VAM).

For further information contact Maxim Shusteff (925) 423-0733 (shusteff1@llnl.gov).