ORNL/TM-2023/2926
CRADA/ NFE-20-08283

CRADA Final Report: CRADA Number NFE-20-08283 with Actinic LLC

Joe Fortenbaugh

Date May 3, 2023

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

ORNL/TM-2023/2926
CRADA/ NFE-20-08283

CRADA Final Report: CRADA Number NFE-20-08283 with Actinic LLC

Joe Fortenbaugh

Date Published:
May 3, 2023

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

Approved for Public Release

1. Abstract

Significant advances have been made in the additive manufacturing (AM) of thermoplastics and optically cured thermosets; however, AM of thermally cured thermosets has lagged. Materials belonging to this class of thermosets, such as silicone rubbers and polyurethanes, are not well represented in the AM space despite their widespread use in medical, defense, and other fields. Ideally, a solution would enable AM of current commercially viable thermally cured thermosets with a speed that is comparable to those already realized for thermoplastics and optically cured thermosets. Realizing this goal will provide several benefits, including:

1. Make thermally cured thermoset designs impossible via casting.
2. Iteration of part designs without investment in new molds.
3. Devices and personal protection equipment, custom-fit to the end-user.
4. Ability to print multifunctional composite materials.
5. Rapid production ability for DoD personnel deployed at forward locations.
6. Simplify supply chains and replace multiple parts with a single raw material.

These benefits motivate the development of a commercially viable 3D printer for thermally cured thermosets, based on the technique of photothermal curing. This project further developed a printer capable of printing composites containing commercially available thermally cured polydimethylsiloxane (PDMS), directly yielding cured parts such as boxes, walls, and free-standing overhangs.

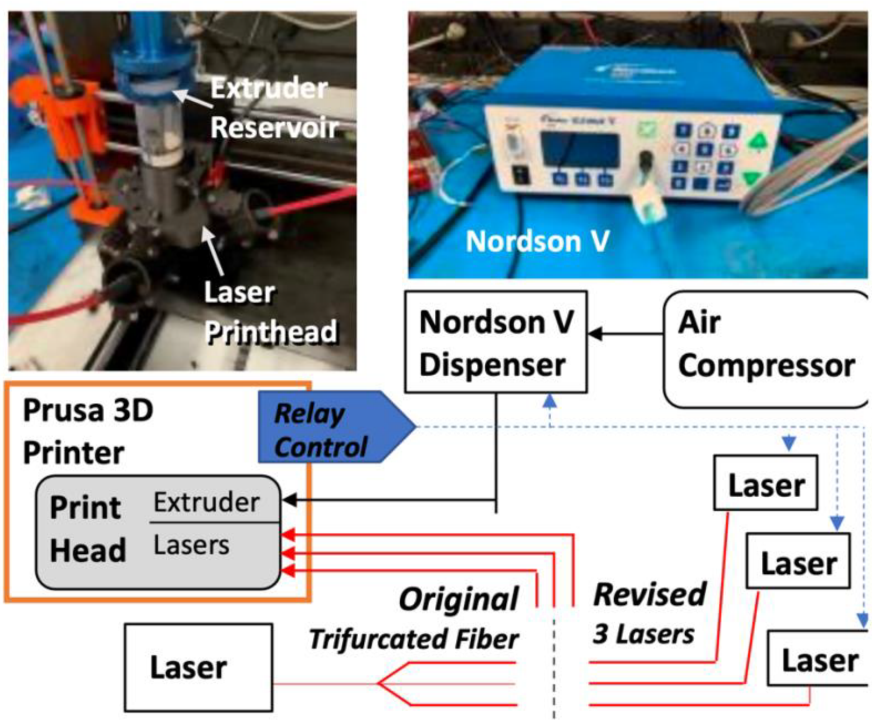

Figure 1: System diagram and pictures of dispenser and printhead on printer.

2. <u>Statement of Objectives</u>

<u>Objective 1</u>: Silicone 3D printer prototype

<u>Description</u>

The first task will be fabrication of a 3D printer for silicone. A prior 3D printing design for silicones, developed by Actinic, will be adopted to existing 3D printing technology at ORNL. In general, the system will consist of a light delivery system (laser diode and fiber optics) integrated into resin extrusion system (e.g. Viscotec dispenser or Nordson Ultimus) mounted to a 3D printer (e.g. Prusa i3). Prior design had pre-mixed two-part silicone with the photothermal agent and extruded mixture through a single nozzle (working time, 8 hrs), but it would be valuable to also develop a two-component extruder system. The 3D printer should be designed to have a print build volume of about 15 x 15 x 10 cm, capable of printing at rates of 50 mm/s, with tolerances of □100 □m, and wall thicknesses □ 0.3 mm. It should be noted though that the primary focus will be on designing a 3D printing system with control over print parameters required to build geometries which target certain final material properties, such as tensile strength, elasticity, durometer, interlayer adhesion, and cost, which will provide the most compelling case for commercial success. In addition, this design will also provide us with a 3D printer design and platform for future use with other thermoset materials. That is, by building the printer for one thermoset, we will better understand what is needed for future formulations.

Task 1 Summary:

Task 1.1 – Refine 3D printer design in collaboration with ORNL PI and other ORNL engineers and researchers
Task 1.2 – Fabricate updated 3D printer design, combining light delivery system, liquid resin dispensing system, and mechanical aspects of 3D printer
Task 1.3 – Rheological, thermomechanical, and material testing
Task 1.4 – Print different silicone test coupons for tensile, flexural, and torsion testing and other 3D printing ‘stress tests’ to demonstrate print capabilities
Task 1.5 – Ongoing iterative refinement of printhead design based on performance of task 1.4

<u>Objective 2</u>: Testing of new thermoset materials for 3D printing

<u>Description</u>

The second task will be to expand the portfolio of thermoset materials capable of being 3D printed to at least one new composite formulation of phenol-formaldehyde. First, we will formulate stable reactive samples (often made of polymer precursors) with the photothermal agent of choice, and then allow these samples to react in the presence or absence of light. By comparing these two conditions, we isolate the efficacy of the photothermal effect for driving the reaction. In all cases, we are concerned with three aspects of the cured polymer: (i) the rate at which it was cured, as determined using infrared and Raman spectroscopy, (ii) the chemical identity of the final products, as determined using MS, NMR, and GC, and (iii) the final properties of the cured film, as determined using MS, gel swelling, gel fractionation, DMA, DSC, and measurements of tensile strength and Young's modulus.

Task 2 Summary:

Task 2.1 – Formulation of stable photothermal thermoset resins
Task 2.2 – Measurements of rates of curing of thermoset resin
Task 2.3 – Testing of rheological and material properties of resins and cured thermoset materials

<u>Objective 3</u>: Design and prototype fabrication of 3D printer for other thermoset materials

<u>Description</u>
The third task will be similar to the first task except that the 3D printer will be designed around the phenol-formaldehyde formulation developed in the second task. As much as possible, the 3D printing system will have the same design specifications as the first technical milestone and will be built from existing 3D printing technology at ORNL. In general, the system will consist of a light delivery system (laser diode and fiber optics) integrated into 2-component resin extrusion system (e.g. Viscotec dispenser or Nordson Ultimus) mounted to a 3D printer (e.g. Prusa i3). The 3D printer should be designed to have a print build volume of about 15 x 15 x 10 cm, capable of printing at rates of 50 mm/s, with tolerances of □100 □m, and wall thicknesses □ 0.3 mm. It should be noted though that the primary focus will be on designing a 3D printing system with control over print parameters required to build geometries which target certain final material properties, such as tensile strength, elasticity, durometer, interlayer adhesion, and cost, which will provide the most compelling case for commercial success.

Task 3 Summary:

Task 3.1 – Refine 3D printer design in collaboration with ORNL PI and other ORNL engineers and researchers
Task 3.2 – Fabricate updated 3D printer design, combining light delivery system, liquid resin dispensing system, and mechanical aspects of 3D printer
Task 3.3 – Rheological, thermomechanical, and material testing
Task 3.4 – Print different silicone test coupons for tensile, flexural, and torsion testing and other 3D printing 'stress tests' to demonstrate print capabilities
Task 3.5 – Ongoing iterative refinement of printhead design based on performance of task 3.4

3. <u>Benefits to the Funding DOE Office's Mission</u>

The development of photothermal curing as a general tool for on-demand curing of thermally cured thermoset polymers and composites would represent a major advance for both coatings and additive manufacturing, while serving the needs of ORNL for more advanced processing and usage of these materials.

4. Technical Discussion of Work Performed by All Parties

Laser-induced curing of carbon-loaded PDMS (cPDMS) was initially performed on hemispheres (drops) on glass plates using diode lasers operating from 405-808 nm. Optical power was measured with a power meter (Thorlabs S415C) and infrared (IR) beam diameter was measured using a fluorescing target. The minimum fluence for full curing was > 8 J/cm2, corresponding to a 2 W laser power with a 4 mm spot size and 100 ms duration. Because the beam intensity is not flat across its cross-section, line curing with a moving laser is more complex than drops, and additional curing of cPDMS lines was done.

Due to the high-power limit of the 808 nm laser (QPC BrightLase), it was used for all subsequent testing and printing. An IR camera (FLIR 450Sc) recorded surface temperature of the cPDMS during line tests performed at 15 mm/s (laser power 1-6W, beam diameter 3.5 mm).

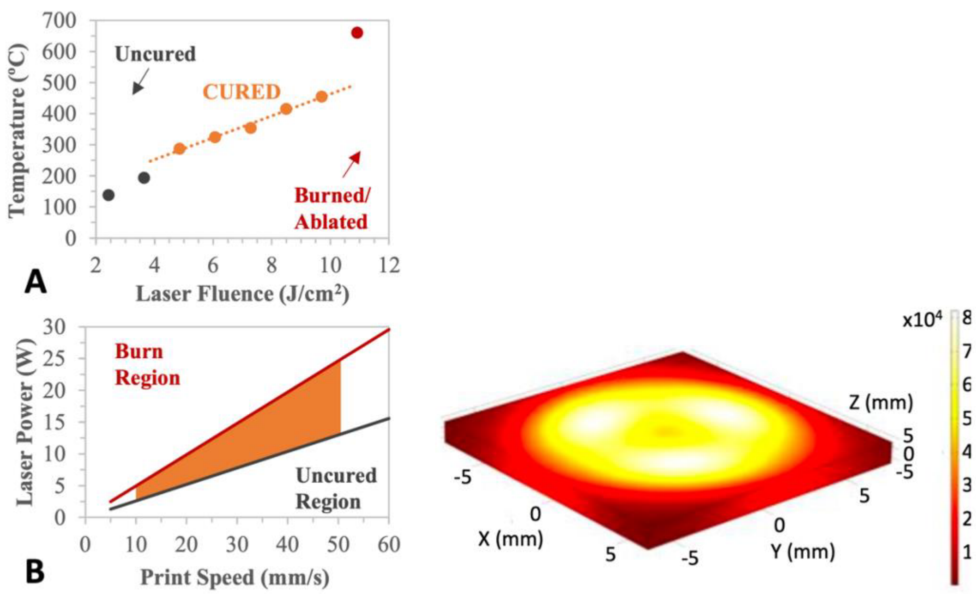

Figure 2: (Left) (A) Peak cPDMS temperature relative to laser fluence correlates well with curing or burning. (B) Extrapolation of operating regime (orange) based on fluence range shows 15-20 W laser power sufficient for printing at 50 mm/s. (Right) Flux calculated from 3 laser sources with 6.5 mm focused beams via COMSOL. An annular profile is seen around the central nozzle region.

A Nordson V dispenser was integrated with the Prusa 3D printer and was capable of controlled extrusion (start/stop) of the resin – without dripping – as toggled through the Prusa PCB fan output and object print code (g-code). Printing was performed through manual addition of 'print directive' code into each g-code file produced after initial slicing with Simplify3D® software. The added code toggled fan power on/off, which in turn controlled extrusion and laser on/off. Forward pressure and nozzle tip diameter of the Nordson directly related to extrusion rate and line width, and the back pressure eliminated resin leakage during pause. Working time for the mixed PDMS was 8 hours and could be extended to 100 hours at 4-5°C.

Hundreds of lines were printed at speeds between 10-25 mm/s, including single lines and walls (see Figure 3) – with resolutions down to 1 ± 0.1 mm. Based on parameters developed in Task 1, individual lines were first printed and characterized. AMI's Keyence IM-6020 scanning system was used to measure the tolerance of the lines which confirmed line resolution. By adjusting the laser power and using a 0.32 mm nozzle tip, lines widths at a resolution of 1 ± 0.1 mm were achieved. Layer thicknesses of 0.4 mm were achieved, and wall heights of over 30 layers were produced with lengths up to 5 cm (see Figure 3). However, one issue using this method was that this lateral resolution was only achievable in one axis, given that only one laser was available. Because of inadequate angulation in other axes, shadowing caused a small amount of 'bleeding,' which limited line widths in other axes to 1.6-2.2 mm.

A 2x2x2 cm box (see Figure 3) was printed at a 10 mm/s with a 400 μm layer height and mass of 2.64 g. This corresponds to a layer width of 1.67 mm, which is consistent with the 1.6 mm average dimensional measurement made. The resin reservoir contained > 20 g of resin, though less than that is needed for a 3 cm box – the expected mass is 3.27-4.12 g. Although the size was slightly smaller, the 2 cm box showed the shape and speed capability of the system. Higher heights and finer linewidths are expected with integration of all three 40 W lasers.

Due to the complexity and length of the manual line-by-line coding methodology adopted during Phase I, using this approach to modify the 3DBenchy g-code was not practical at this time. The 3DBenchy g-code is in the range of 142,000 lines (varying slightly with slicer software). This is a hurdle that will be addressed with an automated code in Phase II. Additionally, the single high-power laser would not necessarily produce an adequate representation of all the 3DBenchy features given the many print directions, relative to the proposed three lasers. Therefore, several other objects were printed to demonstrate individual shapes and features comparable to the 3DBenchy – all using print speeds of 10-15 mm/s with no post-curing. Objects were printed including a tube, 'house', overhanging lines, and lattice (see Figure 3). The dimensions of the walls and overhangs were within 10% of expected (programmed) values. The box and 'house' did exhibit slumping on two sides due to the use of the single layer. The other two sides varied by slightly more than 10%, which was most likely due to the stresses from the slumping sides.

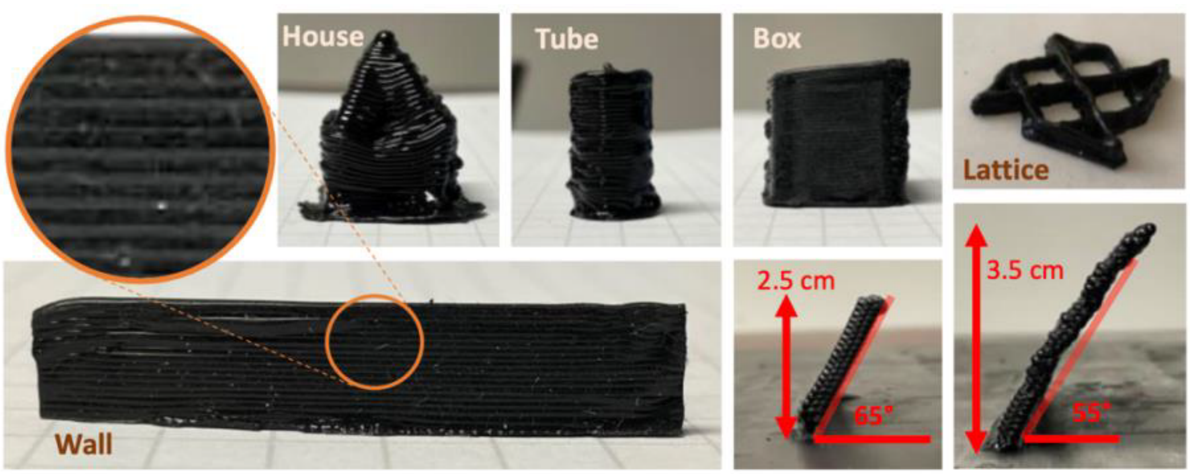

Figure 3: Example of cPDMS shapes printed at 10-15 mm/s with no post-curing – wall, box, lattice, 'house' with unsupported top, and cylinder. Overhangs were printed at angles of up to 45° and were cured at point of extrusion with no supports needed.

5. Subject Inventions (As defined in the CRADA)

None

6. Commercialization Possibilities

I led all research efforts, managed employees, and contracted with partner companies for labor and access to facilities and equipment to meet deliverables and milestones for our technology development. We were awarded a Phase I Army STTR during the Innovation Crossroads program and met all deliverables for the project. Notably, until this work, such rapid on-demand thermal curing for bulk-scale materials was not possible, and its absence has led to a dearth of thermally cured thermosets in the additive manufacturing space.

7. Plans for Future Collaboration

During the Innovation Crossroads program, we demonstrated the key aspects of feasibility and potential for the technology to perform AM using a photothermal-cured thermoset based on silicone. The Phase II builds upon this and demonstrates both the broader capability as a platform approach to thermally curing thermoset materials, as well as completing key milestones towards transition into a commercially viable AM system – including ability to print at speeds, resolutions and volumes of commercial printers; development of resins packaged and approved for shipping; and demonstration of key geometries and repeatability metrics.

8. Conclusion

Our technology reduced the amount of energy needed to cure thermoset resins making the process much more energy efficient and reducing the amount of wasted polymer material that goes into landfills. I learned how to manage contracts and budgets, how to hire employees, how to protect IP, and how to communicate our technology to diverse stakeholders. The fellowship provided a great professional opportunity that has prepared me for my future career goals.