Keeping cool under pressure: High-Area, Rapid Printing enabled through Thermostatic Control

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3D printing is disrupting the field of manufacturing, enabling the creation of new products and altering supply chains. The ability to take a concept from ideation to end manufacturing on a single technological platform is incredibly powerful. The deployment of this technology in conjunction with other emerging digital fields, such as machine learning, has led to the belief that we are in the midst of a digital manufacturing revolution (*i.e.*, Industry 4.0) (1).

Nevertheless, 3D printing is not a new technology – it has been around for over 30 years. It has seen the rise of the internet, supercomputers, and artificial intelligence yet has remained limited in its application. In part, this limitation has come from a lack of innovation within the field. With the expiration of key patents over the past decade (2-4), a flurry of invention ensued leading to great leaps in technology. It was during this Renaissance of additive manufacturing that DeSimone and co-workers achieved one of the key technological milestones within the field of stereolithography. In 2015, they unveiled CLIP, or 'Continuous Liquid-Interface Printing,' in the journal *Science* and proselytized the technology in a TED talk. (5,6) This lecture marked a change in perspective on the field of 3D printing, as CLIP was able to demonstrate incredibly fast print speeds while simultaneously being able to produce material properties rivaling injection molded plastics. CLIP was the first technology to make the case that 3D printing could be expanded beyond prototyping and make inroads into the manufacturing sector.

CLIP operates with the principle of a quenching 'dead-layer,' which prevents adhesion between the emerging 3D printed part and the bottom of the print vat. In short, an oxygen-permeable membrane supports a pool of liquid, photo-responsive resin. Oxygen gas feeds into the pool of resin through the membrane, quenching any radical initiation near the resin/membrane interface. Deeper into the vat and further away from the membrane, the oxygen concentration is lower and photoinitiators can overcome the oxygen inhibition and initiate solidification of the liquid photopolymer resin. This lack of adhesion to the bottom of the print vat enabled CLIP to do two things. First, it was able to print at incredibly fast vertical print speeds. Second, it was able to pull the part continuously and produce parts with isotropic (uniform) material properties throughout regardless of print orientation. This last point is crucial, as many stereolithographic parts up to this point were essentially laminates made up of a series of discrete 2D layers that were weakly bonded together.

Despite this incredible advance, the applications of CLIP have remained limited. These limitations are caused, in part, by an exotherm (release of heat) during the photopolymerization reaction (7). Prior to CLIP, no other technique was printing quickly enough to require active heat dissipation as natural convection was sufficient. Once one reached the vertical print speeds of CLIP, the exotherm became apparent. The effect of this heat production was only amplified as researchers attempted to expand the print area of the CLIP printer, as the rate of heat production was directly proportional to the volumetric throughput of the printer. Unfortunately, the ideal location for the placement of a cooling apparatus on such a printer would be across the bottom of the print vat and would, in turn, hinder the delivery of oxygen through the membrane central to CLIP's operation. Because of this, CLIP has been limited to

peripheral cooling techniques, which cause a thermal gradient across the print vat and varying reaction rates.

In 2019, we reported a new continuous 3D printing approach that, in contrast to CLIP, does not rely upon an oxygen dead-layer for its operation (8). Resultantly, it is capable of being cooled to control the temperature during the print process and dissipate the heat produced. By maintaining this thermostatic control, the printer was scaled to much higher areas and resulted in a record-breaking throughput for this style of printing (over 100 L/hr). This technique was given the moniker HARP, standing for 'High-Area Rapid Printing.' The process operates on the principle of floating a UV-curable resin upon a bed of flowing immiscible oil (Figure 1). The oil is a high-density fluorinated liquid that remains at the bottom of the vat. Additionally, because the oil is highly de-wetting to the photo-resin and in motion, a slip-boundary arises at the liquid-liquid interface. The motion and properties of the oil make its adhesion to the emerging 3D printed part very low and enables a continuous pull mechanism. Additionally, the oil can be pumped through the bottom of the print vat, filtered, and then cooled before being returned to the print vat. In this way, one can control the temperature at the liquid-liquid interface where the 3D printed part is formed and heat is emitted.

The effect of this thermal control is shown in Figure 2. Here the first row is a 50 cm by 50 cm truss being printed without flowing the oil. The heat of the reaction causes the part to quickly overheat, smoke, and eventually crack due to the thermal expansion of the polymer at these high temperatures. The cracking motion can be seen in the last frame of the row where the displacement is emphasized by white guidelines. Alternatively, simply flowing the oil in the recirculation loop (middle row) allows for the heat to be dissipated into the oil of the system. Eventually, the temperature of the oil begins to rise.This can be offset by a chiller unit, which leads to a thermally stable print condition (bottom row).

An additional benefit of HARP is that it remains compatible with a wide range of photopolymer chemistries. The fluorinated oil is immiscible with aqueous, organic, and silicone liquids. Additionally, owing to the fact that HARP relies upon a physical technique to limit adhesion instead of a chemical technique (i.e. does not rely upon oxygen quenching and the production of a dead-layer), it is compatible with both oxygen-sensitive and oxygen-insensitive resin systems, such as photo-cationic polymerization or thiol-ene Michael additions. Through this combination of traditional and non-traditional reaction chemistries, HARP can print a wide range of materials, including rigid plastics, elastomers, and pre-ceramic polymers (Figure 3).

While HARP addresses several challenges in extending 3D printing into the manufacturing sector, many challenges remain. These include the development of high-intensity optical systems capable of maintaining high lateral resolutions across such large print vats. In addition to the thermal transport limits discussed above, the need for resin replenishment under the part gives rise to fluid dynamic transport limitations. Resultantly, the development of low-viscosity photopolymers with industrially relevant properties is necessary to enable continuous printing at high speeds.

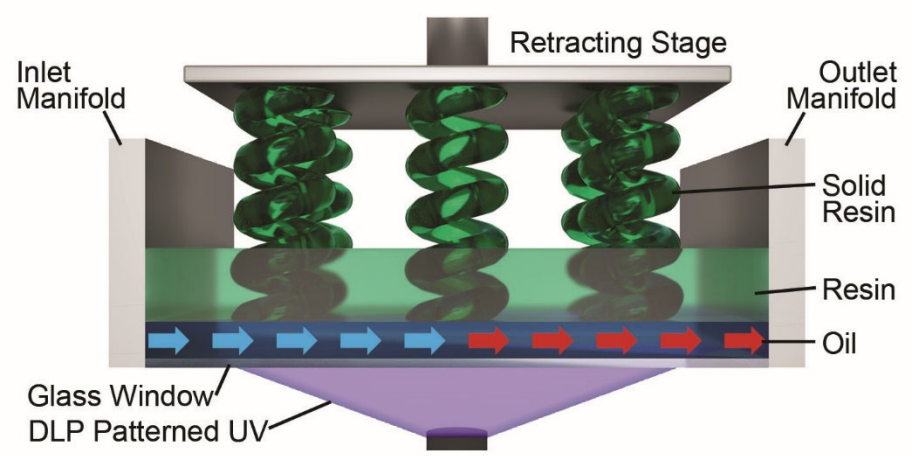

Figure 1. Scheme of HARP 3D Printer. Photo-responsive resin floats on top of a fluorinated oil layer. Inlet and outlet manifolds pump the oil into the vat, across the bottom of the vat under the resin, and then out of the vat to be chilled. As a result, cold oil enters the print vat and hot oil is removed. UV light is patterned using DLP projection optics. From Ref (8). Reprinted with permission from AAAS.

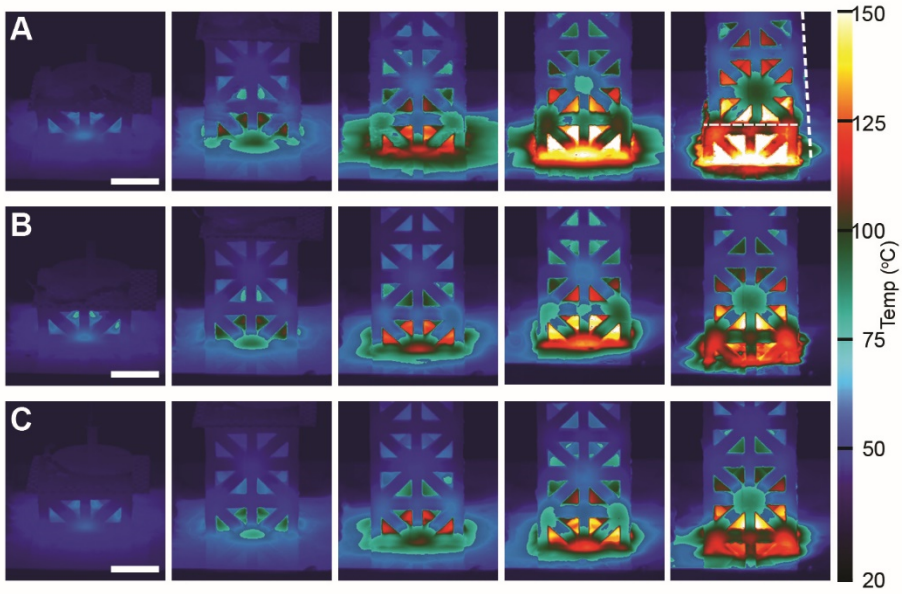

Figure 2. Infrared Thermal Imaging of 3D print process with (A) no flowing oil, (B) flowing oil, and (C) flowing cool oil. Scale bars are 25mm, print speeds are 120 µm/s (~17”/hr), and elapsed time between panels (left to right) is ~500 s. From (8). Reprinted with permission from AAAS.

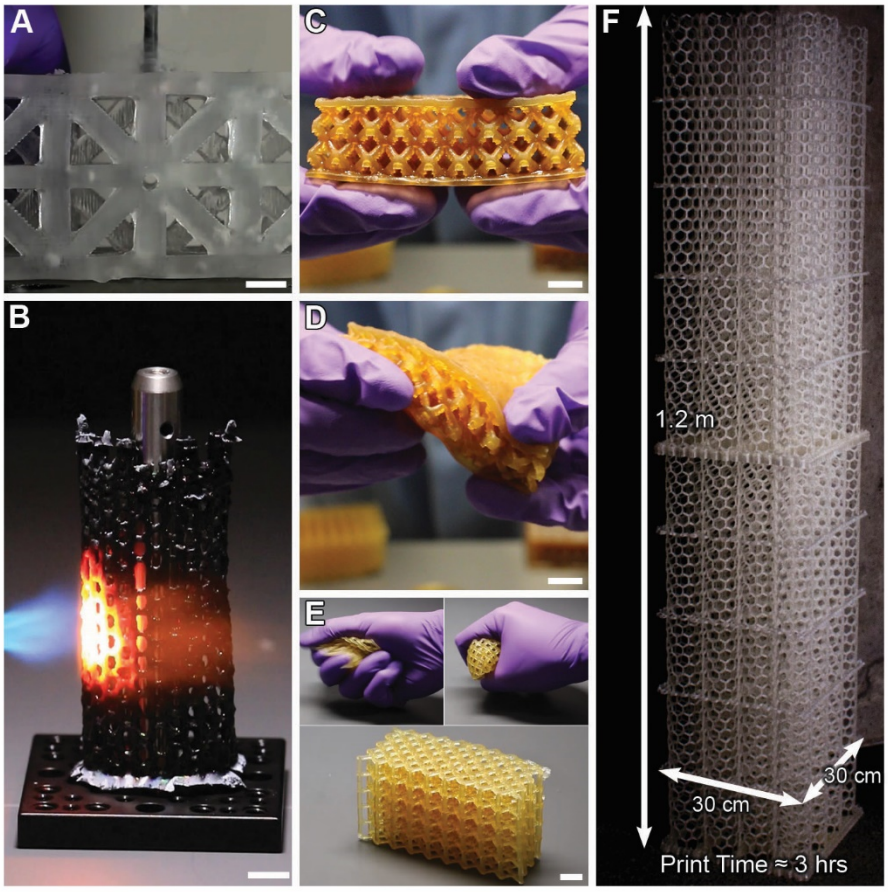

Figure 3. HARP enables a broader palette of resins. (A) Hard, machinable polyurethane acrylate, (B) silica carbide ceramic resulting from 3D printed polymer precursor, and (C-E) a range of elastomeric materials with varying compression properties and moduli. Critically, this range of materials was produced using the same technology used to produce the large lattice pillar (F), which demonstrates the high-throughput capacity of HARP. From Ref (8). Reprinted with permission from AAAS.

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