Feature



 s a metal platform rises from a vat of liquid resin, it pulls an intricate white shape from the liquid – like a waxy creature emerging from a lagoon. This machine is the world's fastest resin-based 3D printer and it can create a plastic structure as large as a person in a few hours, says Chad

Mirkin, a chemist at Northwestern University in Evanston, Illinois. The machine, which Mirkin and his colleagues reported last October¹, is one of a slew of research advances in 3D printing that are broadening the prospects of a technology once viewed as useful mainly for making small, low-quality prototype parts. Not only is 3D printing becoming faster and producing larger products, but scientists are coming up with innovative ways to print and are creating stronger materials, sometimes mixing multiple materials in the same product.



A metal printer at start-up firm Relativity Space, which aims to test a mostly 3D-printed rocket in 2021.

Sportswear firms, aviation and aerospace manufacturers and medical-device companies are eager to take advantage. "You're not going to be sitting in your home, printing out exactly what you want to repair your car any time soon, but major manufacturing companies are really adopting this technology," says Jennifer Lewis, a materials scientist at Harvard University in Cambridge, Massachusetts.

The latest techniques could be lucrative for researchers, many of whom – Lewis and Mirkin among them – are already commercializing their work. They're also fundamentally exciting, says lain Todd, a metallurgist at the University of Sheffield, UK. "We can get performance out of these materials that we didn't think we could get. That's what's really exciting to a materials scientist. This is getting people used to the new weird."

From trinkets to products

The 3D printing technique is also referred to as 'additive manufacturing', because instead of chopping or milling a shape out of a larger block, or casting molten material in a mould, it involves building objects from the bottom up. Its advantages include less waste and an ability to print custom designs, such as intricate lattice structures, that are otherwise hard to create. Low-cost hobbyist machines print by squeezing out thin plastic filaments from heated nozzles, building up a structure layer by layer - a method known as fused deposition modelling (FDM). But the term 3D printing encompasses a much wider range of techniques. One of the oldest uses an ultraviolet laser to scan across and solidify (or 'cure') light-sensitive resin, layer by layer. That concept was described as far back as 1984, in a patent filed by Charles Hull², the founder of a company called 3D Systems in Rock Hill, South Carolina.

The latest techniques – including Mirkin's - still use light-sensitive resin, but are faster and larger-scale, following improvements reported in 2015 by a team led by Joseph DeSimone, a chemist and materials scientist at the University of North Carolina at Chapel Hill³. Early printers were slow, small-scale and prone to producing layered, imperfect and weak structures. These found a niche in rapid prototyping, making plastic model parts as mock-ups for later production by conventional methods. As an area of research, this kind of printing wasn't thrilling, says Timothy Scott, a polymer scientist at Monash University in Melbourne, Australia: "Basically making trinkets and knick-knacks. For a polymer chemist, it was pretty dull."

Then DeSimone unveiled a way to print light-sensitive resin up to 100 times faster than conventional printers³. It uses a stage submerged in a vat of resin. A digital projector shines a pre-programmed image up at the stage through a transparent window in the floor of the vat. The light cures an entire resin layer at once. DeSimone's advance was to make the window permeable to oxygen. This kills the curing reaction and creates a thin buffer layer, or 'dead zone', just above the window's surface so that the resin doesn't stick to the bottom of the vat each time a layer is printed. The stage rises continually, pulling the completed part up through the liquid as new layers are added at the bottom.

Other labs were working on similar concepts at the time, says Lewis. But perhaps most impressive about DeSimone's resins was that they could undergo a second reaction in a post-print heat treatment to strengthen the finished product. "It opens up a much broader array of materials," says Lewis.

Many research groups and firms have since built on the work. Mirkin's printer pumps a laver of clear oil across the bottom of the vat to inhibit the polymer's reactions. This also acts as a coolant, removing heat that can deform a printed part – and it means that the equipment is not limited to printing with resins that are inhibited by oxygen. He says the printer produces material ten times faster than DeSimone's. And last January, Scott and his colleague Mark Burns at the University of Michigan in Ann Arbor reported a printer that inhibits the reactions by mixing into the resin a chemical that can be activated by a second lamp emitting a different wavelength of light⁴. By varying the ratio of the strength of the two light sources, the researchers can control the thickness of the photo-inhibited zone, allowing the creation of more complicated patterns, such as surfaces embossed with seals or logos.

Inventions in 3D printing often have rapid commercial potential: some researchers start forming companies before they publish their

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advances. On the same day DeSimone's paper was published, for instance, he showcased it at a TED talk in Vancouver, Canada, and officially launched his start-up firm Carbon 3D in Redwood City, California, although he had quietly registered the company two years earlier. The firm is now one of the biggest start-ups in 3D printing; it has already raised US\$680 million in publicly disclosed funding rounds, and is reportedly valued at \$2.4 billion. It has high-profile contracts with Adidas to make rubber-like midsoles for athletic shoes, and with sports-gear firm Riddell to manufacture customized helmet padding for American-football players.

Mirkin and his colleagues James Hedrick and David Walker have also launched a start-up, Azul 3D in Evanston, Illinois, to commercialize their technique, which they have dubbed HARP (high-area rapid printing). And Scott and Burns are preparing a commercial prototype printer with their Ann Arbor-based start-up Diplodocal, a name derived from the Greek for 'double beam'.

New resin-printing techniques are still emerging. One begins with a small spinning glass holding liquid resin. As the glass rotates, a projector shines a loop of video onto it that corresponds to 2D slices of the desired object. Within seconds, the final object solidifies inside the liquid resin – no layers necessary⁵. The method is inspired by X-rays and computed-tomography scans, which image

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a cross-section of a solid object. This is the inverse: back-projecting cross-sections to form a 3D object.

Even in this fast-moving field, the technique turned heads for what Lewis calls "the gee-whiz factor". It has significant limitations: the resin used must be transparent, and the printed object must be small enough for light to pass through it to cure it. But it also has a potential advantage: it can handle highly viscous resins, which other resin-based printers struggle to suck through the narrow dead zone. That means it could make stronger materials and more accurate prints.

The approach has garnered substantial interest from industry, says Christopher Spadaccini, a materials and manufacturing engineer at Lawrence Livermore National Laboratory (LLNL) in California. Spadaccini was a member of the team that published the work last January⁵. A group at the Swiss Federal Institute of Technology in Lausanne (EPFL) independently developed the same concept, and has also reported a demonstration of it⁶. Spadaccini thinks the technology has tremendous commercial potential because it has modest hardware requirements. "In the end, really, what you need is a halfway-decent projector and a rotating stage," he says.

Going big

While chemists work on smarter ways to 3D-print intricate resins, engineers are pushing boundaries in 3D printing of concrete – using computers and robots to precisely automate the pouring process.

The world's first 3D-printed concrete pedestrian bridge was made by researchers at the Institute for Advanced Architecture of Catalonia in Barcelona, Spain, and installed in a park in Alcobendas, near Madrid, in 2016. Twelve metres long, the bridge features a lattice structure designed with algorithms that maximize strength and reduce the amount of material needed. Other teams have made similar structures, including a 26-metre-long bridge in Shanghai, China, produced by engineers at Tsinghua University in Beijing. And teams and companies in China and the Netherlands have 3D printed demonstration houses.

Those structures aren't constructed in one print job, however: separate segments are printed and then connected. By producing bridges and houses more cheaply and efficiently, 3D printing could reduce concrete's carbon footprint – but it could also just encourage engineers to build more.

It's not just concrete that is going big: Amsterdam firm MX3D has printed a bridge from stainless steel. First displayed publicly in 2018, the bridge is now being tested and having sensors installed ahead of a planned installation over an Amsterdam canal. And California start-up firm Relativity Space in Los Angeles says it is constructing a nearly fully 3D-printed rocket. The rocket is designed to lift 1,250 kilograms into low Earth orbit, and its first test launch is slated for 2021. Printed metal doesn't always have the same heat-dissipating performance as non-printed metal, says Relativity Space's chief executive, Tim Ellis, but the printing process can add cooling channels in geometries that can't usually be manufactured. Because rockets are used only once or perhaps a few times, they don't have to be as strong in the long term as do alloys in aeroplane parts, which must resist failure over tens of thousands of pressure cycles, Ellis says.

These large-scale metal-printed projects are built with robot arms that feed a thin metal wire to a laser that welds the material into place. Other established ways to print metal use a laser or a beam of electrons to melt or fuse a bed of powder into layers of finished

"There are still some big challenges with 4D printing."



A resin printer from Chad Mirkin's lab at Northwestern University in Illinois can create structures as large as a person in hours.

product. Another technique binds a bed of powder with liquid glue, then sinters the structure in a furnace. And printers designed in the past few years extrude molten metals through nozzles, in much the same way as in FDM.

Aviation firms such as Boeing, Rolls Royce and Pratt & Whitney are using 3D printing to make metal parts, mainly for jet engines. It can be cheaper than milling metal blocks, and the intricate components often weigh less than their conventionally made counterparts.

But 3D-printed metals are prone to defects that can weaken the final products. Spadaccini

and others are trying to use arrays of sensors and high-speed cameras to watch for irregularities such as hotspots of heat or strain – and then make adjustments in real time, he says.

Many scientists are also hoping to improve the intrinsic strength of printed metals, sometimes by controlling the microstructures of the materials. For instance, in October 2017. a US team reported that the intense heat and rapid cooling used in 3D-printing stainless steel could alter the metal's microstructure such that the product is stronger than those cast conventionally⁷. And two months ago, researchers in Australia and the United States reported a titanium-copper alloy with similar strength advantages8. As they solidified, previous 3D-printed titanium alloys tended to form grains that grew in column-like structures. The copper helps to speed up the solidification process, which results in grains that are smaller and sprout in all directions, strengthening the overall structure.

Mark Easton, a materials engineer at RMIT University in Melbourne and one of the leaders of the alloy work, has already had conversations with aerospace companies interested in exploring uses for the material. He says it could also be used in medical implants such as joint replacements.

Many of the printing techniques that work for metals can also be applied to ceramics, with potential applications that include making dental crowns or orthopaedic implants. Moulds for these objects are already made by 3D printing, with the material cast in the conventional way. But 3D-printing the entire object could save time at the dentist or surgeon's office.

However, it is harder to control the microstructure of 3D-printed ceramics, says Eduardo Saiz, a materials scientist and ceramicist at Imperial College London. And nearly all practical ceramic printing techniques involve extensive post-print sintering that can warp or deform the part. "In my opinion, ceramics is way behind polymers and metals in terms of practical applications," he says.

Change over time

The field's future could also lie in '4D printing' – 3D-printed objects that also have the ability to perform some mechanical action, akin to artificial muscles. Often, these incorporate shape-memory polymers, materials that can react to changes in their environment such as heat or moisture.

In May 2018, researchers at the Swiss Federal Institute of Technology (ETH) in Zurich and the California Institute of Technology in Pasadena reported printing a submarine that propels itself forward using paddles that snap backwards when placed in warm water⁹. The work could lead to microrobots that can explore the oceans autonomously. But for the moment, the paddles must be reset after each



These multi-material print heads can switch between printing hard and soft materials in one object.

stroke. Such devices could use battery power to reset themselves, but that makes the machine less efficient than one made conventionally, says Geoff Spinks, a materials engineer at the University of Wollongong in Australia. "There are still some big challenges with 4D printing," he says.

Another approach to 4D-printed devices involves triggering the action with a changing external magnetic field. US researchers have 3D-printed lattice structures filled with a liquid that changes stiffness in response to a magnetic field¹⁰ – which could perhaps be used to help car seats stiffen on impact.

Other, more passive potential 4D printing applications include stents, which could be compressed to be implanted then expanded on reaching the desired site in a blood vessel to prop it open. Last July, researchers in Switzerland and Italy described a 4D-printed stent that is just 50 micrometres wide¹¹, much smaller than conventional ones. The devices are so small, the team says, they could one day be used to treat complications in fetuses, such as strictures in the urinary tract, which can sometimes be fatal.

Perhaps the most ambitious example of 4D printing is matter that not only moves, but is alive. Currently, techniques for such bioprinting can print tissue, such as human skin, that is suitable for lab research, as well as patches of tissue for livers and other organs that have been successfully implanted in rats. But such techniques are still far from ready to integrate into a human body. Researchers dream of printing fully functioning organs that could alleviate long wait lists for organ donors. "I personally feel we're a decade-plus away from that, at least, if ever," says Lewis.

All together now

Many inventive ideas about printing matter that moves or changes rely on printing multiple materials together. "That's absolutely where the field is heading," says Scott.

Last November, Lewis and her lab described a printer that can rapidly switch between different polymer inks or mix them as it prints a single object¹². This means objects can be printed with both flexible and rigid parts. Lewis has spun off previous work on multi-material printers into a firm called Voxel8, a start-up in Somerville, Massachusetts. Her multi-material printer could help with the athletics wear that Voxel8 is developing, says Lewis. Wearable devices need to be flexible around joints while also having rigid parts to house electronics. Saiz calls the printer "beautiful work", adding wistfully: "There's nothing like that for ceramics or metal."

And in March 2018, a team led by Jerry Qi, a materials engineer at Georgia Institute of Technology in Atlanta, unveiled a four-in-one printer. This combines a nozzle that extrudes molten polymer with one that prints light-sensitive resin, ready to be cured by ultraviolet lamps or lasers, and two that print wires and circuitry from tiny dots of metal¹³. The print heads work together to make integrated devices with circuits embedded on a rigid board or inside a flexible polymer enclosure. Qi says his group is now collaborating with electronics companies interested in printing circuit-board prototypes faster than conventional methods. It wasn't as simple as bolting four different printers into one platform: the researchers also needed to develop software that would allow each print head to communicate with the others and keep track of the progress.

The field is still far from delivering on early visions of bringing mass manufacturing into people's homes. For now, sophisticated printers are too expensive to appeal to non-specialists. But 3D printing has come a long way in the past 20 years. Todd remembers people touring his lab in the early 2000s to see his technique to fuse specks of metal dust together to grow parts. Compared with the conventional milling machines and metal-cutting systems in neighbouring labs, his 3D-printing machines struck visitors as a complete oddity. "It was like we were some sort of a dog playing a piano in a bar," he recalls. Now, for many firms, that trick is standard practice.

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- 1. Walker, D. A., Hedrick, J. L. & Mirkin, C. A. Science **366**, 360–364 (2019).
- Hull, C. W. Apparatus for production of three-dimensional objects by stereolithography. US patent 4575330A (1984).
 Tumbleston, J. R. et al. Science 347, 1349–1352 (2015).
- Tumbleston, J. R. et al. Science 347, 1349–1352
 de Beer, M. P. et al. Sci. Adv. 5, eaau8723 (2019).
- Kelly, B. E. et al. Science 363, 1075–1079 (2019).
- Loterie, D., Deirot, P. & Moser, C. Preprint at ResearchGate https://doi.org/10.13140/RG.2.2.20027.46889 (2018).
- 7. Wang, Y. M. et al. Nature Mater. 17, 63–71 (2018).
- 8. Zhang, D. et al. Nature **576**, 91–95 (2019).
- Chen, T., Bilal, O. R., Shea, K. & Daraio, C. Proc. Natl Acad. Sci. USA 115, 5698–5702 (2018).
 - 10. Jackson, J. A. et al. Sci. Adv. **4**, eaau6419 (2018).
 - de Marco, C. et al. Adv. Mater. Technol. 4, 1900332 (2019).
 Skylar-Scott, M. A., Mueller, J., Visser, C. W. & Lewis, J. A.
 - Nature **575**, 330–335 (2019).
 - 13. Roach, J. D. et al. Add. Manuf. 29, 100819 (2019).

Correction The new 3D printing

This story erroneously stated that Relativity Space intended to do a test launch this year, and misstated the timeline for the development of the printing technique that forms a 3D object in a spinning resin.