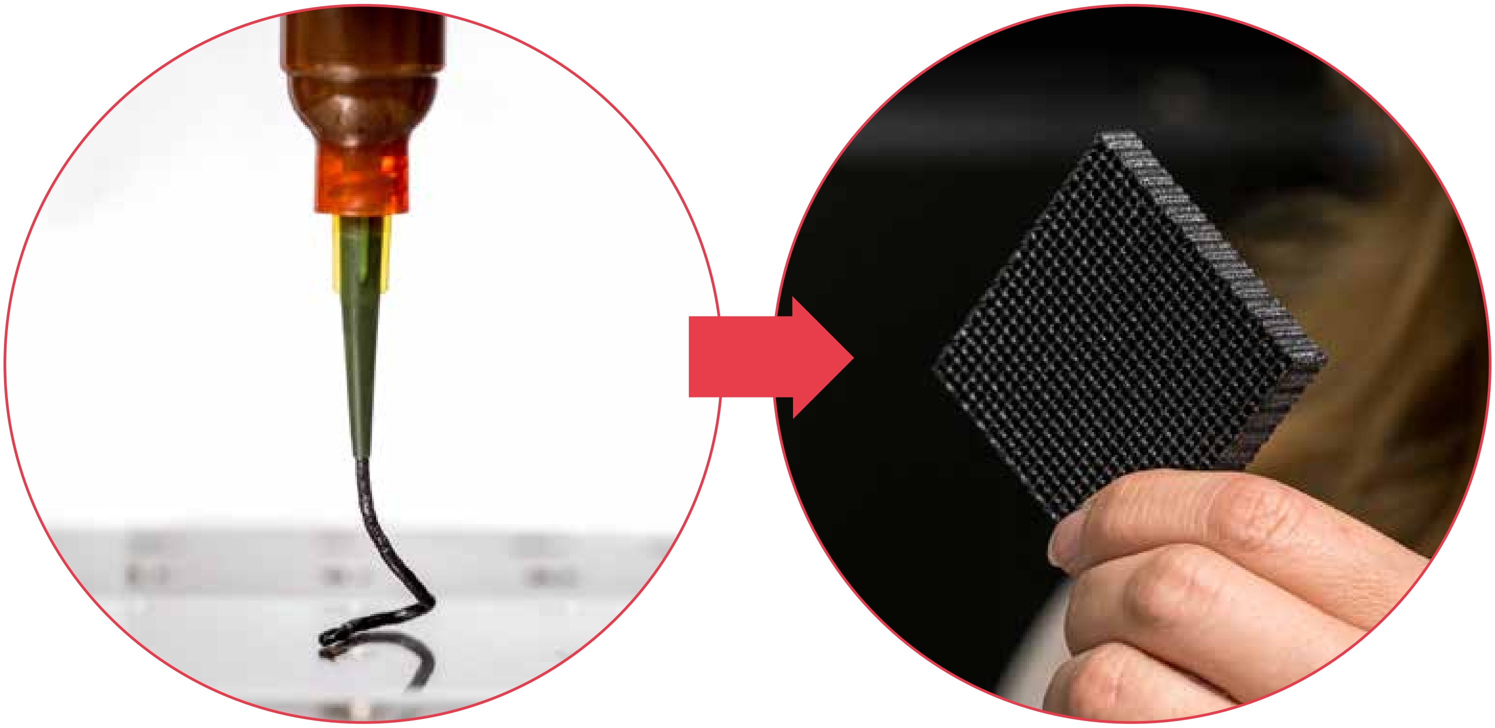
A NEW COMPOSITE-MANUFACTURING **Approach Takes Shape**

Jennifer Rodriguez and James Lewicki examine a three-dimensionally (3D) printed carbon fiber part created using a Livermore-developed direct ink writing (DIW) process.

STRONGER than steel yet lightweight as plastic, electrically conductive and highly temperature resistant, carbon fiber composites have become the material of choice for many applications in aerospace, transportation, defense (see *S&TR*, March 2013, pp. 4–9), and energy storage. The heterogeneous nature of these mixtures of carbon fibers and resin allows for greater customization of structure and properties than with more homogenous materials, such as steel. However, the materials



In DIW, a type of additive manufacturing, (left) a tiny nozzle extrudes a liquid combining carbon fiber and polymer resin onto a platform in a pattern prescribed by a computer file. Layer by layer, as the 3D structure is built, the "ink" must extrude smoothly and solidify quickly to support the growing structure. (right) A completed 3D-printed part is shown.

also pose significant manufacturing challenges. For instance, variability within and between parts can be greater than with homogeneous materials, and such variations can affect a part's properties and performance, which depend heavily on fiber orientation and distribution. Fabricators can compensate for this variability with a higher ratio of fiber to resin, but doing so makes the parts heavier and costlier and the process more wasteful than necessary.

Additive manufacturing (AM)—commonly known as three-dimensional (3D) printing—could eliminate many of these manufacturing concerns. By depositing a material layer by layer in a precise sequence specified in a computer file, AM enables greater precision, design flexibility, and repeatability than conventional manufacturing techniques. Plastic and metal AM technologies are well established, but printing carbon fiber composites is a tangle that scientists and engineers have only begun to unravel over the past few years.

Livermore chemist James Lewicki says, "Carbon fiber is the ultimate structural material. If we could make everything out of carbon fiber, we probably would, but it's been waiting in the wings for years because it's so difficult to make in complex shapes. With 3D printing, however, we could potentially make any shape." Lewicki leads a team of chemists, engineers, materials scientists, and computational experts who—with funding from the Laboratory Directed Research and Development Program—are working to improve the versatility and predictability of carbon fiber 3D printing and the performance of the resulting parts. Combining computational modeling and novel materials chemistry with AM techniques, the team has successfully demonstrated a new approach to producing high-performance carbon fiber composites.

A Better Glue

Carbon fiber composites are made of fibers just 5 to 10 micrometers in diameter, set in a polymer matrix known as a resin. The carbon fibers provide most of the material's strength and other performance characteristics. The resin binds the fibers together to prevent buckling but also represents one of the biggest obstacles to the 3D printing of high-performance parts using direct ink writing

(DIW). DIW is a high-speed, low-cost AM technique in which "ink"—a material in liquid form—is extruded through a tiny nozzle and onto a platform that is moved to deposit the ink where needed to build up the desired object, layer by layer, in three dimensions. (See *S&TR*, March 2012, pp. 14–20.) With DIW, manufacturers can print a wider variety of structures, geometries, and patterns than with conventional approaches, but existing DIW resins are not strong enough for high-performance applications such as aerospace. Nor are most high-performance resins suitable in another important regard—curing time. Conventional resins can take hours or days to harden, while the DIW process requires a resin that can hold its shape as the component is built up. Furthermore, most conventional composites would clog the nozzle of a DIW printer rather than extrude smoothly and continuously.

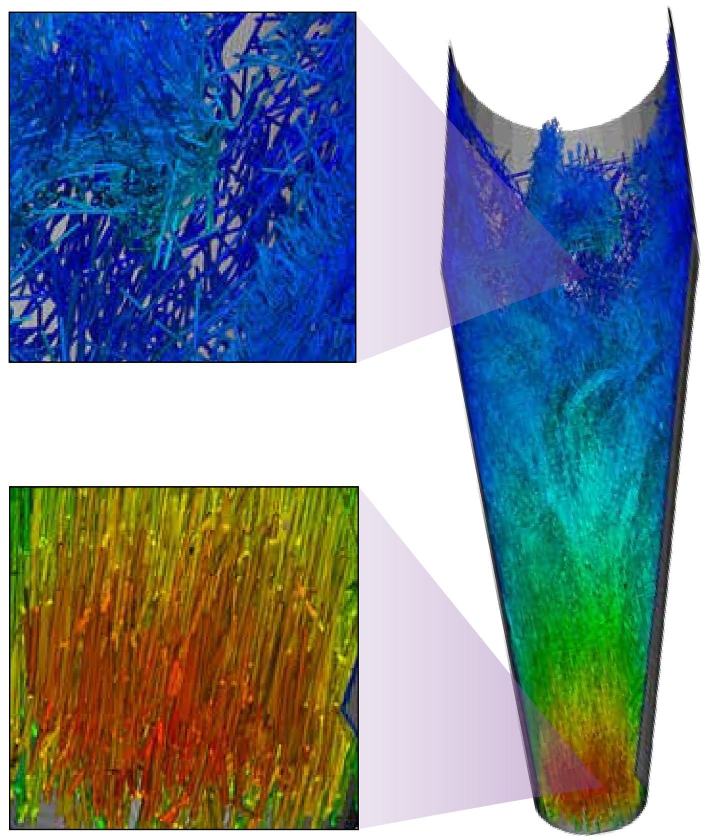
With no commercially available resin to meet their needs, Lewicki and his team created a resin specifically for high-performance component printing—one that gels in 5 seconds or less, fully cures with heat in 10 minutes, and offers flow characteristics suitable for AM. A low volume of high-surface-area silica nanoparticles yields an optimal resin consistency and allows the carbon fibers to orient themselves in the direction of the flow as they are squeezed through the nozzle, preventing clogging.

The resin formula is as much a product of computer simulation as innovative chemistry. In developing the resin, the team's computational experts used Livermore supercomputers to model the flow of carbon fibers through the ink nozzle at several scales. Lewicki notes, "Simulations of the actual printing process were important early on, as they helped show us the path forward with fewer experimental iterations." Fluid analyst Yuliya Kanarska adds, "With our code, we can simulate the evolution of the fiber orientations in 3D under different printing conditions to find the optimal fiber length and optimal performance." Simulation results both validated and explained what was observed experimentally—that with the right ingredients in the right ratio and the right nozzle size and shape, the resin can efficiently deliver carbon fibers without clogging the printer.

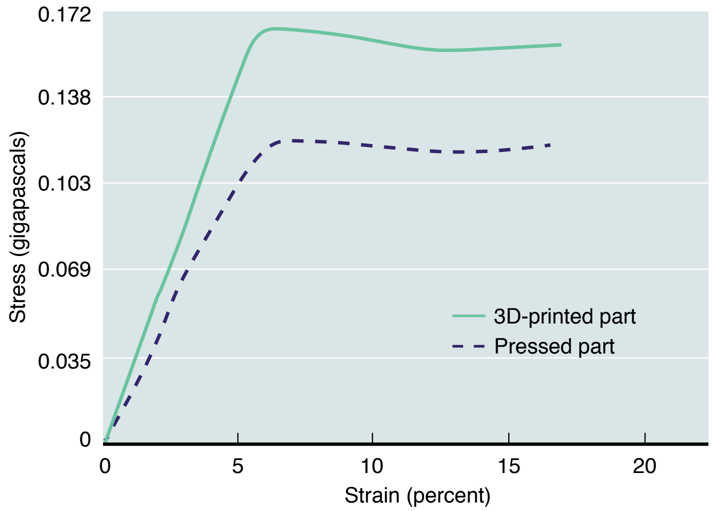
Designer Parts

Standard mold-based manufacturing methods and even some other DIW formulations produce parts with a more random fiber distribution and alignment than Livermore's approach does. Livermore parts, with fibers more consistently aligned in the flow direction, have superior mechanical properties compared to those with the same density of fibers produced by other methods. Recognizing this advantage, the team has gradually increased the volume of carbon fiber in their formula and can now create parts with the same level of performance as traditionally manufactured parts but with just one-third the carbon fiber volume that would be required by other carbon fiber composites. Engineer Michael King states, "We are now confident we can design parts that perform better on a per-fiber and an overall-part basis than other methods can."

Precise yet flexible, DIW offers researchers the freedom—and challenge—of tailoring a part's electrical, mechanical, and thermal response to a given application. Lewicki says, "With chemistry



To avoid nozzle clogging in DIW printing, Livermore researchers use high-resolution numerical simulations of carbon fiber "ink" to study the evolution of fiber orientations in three dimensions. The simulations, such as the one shown here, have helped researchers understand the relationship between fiber length, nozzle diameter, and degree of fiber alignment relative to flow direction. Colors reflect degree of alignment, with warmer colors indicating greater levels of alignment than cooler colors. Fibers approaching the nozzle at bottom start to orient with the direction of flow.



In mechanical testing, 3D-printed parts made with the Laboratory's carbon fiber composite—in which fibers are oriented in the printing direction—outperform conventional pressed parts, which contain randomly aligned fibers.

and engineering, we can purposely put carbon fiber exactly where we want it in a part, more so than other research groups can do. But then the question is, where *should* we put the material for the best performance?" For example, satellite components could be printed to be insulated on one side and conductive on the other to compensate for heat-induced warping.

Because no existing composite-design algorithms could satisfactorily optimize performance, the team has been writing their own, building on team and institutional expertise in multiscale material modeling and systems optimization. Subsequent efforts to optimize fiber layout for greater strength and stiffness in certain directions yielded a 15 percent improvement in mechanical properties, with the potential for even greater improvements.

Computational optimization is an essential step towards making carbon fiber 3D printing predictable, repeatable, and highly customizable. Although still in its infancy, this effort aims to integrate process modeling and computational optimization with in-house tool-path planning algorithms, for a workflow of robust, computationally aided design, development, and manufacturing. The tool-path planning currently under way will assess a part's optimized design, confirm that the design is printable, and then translate the design parameters into instructions that the 3D printer understands. King says, "Essentially, we are building thousands of parts virtually to produce optimized machine instructions, so that we can ultimately get a highly buildable part." To this end, the team continues to investigate the structure and properties of the composite ink when used in DIW manufacturing. Characterization and modeling aim to better understand and control the properties and performance of the resulting AM structures.

From Idea to Product

With enhanced design flexibility, manufacturing repeatability, and part performance, AM technology is expected to spur wider adoption of the team's versatile carbon composite. Lewicki has been working with Genaro Mempin in the Laboratory's Industrial Partnerships Office to develop a commercialization strategy, including filing records of invention (ROIs)—the first formal step on the path to a patent. The ROIs expand Livermore's already sizable portfolio of AM-related innovations, underscoring the institution's core competency in advanced materials and manufacturing. Mempin says, "We have received more than 90 ROIs in AM from Livermore inventors since 2009. The Laboratory has filed patent applications for more than two-thirds of these ROIs, and more are in the pipeline being prepared to file."

Lewicki notes, "So many people are interested in a better, faster, cheaper way to make carbon fiber composites. To take this project further, however, we need to make the transition from scientifically interesting material to practical industrial product. For this, we need collaboration." The research team is exploring a range of opportunities. Other Livermore teams engaged in national and energy security research, along with potential U.S. defense partners and potential licensees in commercial aerospace, have already expressed an interest in Livermore's resin formulation and AM process optimization.

The secret formula behind the team's innovations, according to King, is actually quite simple: "We have a tight collaboration between computational experts, chemists, and engineers. Multidisciplinary teams are something the Laboratory does well and are what has allowed us to create a practical, high-quality technology."

—*Rose Hansen*

Key Words: additive manufacturing (AM), carbon fiber composite, design optimization, direct ink writing (DIW), Industrial Partnerships Office, Laboratory Directed Research and Development Program, record of invention (ROI), resin, silica nanoparticle, three-dimensional (3D) printing, tool-path planning.

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