Potential Applications of 3-D Printed Active Composite Materials

Introduction

With the advent of 3-D printing, structurally complex objects that were once unbuildable can now be easily manufactured. However, what if these objects could be designed and manufactured to respond or change in predictable or pre-programmed ways to a stimulus applied after their production? Enter 4-D printing.

The term “4-D printing” was coined in February 2013 [1]. The first academic paper to address the concept appeared seven months later [2], describing how 3-D printing techniques can combine with active or smart materials to form 4-D printed objects whose shape, properties, and functionalities can be deliberately changed after printing [3,4]. 3-D printing is a process of rapidly creating three-dimensional objects in a layer-by-layer fashion. Today, many different technologies exist to implement 3-D printing, including powder bed laser melting (where material powders are melted by a raster laser to form a layer of solid material with a well-defined geometry) and vat photopolymerization, which takes a layer of polymer resin and converts it to a layer of solid by a raster laser or a projector. Figure 1 depicts another method, polyjet 3-D printing technology, which is used by researchers in the Mechanics of Soft Materials Laboratory at Georgia Institute of Technology (Georgia Tech). In this method, several inkjet print heads are used to jet different polymer resins (in a manner similar to how different color inks are jetted onto paper in an inkjet printer), after which the resin is cured (or solidified) using ultraviolet light.

In traditional 3-D printing, an object is formed with a fixed shape, and that shape is not intended to change. 4-D printing enables a 3-D printed object to change its shape or form well after the printing process has been completed via exposure to a specific trigger stimulus. Researchers typically rely on environmental free energies such as moisture [5,6], temperature [7-10], light [11-13], or a combination of these [14-16] to provide the stimulus for the activation of a 4-D printed object. Non-free energies like a specific electrical current or chemical stimuli have also been used to activate a 4-D object [17,18]. The use of a highly specific (or proprietary) triggering energy could be used to prevent unauthorized use or activation of a 4-D object. It should be noted that just as the concept of 3-D printing now encompasses many different implementation methods, some of which do not directly involve jet-based printing, 4-D printing is a similarly broad concept. Most of all, however, the 4-D printing concept is defined by its emphasis on the time evolution factor or shape change of an object, rather than the details of the technologies or methods used to achieve shape change.

4-D printing is typically achieved through multi-material (m²) 3-D printing techniques in which different materials can be precisely placed in space. The most common method used in m² 3-D printing is the polyjet method [19] (see Figure 1). The direct-write method is another common technique [20]. 4-D printing typically uses two or more materials, at least one of which is active and can respond to a trigger stimulus. Active, or smart materials, include a wide variety of substances that can change their appearance, material properties, and/or shape in a controlled manner in response to an external stimulus. Here, “active” or “smart” refers...
Potential Applications of 3-D Printed Active Composite Materials

HDIAC Journal • Volume 4 • Issue 4 • Winter 2017 • 21
www.hdiac.org

Potential Applications of 3-D Printed Active Composite Materials

To the fact that these materials can "sense" their environment, so to speak, reacting to changes in environmental conditions such as temperature and/or humidity change or ultraviolet irradiation. Based on the type and intensity of the trigger stimulus, smart materials can change their physical state, such as deforming from the shape in which the material was manufactured into a different shape—one programmed in advance by a human operator.

To date, two types of active materials are under investigation for use in 4-D printing: shape memory polymers (SMPs) and hydrogels. SMPs are used in 3-D printing layered composite structures—also known as printed active composites (PACs)—that contain multiple families of shape memory polymer fibers [2]. Through proper design of the distributions of SMP fibers in the non-SMP matrix, many interesting shape changing properties can be achieved [7,21]. Hydrogels that swell in water or in solution can also be used to produce shape change when used alongside a non-swelling polymer, which converts the swelling force into a biased mechanics field [14,22]. Research into 4-D printing applications has already accomplished one-way activation in an object from an initial, programmed state, into a permanent final state [2]. Subsequent research has allowed for the programming of multiple activation states within a single composite structure [19], and only in the past year have we begun to achieve fully-reversible two-way actuation [17].

These capabilities, combined with the typical advantages offered by 3-D printing (such as agile manufacturing), make 4-D printing a potential future solution for many Department of Defense (DoD) applications. Research into 4-D printing applications has already accomplished one-way activation in an object from an initial, programmed state, into a permanent final state [2]. Subsequent research has allowed for the programming of multiple activation states within a single composite structure [19], and only in the past year have we begun to achieve fully-reversible two-way actuation [17].

Polyjet printing technology allows for printing SMPs with different glass transition or...
activation temperatures, and thus can be used to create active components [21]. An SMP is a polymer that can be programmed (or formed) into a temporary shape and later made to recover its permanent shape upon exposure to its trigger stimulus [28]. To date, temperature is the most commonly used trigger stimulus in SMP-focused studies. In a typical application, the SMP can be programmed into a shape through a thermomechanical loading process in which the SMP is first heated to above its transition temperature (such as glass transition), deformed, and then cooled. Upon unloading at the low temperature, the SMP remains in the temporary, deformed shape. To recover its permanent shape, the SMP is heated to a temperature above the transition temperature. It should be noted that the shape change from temporary to permanent in this example is a one-time event (i.e., the SMP would have to be programmed again by the thermomechanical deformation). However, there are research efforts underway to make multi-use reversible shape changes possible [29,30].

Figure 2A depicts an example of a printed active composite using an SMP that results in bending. This PAC laminate consisted of a single layer of SMP fibers in a soft matrix. After printing, the PAC was programmed with a simple thermal-mechanical programming step (including stretching at a high temperature, cooling to a low temperature (0°C), and releasing the mechanical load), and the PAC object was bent. The resulting bending can be used to create active origami structures such as the self-folding airplane shown in Figure 2B. The 4-D printed active origami structures demonstrated their ability to solve engineering issues related to the packing of large structures into small volumes, for purposes related to storage and transportation. Additionally, this folding/assembly process that was triggered by a stimulus and executed automatically (self-folding or self-assembling) has the advantage of being able to overcome the limitation of requiring manpower to work in extreme environments or urgent/dangerous situations. For example, a printed flat pack structure could deploy into a three-dimensional structure by applying the trigger stimulus, producing, for example, a self-foldable building or tent for immediate use in the field [24]. For another example, the hydrogel-based shape-shifting structures can be used as a rain-expandable structure requiring minimal human involvement to utilize [31].

Wu, et al. [19] took the PAC method one step further in 2015 by incorporating multiple SMP fibers into a 4-D printed object, as shown in Figure 2C. The two fiber types had different activation temperatures, at around 37°C and 57°C. After printing, the PAC was programmed with a simple thermal-mechanical programming step as described above. After programmed, the PAC could “memorize” two temporary shapes and would recover to the flat, permanent shape when stimulated by heat. Figure 2D shows the shapes of the PAC activated at different temperatures.

Many interesting applications for active structures could be realized using PACs. Figure 2E shows an active hook: the flat hook could morph into semi-circular shapes when immersed in 30°C water and lift a small box. Subsequently, upon immersion in 70°C water, the hook returned to a straight shape, releasing the box. The capability of changing shape from one to another under moderate temperature change and then returning to the initial shape under a higher temperature offers a significant advantage in many DoD applications. For example, such a design could be used as a suture to tighten wounds or as a fixture to attach devices under relatively moderate temperature in the battlefield; once the warfighter or...
the devices return to the hospital or service center, a higher temperature can be applied to quickly release the fixture [32]. In addition, such a design could be used for soft robotics, where a robot made of soft materials can change its configuration dramatically to meet different application requirements. By using the multiple-shape or dual-programmed PAC, the temporary intermediate shape could be used for the soft robots to pass obstacles, like a barricade or small opening, before recovering to its original shape for use in its final location.

PACs do have some limitations. For example, the PACs illustrated in Figure 2 are successful in creating active structures; however, they require extensive programming using the multiple-step thermal-mechanical process (including heating, deforming, cooling, and removing load) before actuation. In addition, the actuation is single-use; achieving reversible or two-way shape change would require special designs or mechanisms.

**Direct 4-D Printing Using Printed Active Composites**

Recently, our research group and collaborators developed a new method such that a composite can be directly activated and made to maintain a new shape through simple heating [10]. Here, we utilized the residual strain induced during 3-D printing, which was controlled by the material composition and printing process parameters. When a laminated strip with an SMP in conjunction with an elastomer was printed (the printing method is similar to the one used in the PAC discussed above), the elastomer was imbedded with the residual strain created by the 3-D printing process. After it was removed from the printing tray and heated, the laminate object bent due to the residual strain and the thermal expansion mismatch of the two materials (see Figure 3A). This new bent shape is permanent; the strip would not change upon further cooling and heating after it was first bent.

This simple bending process could be used to create more complex shape changes, such as the expanding lattice shown in Figure 3B or the shrinking lattice shown in Figure 3C. The difference between Figure 3B and Figure 3C lies in where the elastomers are placed, which indicates the large degree of design freedom that 3-D printing offers. Figure 3D depicts a 4-D printed object that was designed to be printed flat but raises up and expands to form a dome upon heating. In Figure 3E, initially flat petals bend and form a closing flower.

As discussed above, in this direct 4-D printing method, the shape assumed after heating is permanent. An obvious advantage of this new method is the decreased cost in supporting materials and printing time. For example, for the dome structure, conventional 3-D printing requires a supporting material underneath the dome, which also takes additional time to print. We estimate that 4-D printing can save approximately 70 percent of materials and time for a dome or similar structure formed with thin lattices. In addition, this new method is very simple to implement and could be used for a wide range of DoD applications. For example, the lattice structures illustrated in Figures 3B and 3C can potentially be used as quickly expandable fencing or as metamaterials with tunable bandgap for acoustic applications.

**Internal Shrinkage, Stress-Induced Shape Change**

Volume shrinkage is a common event when a polymer is cured (changed from a liquid resin to a solid polymer); therefore, it occurs in many 3-D printing processes, especially when photopolymerization is used. Volume shrinkage in general should be avoided in 3-D printing techniques, as it can cause shape distortion if the geometry of the printed part is especially complex. However, if such a volume change can be precisely controlled, its occurrence can be advantageous for creating shape-changing structures [11,34].

Our research group developed a simple method to fabricate thin film structures by utilizing the volume shrinkage stress induced during the photopolymerization process [35] (see Figure 4A). A commercial projector was used as the light source. Photoabsorbers were added into the resin to attenuate the light, creating a light intensity gradient across the thickness direction within the liquid resin. Therefore, the material directly exposed to the light (the bottom of the resin shown in Figure 4A) was cured faster than the material further from the light, resulting in a nonuniform volume shrinkage and stress gradient in the cured polymer. Once the material was removed from the

---

**Figure 3:** (A) The concept of direct 4-D printing where two layers of different materials are printed together, and the difference of the thermal expansion coefficients and the printing-induced internal strain can induce shape changing behavior (B) A lattice structure that expands greatly upon heating (C) A lattice that can shrink upon exposure to heat (D) A flat structure that can expand upon heating to create a dome structure (E) Printed flower blooms into a configuration where petals at different layers assume final configurations with different curvatures. Adapted from [10].
curing stage, the cured polymer sheet was activated and bent toward the less cured portion (the top surface in Figure 4A).

Further experiments demonstrated that the bending curvature depended on the illumination energy, which can be controlled by the intensity of the light, the length of illumination, or both (see Figure 4B). The light intensity was related to the grayscale in the CAD drawing; as a result, by precisely controlling the spatial distribution of the designed grayscale pattern, we easily created complex 3-D origami structures. Figure 4C illustrates a flat polymer sheet after photopolymerization (using the pattern in the inset), and Figure 4D illustrates the bending shape achieved after removal from the printing stage. Complex polyhedron structures may also be fabricated, as illustrated in Figures 4E and 4F.

To extend the application of this method, a two-sided illumination procedure was proposed, as illustrated in Figure 4G. After the first illumination step, the material was flipped, and a second gray level pattern was projected. Using this method, origami structures that require bending deformation toward different directions can be printed (see Figure 4H). One advantage of this method is that it can quickly produce 3-D printed thin film structures by using a commercial projector. One potential application is to fabricate contact lenses, as illustrated in Figure 4I. It should be noted that this method creates shape changes that are currently irreversible and single-use only. Recently, we extended this method to program reversible shape changes into objects by tuning the materials used in this approach [11].

Hydrogel for 4-D Printing of Reversible Shape Changing Structures

Some highly absorbent materials, such as hydrogels, yield large volume changes upon introduction to solvents in a process called swelling. The swelling and de-swelling behavior of hydrogels can be used to force shape change in 4-D printed structures [5, 7, 20]. However, one disadvantage of hydrogels is their softness, with Young’s modulus in the range of a few tens to hundreds of kPas (although their bulk modulus could be very high).

In 2015, our research group developed a new design that utilized the swelling of a hydrogel as the driving force and the temperature dependent modulus change of a SMP as a switch to create shape change components capable of being stiff in two different configurations [7]. Figure 5A illustrates a design in which the hydrogel was sandwiched between an SMP layer and an elastomer layer. The elastomer was also deposited in columns to convert the hydrogel’s swelling to in-plane expansion. Figure 5B illustrates the deformation process. The hydrogel sample was first printed according to the design in Figure 5A. It was then immersed in cold water (~0°C) for ~12 hours (see S1 in Figure 5B), allowing the hydrogel to absorb water. Because the temperature was low, the SMP had a very high modulus, which prevented the strip from deforming. The strip was then moved to a hot water bath (see S2 in Figure 5B). The modulus of the SMP strongly depended on temperature. Because of the temperature rise, the modulus of the SMP dropped by approximately three orders of magnitude, which led to a quick bending of the strip (typically within 10–20 seconds). The strip was then heated again, it returned to its straight, unbent shape.

Figure 6: This image is one in a series of images showing the transformation of a 4-D-printed hydrogel composite structure after its submersion in water. (Source: National Science Foundation)
This process could easily be used in more complicated designs. For example, our research team also printed a flower design (see Figure 5C). The flower closed its petals once immersed in cold water. The flower also carried a load of 25 grams at low temperature (see Figure 5D). This new design was capable of reversible shape changes, fast deployment speeds (within ~10 seconds), and a high degree of stiffness. This makes it a good candidate for DoD applications, such as for use in micro unmanned aerial vehicles (UAVs) or small UAVs (SUAVs) for surveillance. For example, the aforementioned steps (see S1–S4 in Figure 5B) could be performed on an SUAV promptly after fabrication. The SUAV could then be deployed into a flying configuration once activated by temperature (set either to an environment change or through remotely controlled electrical heating).

**Future Possibilities**

The field of 4-D printing is rapidly developing. It enables the targeted evolution of a 3-D printed structure’s shape, property, and functionality over time through the use of printable active materials. This article discussed several recently developed and facilely approached methods from our research group and collaborators, including shape-memory polymer-based unconstrained-thermo-mechanics; internal stress-based constrained-thermo-mechanics; and hydrogel-based hydro-mechanics. The use of active materials, realized through 3-D printing, enables innovative applications previously unachievable by conventional manufacturing processes. For example, potential military applications for 4-D printed hydrogel structures could be pursued in key areas including, but not limited to, improved battlefield medical devices for wound healing [36,37], drug delivery systems [38], wearable electronics [39], and energy-storing supercapacitors [40]. However, as with any emerging field of research and development, 4-D printing still faces many challenges. Each class of potential applications presents a different set of requirements that the material system must satisfy. For instance, biomedical devices must be fabricated from a bio-compatible polymer so that they may be introduced into the body without triggering harmful response [41,42]. Similarly, a major roadblock in the widespread implementation of flexible, wearable electronics is the lack of a proper energy storage system that can withstand constant mechanical deformation from the wearer’s movement [43]. Another challenge associated with 4-D printing is that most printing processes deploy thin structures in order to produce a large shape change relative to their size. Although thin structures are routinely pursued in DoD applications for lightweight equipment, it will also be important to achieve shape change...
Further types of application may be brought to fruition if this technology is implemented with other advances, such as color-shifting textiles intended to help warfighters conceal themselves by bending the light reflected from the clothing [47]. To better implement and maximize the potential applications of 4-D printing, further research should be aimed at developing novel, stronger, and more durable printable active materials, and producing new 4-D printing concepts and predictive design tools based on theory. With these efforts, 4-D printing may become beneficial for many future DoD applications. ■

Acknowledgment

The authors are grateful for the financial support from the Air Force Office of Scientific Research (FA9550-13-1-0088 (expired in 2016), FA9550-16-1-0169; Dr. B.-L. “Les” Lee, Program Manager) and a DURIP grant from AFOSR (FA9550-16-1-0170; “Les” Lee, Program Manager), and from the National Science Foundation (grant CMMI-1462895, CMMI-1462894).

References


in large, thicker structures for more durable applications. Therefore, it is necessary for the 4-D printing processes discussed in this article to be closely tailored to a given structure’s end-use applications and environmental requirements.

The potential benefits of using applications of 4-D objects go well beyond the feature of simple shape-shifting. Other stimulus-responsive properties, such as self-healing and self-sensing, are beginning to be incorporated into 4-D printed structures [44-46].
Devin Roach  
Ph.D. Candidate, Georgia Institute of Technology

Devin Roach is pursuing a Ph.D. in mechanical engineering, conducting research in the Mechanics of Soft Materials and 3-D Printing Laboratory under H. Jerry Qi (B.S., Georgia Institute of Technology). His research interests include soft-active polymers, 3-D printing, and how they can be integrated to form novel structures for use in printed soft robotics and biomedical devices. He has worked on research teams at Sandia National Laboratories, Delta Air Lines, and Airbus Headquarters in Germany.

Craig M. Hamel  
Ph.D. Candidate, Georgia Institute of Technology

Craig M. Hamel is pursuing a Ph.D. in mechanical engineering and is a Paper Science and Engineering Fellow at the Renewable Bioproducts Institute (M.S., New Jersey Institute of Technology; B.S., University of Mississippi). His doctoral research revolves around the cross section of additive manufacturing, renewable materials, theoretical mechanics, and continuum level simulations.

Jiangtao Wu  
Ph.D. Candidate, Georgia Institute of Technology

Jiangtao Wu is pursuing a Ph.D. in mechanical engineering, conducting research in the Mechanics of Soft Materials and 3-D Printing Laboratory under H. Jerry Qi (M.S., University of Chinese Academy of Sciences). Wu's research interests include 3-D printing, smart materials, active structures, and mechanics of polymers.

Xiao Kuang, Ph.D.  
Postdoctoral Associate, Georgia Institute of Technology

Xiao Kuang is a postdoctoral associate in the George Woodruff School of Mechanical Engineering, (Ph.D., Institute of Chemistry Chinese Academy of Sciences; B.S., Beijing University of Chemical Technology). Kuang's research interests include 3-D printing smart (self-healing, shape memory) materials, recyclable 3-D printing, and hybrid materials for high-performance or functional applications.

Martin L. Dunn, Ph.D.  
Professor and Associate Provost for Research, Singapore University of Technology and Design

Martin L. Dunn is a professor and the associate provost for research at the Singapore University of Technology and Design (Ph.D., University of Washington). Before joining Singapore University of Technology and Design, he directed the Mechanics of Materials and Design Engineering Materials programs at the U.S. National Science Foundation. Dunn has also served as associate dean for research in the College of Engineering at the University of Colorado, Boulder (CU Boulder). Also at CU Boulder, he was a professor of mechanical engineering, chair of the Department of Engineering, and held the Victor Schelke Endowed Chair. He has held positions at Sandia National Laboratories and the Boeing Company. His primary research interests include multiphysics modeling of materials, computational design, and additive manufacturing.

H. Jerry Qi, Ph.D.  
Professor, Georgia Institute of Technology

H. Jerry Qi is a professor in the George W. Woodruff School of Mechanical Engineering (Sc.D., Massachusetts Institute of Technology). Before joining Georgia Tech, he was an associate professor at the University of Colorado, Boulder (2004-2013) and was a postdoctoral fellow at MIT (2003-2004). Qi is also an ASME Fellow and Woodruff School of Mechanical Engineering Fellow. His research primarily focuses on modeling, development, and 3-D printing of soft active materials. Specifically, his current research focuses on developing 3-D printing technologies for high performance polymers, 4-D printing of active materials, mechanics in 3-D printing, and active polymer design and manufacturing.