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Chapter 16

FROM 3D TO 4D-PRINTING: ON THE ROAD TO SMART 3D-PRINTED POLYMER DEVICES

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ABSTRACT

The scientific and technological progress reached a point that allows for exciting 3D printing technologies. Applied to the additive manufacturing industry, said technologies offer the possibility to create polymer devices with controlled architectures such as personalized prototypes, hydrogels, biomedical and flexible electronic devices, as well as sensors and actuators with controlled properties and a specific set of desired functionalities. Alongside this advancement, a new class of polymers defined as "smart polymer materials", are described, with a main utility built around the capacity to exhibit adaptive properties that fulfill previously impossible functions post application of environmental changes. Direct 3D printing of such stimuli-responsive materials allowed the development of a brand new 4D printing technology with an outlined time dimension. This chapter will cover a comparative review of the two most frequently explored AM technologies - fused deposition modeling and stereolithography with a specific focus on

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the practical use in “smart materials” 3D printing. Potential applications for the printed parts and some critical remarks are also mentioned.

Keywords: smart polymers, additive manufacturing, fused deposition modeling, stereolithography, 3D-printing, 4D-printing

INTRODUCTION

1. From Additive Manufacturing to Smart Materials

Slowly yet steadily, additive manufacturing (AM) technologies have become a major player in the fabrication of polymer devices. Private companies, government and public sector have openly declared an interest into applying this method in smart devices fabrication while pursuing direct practical. AM also known as 3D printing, has been herein recognized as a milestone technology for future advances in manufacturing [1-4]. Based on a layer by layer fabrication, with resolution in the range in micro- and nanometers per layer, the computer-assisted printing significantly speeds up the development of custom 3D objects without actually inflating the costs. AM technologies using polymeric materials include selective laser sintering [5], fused deposition modeling (FDM) [6] and stereolithography (SLA) [7] techniques. While FDM is the most promising candidate for fabricating parts out of multi-materials, SLA offers the highest versatility with respect to the freedom in material development, scalability and speed of fabrication.

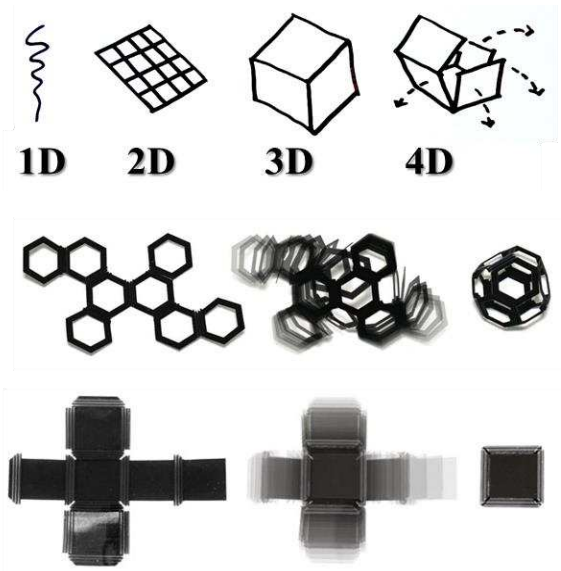


Figure 1. Schematic illustration of the 4D printing concept whereas the 3D-printed structure can change shape over time given external stimulus [8, 9].

Despite the irrefutable progress made around 3D printing and its unquestionable potential benefits, the technique still suffers from rigid and static properties of the printed parts and a difficulty with the actuation or transformation to a desirable shape. However, the emergence of a new class of polymers defined as "smart materials" has somewhat changed the accepted way to conceptualize and design polymer devices. Generally, the term "smart material" is used to describe a material capable of responding to an external stimulus by changing its shape, volume and physical properties, such as Young's modulus, stiffness, and resistance [10]. By attaching this additional attribute of "smartness", new functional systems are linked to various polymeric devices - sensors, actuators and soft-robotics. Combining these stimuli-responsive materials and AM techniques resulted in 3D objects that carry unique responses to a variety of external or environmental stimuli such as changes in temperature, humidity, pH, solvent vapor, *etc.* [11, 12]. This progress gave birth to the 4D printing technology with a fourth dimension defined as the material's transformation over time (Figure 1) [8, 9]. The key element here is the time, where the actuation, the sensor properties and the programmability are directly embedded into the material structure and occur in desired time frames. The resulting new properties mainly rely on an appropriate combination of "smart materials" in the right three-dimensional geometry. Subsequently, shape-changing, self-actuating, self-healing or any other multi-functionality can be obtained as an expected response triggered by changes in the environment. This approach has immediate potential implications in e.g., robotics, biomedical devices, building construction, aerospace, electronics and sensors. As an example, the U.S. Army has already virtually adapted the technology to produce woodland camouflage fabrics, able to mimic natural or even artificial backgrounds by bending the light reflected from the clothing [13].

In this chapter, the focus would be on some of the most recent advancements in AM techniques, with an accent on 3D printing for the design of "smart polymer" materials. A special mention would go to the 4D printing methodology. The discussion would be built around FDM and SLA, the two most well-established techniques in the field. More information about other currently existing AM processing methods is available in Chapter 10 "Polymers for Additive Manufacturing" of this book and readers are kindly invited to refer its content. At the end of the chapter, some practical daily life applications are described and envisioned, and future perspectives and critical remarks are also outlined.

2. 3D Printing

2.1. Fused Deposition Modeling

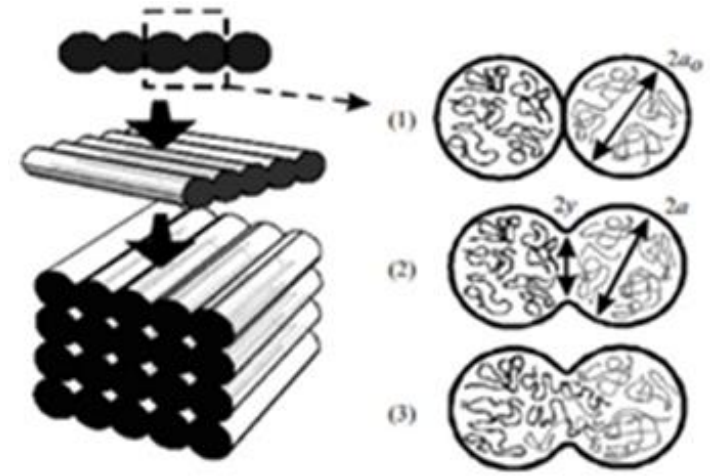
FDM as part of the AM industry is a fast-growing prototyping technology, offering an opportunity to create functional parts with complex geometrical shape within an

acceptable time frames. The core of the process is melting a uniform mono-filament to a semi-liquid state, followed by a layer-by-layer extrusion onto an adapted platform. The adhesion between the layers is guaranteed by a simple contact between the deposited filaments solidifying in the final object [14]. FDM usable materials are limited to most commonly used commercially available thermoplastic polymers (polylactide - PLA, acrylonitrile-butadiene-styrene, polyethylene terephthalate, Nylon®, thermoplastic polyurethane and polycarbonate). Main beneficial factors for those are a low melting temperature, biocompatibility, resorbability and large scale industrial production. For the correct application of FDM, the melt viscosity of the material is of great importance. It should be high enough to ensure structural support, while simultaneously being low enough to enable the layer-to-layer deposition [15]. Some advantages of FDM-based printers are the low cost, high speed and simplicity of the process. However, one common difficulty is that the polymer or the composite material should be prepared in filament shape with a specific diameter (generally 1.75 mm) and capable of undergoing the extrusion process. In cases where nanofillers are loaded in the polymer matrix, their homogeneous dispersion ends up being of particular importance for the final properties of the printed part.

Currently, some advances in the development of composite 3D methodology also allow for the use of pre-blended materials and polymer nanocomposites. Various nanofillers such as carbon fiber [16], carbon black [17], short fibers (including chopped carbon fibers) [18], polymer fibrils [19], carbon nanotubes [10], and glass fibers [20] were mixed into thermoplastic filaments for direct use. The result was a notable reinforcement of the materials in term of mechanical properties. Using 3D printers with two or more printer nozzles enables the production of smart polymer systems for everyday materials. It should be noted that the process parameters (such as working temperature, layer thickness, printing orientation, raster width and angle and air gap) and their direct impact on the final device morphology and properties are not in the scope of this chapter. Detailed information can be found in the study published by Sood et al. [21].

Even though AM through material extrusion is a convenient method for the manufacturing thermoplastic components, a key obstacle facing the 3D-printed plastic parts is the weak welding between adjacent filaments. Often when using FDM, the adhesion between the adjacent filaments in the final 3D-printed device is a result of simple surface contact to contact of the molten material. There are several important difficulties that need to be dealt with: (*i*) fast surface cooling of the previously deposed filament decreases the possibility to interact with the subsequent deposited molten filament, (*ii*) the formation of crystalline phase in the previously deposited filaments during their cooling (decreased mobile amorphous phase of the macromolecules and low probability to interact with the subsequent filament) and (*iii*) an irregular volume contraction alongside the deposited filaments resulting in “wave”-shaped profile instead of straight one. All these effects could lead to delamination of the filament layers and the

subsequent mechanical failure of the final product and limited engineering application. These anisotropic mechanical properties often measure different volume strength when stress is applied: greater along the filament length deposition and weaker in any other direction (Figure 2). In addition to that, some limitations related to the mechanical construction of the equipment are present such as: printing direction (x and y) deviation and vibrations during the printing process. By combining the knowledge acquired in various scientific fields and the expertise of the technological progress linked to the FDM machine construction. In this context, several scientific studies were published with the goal of increasing the interface between the individual filaments. Some scientific projects are focused on the post-treatment of the filament (heating or coating) or on the formation of covalent bonds between the filaments, e.g., thermoreversible reactions.



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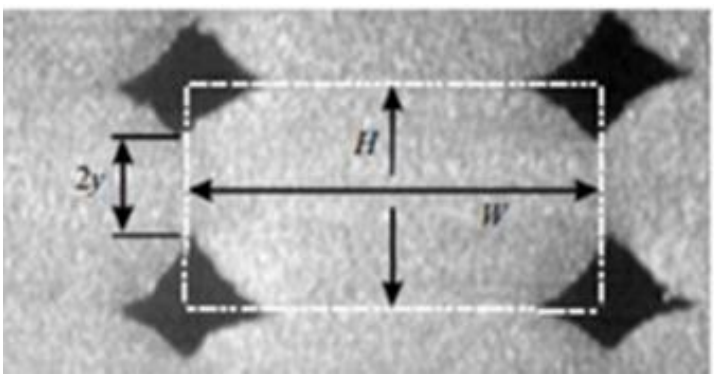

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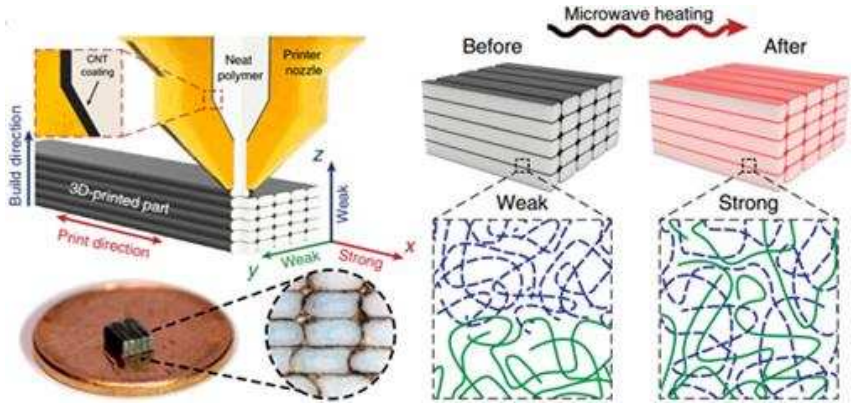
Figure 2. Different degree of contacts between two adjacent filaments: 1-surface contacting, 2-neck growth, 3-molecular diffusion at interface and randomization (A) and SEM microphotograph of the cross-sectional area of the filaments (B) [23].

In the literature, several approaches were proposed to improve the strength of FDM fabricated parts. The focus is on the bead width, the air gap, the working temperature and the faster orientation while goal is to increase the surface contacting the filaments interface, its' the neck growth and molecular diffusion (Figure 2).

Another promising setup is to perform microwave irradiation assisted FDM. This idea has been investigated by Sweeney et al. The experiment used PLA filaments coated with multiwalled carbon nanotubes (0.5 - 20 wt%) for their local heating properties and percolation network [22]. Specifically, localized nanofillers only at the surface of the filaments allowed the production of 3D-printed parts with properties approaching those made from conventional manufacturing such as injection-molding. The presence of microwave-responsive heating elements on the fibers surface, allowed the local selective heat and relaxation of the polymer macromolecules thus increasing their interfaces entanglement (Figure 3A). As a result, enhanced adhesion between the filaments and improved weld fracture strength by 275% were obtained. The authors successfully demonstrated a technique for designing new 3D-printed materials with enhanced mechanical properties resulting in nanomaterial networks.



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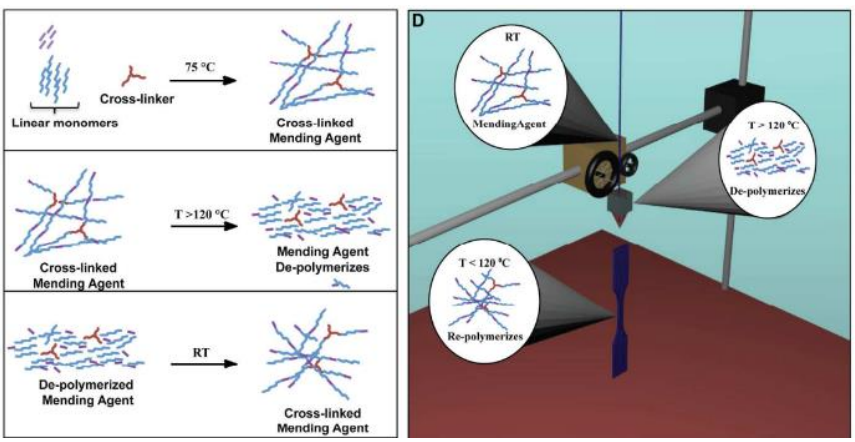

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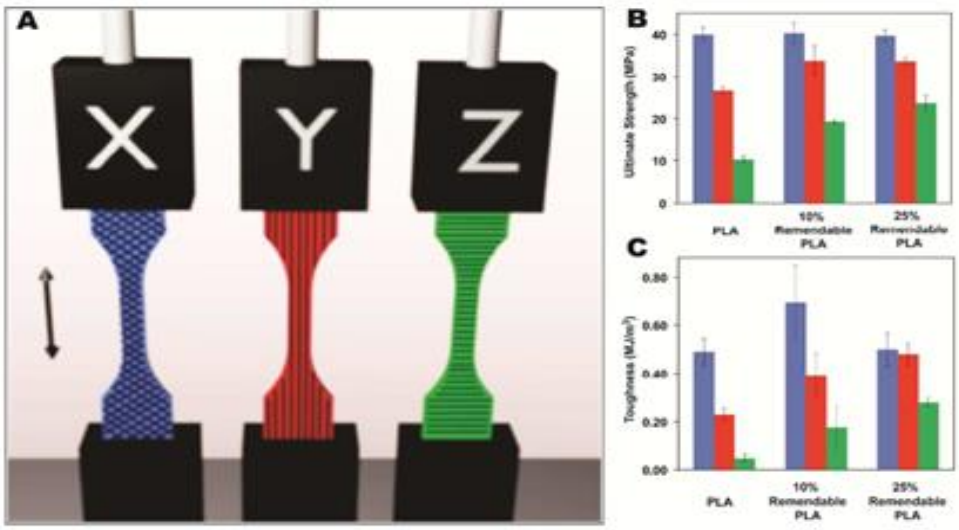

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Figure 3. Different approaches for filament adhesion enhancement: cahin interpenetration (A) or covalent bonding (B and C) [22, 24, 25].

Another possibility to improve the materials mechanical-properties is to explore the fibers interface chemistry. Monomers, oligomers and small molecules playing the role of crosslinker are a valid path in this scenario. Their functionalization with moieties capable of undergoing thermally reversible dynamic Diels-Alder has shown some promising results [24, 26]. To address the covalent chemical adhesion at a molecular level, PLA functionalized with maleimide moieties and a furan-containing mending agent as crosslinker have been used (Figure 3B). The advantage of this approach is that the thermo-reversible network in the extruded filament thermally *de*-polymerizes during the heat cycle of the print process and *re*-polymerizes during the cooling step. When different dogbone type patterns (X, Y, Z) were tested, depending on the direction of the deposited filaments (Figure 3C), it was established that both strength and toughness end up being improved (130% and 460%, respectively along the *z*-axe). Recycling of the polymer matrix was also possible without its additional chemical modifications. Such self-healing mechanisms have also been described by Yang et al. where new covalent bonds occurred within the polymer structure by using multi-furan monomer and bismaleimide [25]. In this case, isotropic 3D thermoset parts in terms of mechanical properties and with more than 95% interlayer adhesion were designed. In advantage to the multi-axial toughness, a smooth surface of the finished product was obtained. Improvement of the printed parts' mechanical properties can be reached when an inert gas atmosphere is used during the print process. Acrylonitrile-butadiene-styrene and polyamide materials demonstrated high mechanical load (increase in elongation at break and tensile strength up to 30%) due to the absence of the macromolecular chain oxidation processes and related-polymer degradation when exposed at high printing temperature [27]. Another possibility to

overcome the anisotropic mechanical effect (improved interfilamentous junctions) is to introduce crosslinks among the polymer chains by exposing 3D-printed copolymer blends to ionizing radiation. Shaffer et al. demonstrated that gamma rays irradiation of polymer/radiation sensitizers (i.e., trimethylolpropane triacrylate and triallyisocyanurate) blends during the printing process, induce crosslinking of the parts resulting in enhanced thermomechanical properties of the final PLA-based material [28]. All these approaches ensure good adhesion between the individual filaments, which is of importance for the successful producing of 3D-printed parts with sufficient mechanical properties and reproducible functionalities in the case of shape memory systems such as actuators.

Of particular interest are the custom-design polymer devices with predefined structure and unique functionality such as self-healing and-deployable structure, actuators, origami structures, biosensor, fixation and fitting parts and others. These polymers are also suitable for smart robotic mechanisms and soft actuation. For their fabrication, a new class of polymers can be used - shape memory polymers (SMPs) capable to memorize their original shape, to acquire a metastable temporary one upon deformation and to revert back to the permanent shape when exposed to an appropriate stimulus. The polymer material's ability to achieve shape recovery from the fixed temporary shape to the initial one is defined as shape-memory effect (SME). This property can be quantified using the shape fixity ratio (R_f) or the ability of the material to fix the temporary shape and the shape recovery ratio (R_r), which represents the extent to get back to the original shape. Usually, the major actuation is directly related to the thermal transitions glass temperature (T_g) or melting temperature (T_m) of the polymeric matrix. In addition, full shape recovery may be caused by other stimuli such as magnetic field, light and electrical current where functional nanofillers (magnetic, plasmonic nanoparticles, carbon nanotubes) are incorporated in the nanocomposite material [29]. In the present chapter, we will define smart 3D materials as materials produced by a 3D technique and capable of recovering their initial shape when exposed to diverse stimuli, while 4D materials would be those capable to change their shape over time once they are 3D-printed and this without external force.

The emergence of SMPs opens the door to the production of new type of filaments from non-commercially available polymers with good processability. Extruded mono-filaments from ternary blends between styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene, polyethylene wax and low-density polyethylene were produced by Chen et al. [30]. The 3D smart materials had the advantage to memorize at least three temporary shapes at specific temperatures via dual, triple and quadruple heating process (Figure 4A). This gradual shape recovery was explained with the presence of multiple individual melting peaks characteristic for polymer matrix composition (heterogeneous microstructures),

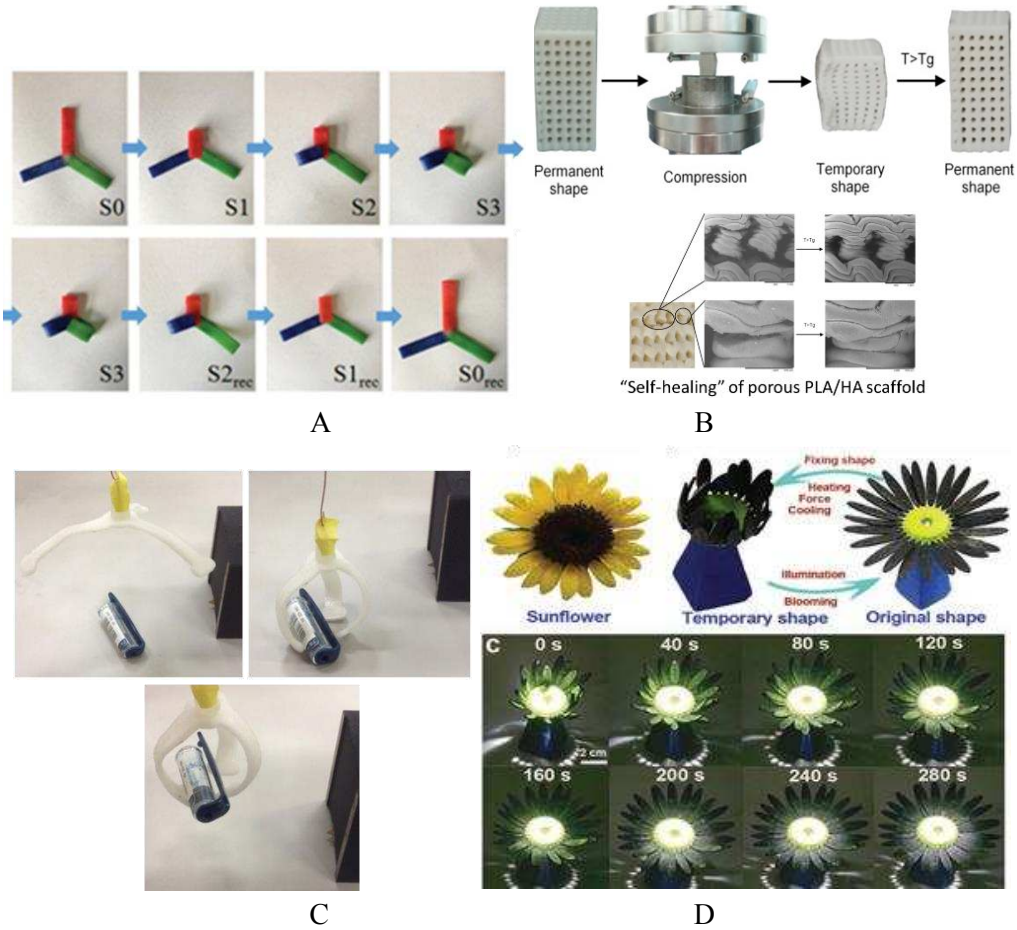


Figure 4. Digital images of 3D-printed SMPs by FDM with quadruple shape memory effect thought bending test (A) [30], with self-healing properties (B) [31] or for catching and transport of objects (C) [33]; Photo-responsive materials with light-triggered shape recovery (D) [34].

offering broad thermally switching transitions. As a consequence, it was demonstrated that 3D-printed objects for rapid prototyping with tunable SME can be easily prepared with specific topological structures, particularly in comparison to other conventionally used thermoplastic-shaping techniques (such as casting or molding). Another nanofiller used for SMP filaments production was hydroxyapatite (HA, 15 wt%) [31]. In this case the porous scaffolds (with an average pore size and porosity of 700 μm and 30 vol%) were reinforced by the dispersed HA particles acting as nucleation agents on PLA phase. The incorporation of the ceramic particles inhibited the growth of cracks during compression-heating-compression cycles revealing the self-healing properties of the material (Figure 4B). The authors then established the advantage of FDM as a disruptive technique for the production of personalized porous scaffolds and implants as self-fitting small bone defect replacements with R_r of 98% and absence of delamination.

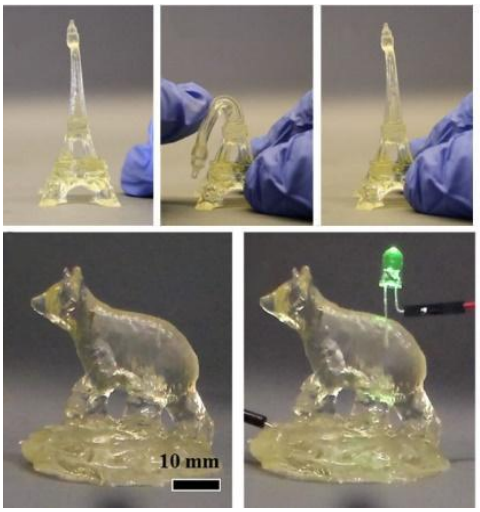
Themally-trigered parts can be done from filaments made of an ionomeric thermoplastic SMP-zinc-neutralized poly(ethylene-*co*-methacrylic acid) [32]. In this case, the shape-memory effect is obtained via two networks: nanodomains with long relaxation times of supramolecular crosslinks formed by ionic bonds (permanent network) and ethylene crystals (temporary network). Printed parts with more complex geometry can be used for catching and transporting objects as presented in Figure 4C [33]. In this study, the filaments were produced from polyurethanes with various T_g (i.e., form 145°C to 195°C).

FDM also finds an application in the fabrication of light triggered devices, where the chemical stability and properties of the photo-sensible compounds are preserved during the printing process by avoiding their UV illumination, as in the case of SLA. Photo-responsive shape memory (nano)composites from polyurethane as smart polymer with advisable T_m and carbon black for its excellent photo-thermal conversion efficiency were described [34]. Remote light control (light source or sunshine) of the printed parts was demonstrated using complex geometric shapes such as a cubic frame and a sun flower-shaped structure (Figure 4D). In both cases the original shape recovered fast (within few minutes with good R_r) due to the effective conversion of light into heat. This approach confirms the potential application of 3D-printed materials as biomimetic solar tracking sensors or smart solar cell systems in FDM.

2.2. Stereolithography

Based on a spatially controlled layer by layer solidification of a liquid resin by photo-polymerization, SLA allows a high quality surface resolution, dimensional accuracy, a variety of material options that includes transparent materials and a growing library of compatible materials enabling the fabrication of large-scale 3D objects [7]. The advantages of SLA compared to all other AM techniques regarding accuracy and resolution as micron-sized structures with sub-micron resolution have been established using this setup [35]. Most SLA formulations are based on chain-growth polymerization from concentrated solutions of low molecular weight species that typically form dense, brittle networks [36]. Among the limited commercial availability of liquid resins suitable for SLA, acrylics for their propensity to light-initiated free radical polymerization and epoxies for for their propensity to cationic photopolymerization are commonly used in SLA formulations, together with their high solubility in many common solvents. Thiol-ene photo-curable resins was also tentatively implemented in the SLA area [37]. Multi-functional monomers are then typically used to introduce more crosslinking sites and tune the mechanical properties of the resulting cured resins. While the number of available photo-curable resins is now rapidly expanding, a customizable manufacturing setup is currently being developed, as a way to cover the printability of other range of materials, and possibly combining performances of different materials in the resulting 3D objects. For example, Tumbleston et al. [16] recently used acrylate photo-chemistry in a newly developed continuous liquid interface production (Carbon 3D, Inc.). In this study, a

modified version of SLA that can print up to 10 cm scale objects in minutes (instead of hours) by creating an oxygen depletion zone in liquid resins, was presented. Another modified version of SLA includes digital mask projection SLA [38], digital light processing [39], micro-SLA [40] and two-photon polymerization [41] to polymerize



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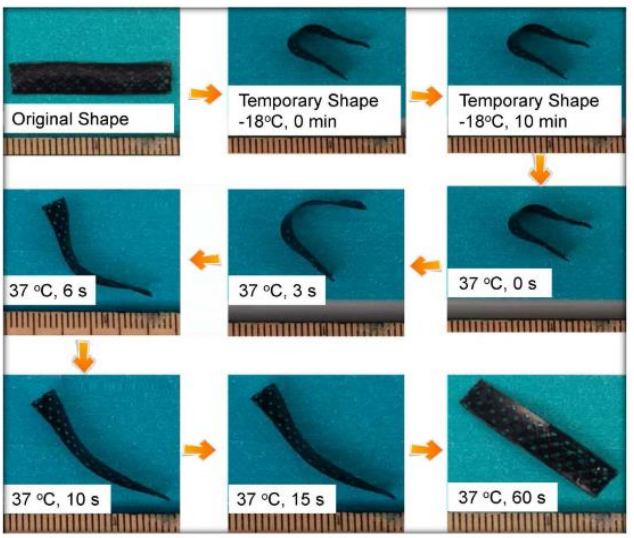

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Figure 5. Digital images of SLA printed materials with shape-memory properties for highly elastic and conductive hydrogels (A) [42], tissue engineering scaffolds (B) [43] and vascular stents fabrication (C) [44].

objects starting from a liquid resin. Scientists are constantly looking for a better solution in order to 3D print parts that are not only structurally sound, but get functionalized with active materials to impart "smartness" into the resulting objects.

As part of said "smart materials", SMPs are a subject of successful SLA printing with various applications. New approach for highly elastic, transparent hydrogels obtained by SLA was proposed by Odent et al. [42] The composite materials presented dynamic and reversible network of ionic interactions resulting in single platform of tunable stiffness, toughness, extensibility, and resiliency. In addition, the presence of silica nanoparticles resulted in the reinforcement of the mechanical performances of the printed material. The electroconductivity of the material conveys a potential application in soft robotics and compliant conductors field (Figure 5A). Composite hydrogels with magnetic responsiveness were designed by Hassen et al. [45]. Poly(ethylene glycol) dimethacrylate was used for its shape-memory properties and the magnetic remote control was provided by adding physically embedded carbonyl iron particles. An interesting approach for biocompatible 3D scaffolds as tissue engineering for human bone marrow mesenchymal stem cells proliferation were proposed by Miao et al. [43]. In this case renewable soybean oil epoxidized acrylate was used as a liquid resin conferring the shape-memory properties of the porous scaffolds. Their shape-recovery is mainly thermally-triggered with T_g of 20°C, offering the possibility to easily generate the glass/rubber phases (permanent/temporary shape) at a temperature close to the human body one (Figure 5B). Cytotoxicity analysis performed on the printed materials had significantly higher cell adhesion and proliferation than traditional polyethylene glycol diacrylate, and had no statistical difference from the widely used polyesters [PLA and poly(ε-caprolactone)]. 3D minimally invasive medical devices such as vascular or tracheal stents with complex geometry and shape-memory effect were shaped from methacrylated macromonomers (Figure 5C) [44] or methacrylated polycaprolactone precursor, respectively [46].

3. 4D Printing

4D-printing adds the fourth dimension of time, whereas the 3D-printed structure can change shape, functionality or properties over time once triggered by an external stimulus [11, 12]. Therefore, "smart materials" can be seen as those which provide a means of achieving stimuli-responsiveness into the resulting 3D object that would have otherwise been lacking. The latter is evident once the fabrication of self-assembling origami, where a 2D structure automatically folds into a complicated 3D component is considered [47, 48]. The development of active materials with desirable properties that are also compatible with printers is then crucial for steady advancements in 4D printing. Usually, a 4D-printed structure is created by combining several active materials in the appropriate distribution into a single, one-time printed structure [49]. At the core of this technology

lies a control over two key capabilities: the *material design* and the *structure design* relates to the transformation of the as-printed object due to the properties of the material and design geometric mechanisms respectively. These will be discussed in additional details in the following sections.

3.1. Structural Design

Designing the orientation and location of "smart materials" into 3D-printed objects can facilitate their structural changes in response to external stimuli. However, the change under these conditions does not always lead to increase their dimensionality - an anisotropy, i.e., inhomogeneity with different magnitudes towards any directions is therefore required to generate a transformation such as bending and twisting. Self-transforming materials could then be achieved either by applying gradients of field to homogeneous materials or by applying non-gradient stimuli to inhomogeneous materials [50]. While self-transforming objects using homogeneous materials is technically complicated, a force gradient must be formed and kept for a long period of time, inhomogeneous materials easily switching configurations thanks to the difference in strength of these constituting components. Herein, it is easily understandable that 3D printing technology is one of the most powerful tools to create complex 3D shapes with varied material distributions through spatial arrangement. Such a structuring approach can be categorized as *uniform distribution*, *gradient distribution* and *special patterns* (Figure 6).

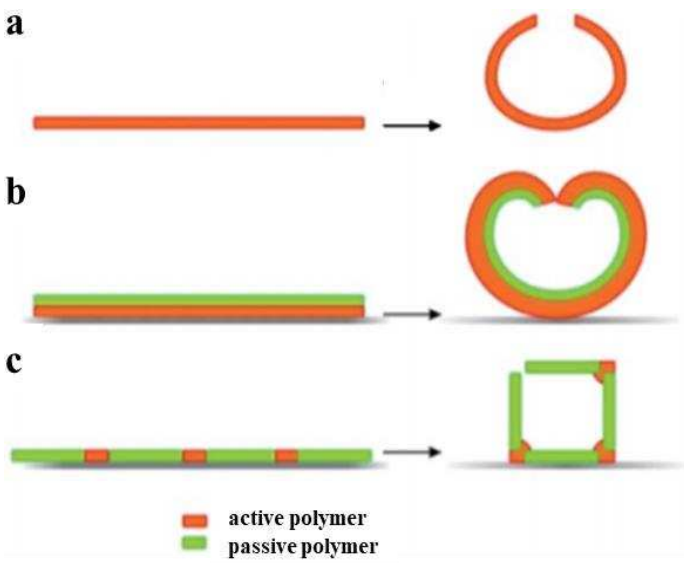


Figure 6. Approaches for structure design of self-transforming materials using uniform distribution (A), gradient distribution (B) and special patterns (C) [50].

3.1.1. Uniform Distribution

This approach is based on homogeneous active materials having directional anisotropy of properties [50]. Among them, shape-shifting materials are probably the most well-known 4D systems of this category having the ability to switch its geometric configuration from one to another in a fully controllable manner when exposed to an appropriate stimulus [51]. In this respect, *shape-changing* (or so-called actuation) should be distinguished from his *shape-memory* counterpart - the former spontaneously change its shape in response to an external stimulus and return to the original shape once the stimulus is turned off. On contrary, the shape-memory effect requires a programming step through deformation of the permanent shape and its fixation in a temporary one, which is retained, until an appropriate stimulus is applied (e.g., moisture, pH change and light) [52, 53]. The use of polymers with multi-responsiveness into a uniformly distributed printed structure therefore allowed the creation of original designs for self-transforming and multi-triggering materials. In this context, details about 4D-printed materials with respect to specific stimuli would be discussed hereafter - the authors kindly return the reader to the appropriate '*Material Design'* section.

3.1.2. Gradient Distribution

The gradient distribution of a single material means that the density of the structure is different at various locations. As a result, the material does not uniformly expand or shrink but folds and unfolds. Bilayers are probably the first structures with gradient distribution - one of the layers is passive, so its properties remain unchanged while the second layer is active and its volume or shape is changed when a stimulus is applied [50]. The proof of concept is demonstrated on the example of star-like patterned polycaprolactone/poly(*N*-isopropylacrylamide) bilayers, capable of controlled capture and release of cells upon heating (Figure 7A) [54]. Fabricating photolithographically patterned bilayer in all the three dimensions is therefore a straightforward way to design and fabricate actuators for repeated sensing in response to continuous environmental change. Several self-folding structures were accordingly created by employing the bilayer design [55-60]. The latter include thermo-responsive SMP/elastomer bilayer laminate in which the shape-change is actuated by the thermal mismatch strain between the two layers upon heating [61]. Likewise, the successful combination of FDM and SLA approaches for the manufacture of complex multi-material magnetic scaffolds in the form of coaxial and bilayer structures suitable for the regeneration of complex tissues were considered [62]. Lastly, Ge et al. investigated the designing variables that are crucial for creating laminate architecture by directly imprinting fibers of SMPs into an elastomeric matrix [48]. 3D-printed flat layered composite structures consisting of multiple active SMP fibers with different T_g in a rubbery matrix to control the transformation of the structure were further developed by Wu et al. (Figure 7B) [63]. Utilizing heat-shrinkable PLA strips, which are printed by FDM on a fixed sheet, Zhang et al. had fabricated smart

3D lightweight structures, whose initial bilayer microstructure can be switched between flat and 3D configuration under appropriate thermal stimuli [64, 65]. Inspired by Nature, Gladman et al. printed composite hydrogel bilayer architectures with programmable anisotropy controlled by the alignment of cellulose fibrils in a soft acrylamide matrix that morph into given target shapes on immersion in water [66].

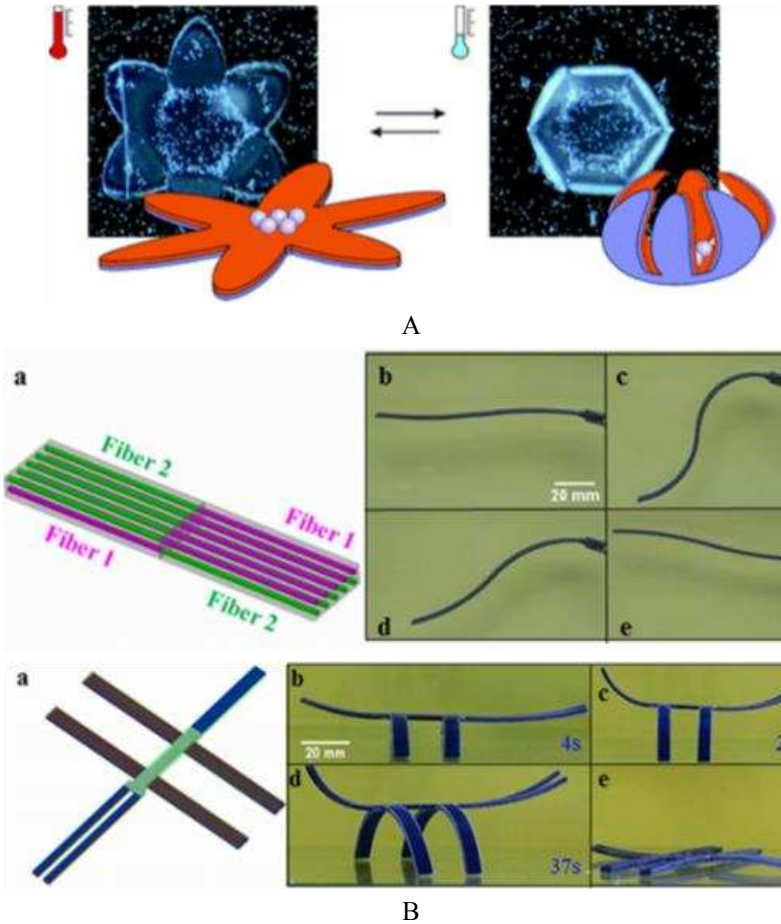


Figure 7. Thermoresponsive star-shaped self-folding capsules in the form of photocrosslinked bilayer (A) [54], and two-layer laminate designed leading to an active "wave" shape when heated or mimicking an insect when immerged in hot water (B) [63].

While the approach is very simple and could be one-step fabricated using a single material, the formed bilayer structures are, hinge-free, i.e., exclusively leading to rounded shapes during the folding. Such limitations pushed researchers to improve the ways to 3D print structural elements in an attempt to convey reliable and large curvature actuation, which is partially covered by gradient-structures or subsequently by special patterns. Usually, gradient materials consist of a layered structure wherein there is a varying layer composition along one axis. One example of such a structurally sound design is shown by

Tibbits et al. using thin surface disk with a gradient distribution of rigid material from the center point to a circumference with full expanding material to fold into otherwise unattainable designed structures depending on the duration of immersion in water (Figure 8) [67]. A method for producing gradient structures with extrusion-type 3D printing was later introduced by Giannatsis et al. following three main steps: (*i*) defining the geometry and material distribution of each layer in the form of a grayscale image, (*ii*) generating a set of points distributed according to the gray tone of the image and (*iii*) constructing a continuous path through the points for guiding material deposition by the 3D printer [68]. Unlike bilayer materials, gradient materials have a continuous change of composition and microstructure along one direction, which helps with avoiding problematic sharp interfaces between discrete layers, a common cause of failure in many engineered parts [69]. Photolithography is a common technique to crosslink and thus permanently preserve a gradient structure. SLA should then outmatch other AM techniques with respect to the fabrication of gradient-structured materials, whereas the time of exposure and the crosslinking density would govern the direction of the gradient.

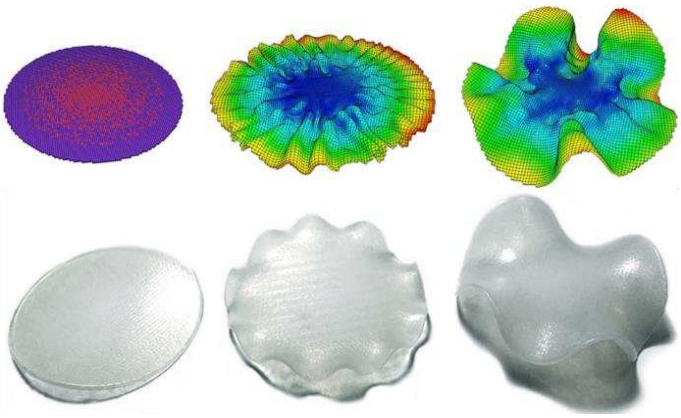
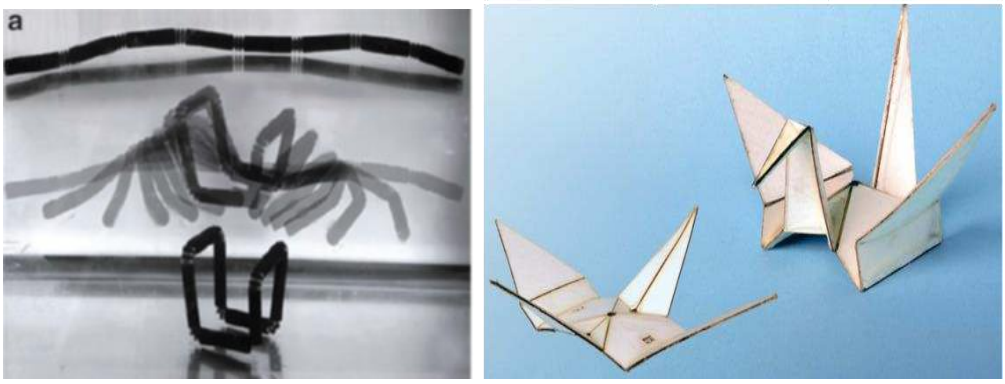


Figure 8. Gradient-structured material and the results of its immersion in water over time [67].

3.1.3. Special Patterns

The approach is based on the use of patterned components of the passive polymer with insertion of an active one. The object's transformation thereby depends on the collective action of those building blocks. For instance, Tibbits et al. combined rigid plastic and active expandable polymer materials in various spatial arrangements in their experiments - the rigid material gives the structure and angle limits for folding while the active material swells after encountering water, forcing the rigid material to bend in its final-state 3D configuration (Figure 9A) [8, 9, 67, 70]. Embedding certain targeted smart hinges inside the structure thereby enable reliable self-transforming behavior. Ge et al. designed self-evolving structures that can be programmed to sense the environment and actively self-deform when exposed to water [47] or even thermomechanically programmed to get complex 3D configurations [48]. Using different combinations of

flexible hinges and rigid segments of metal and polymer thin films, Bassik et al. successfully constructed complex and highly-defined 3D patterned structures [71]. Fabricating such designs is however technically complicated as it might require mask alignment during several steps of photolithography but it also allows fabrication of the broadest range of self-folding structures [72]. Even so, origami-inspired self-folding structures have been recently designed and reviewed by Peraza-Hernandez et al. [73]. Among them, Santangelo et al. focused on understanding the mechanics in which an origami structure can be designed to fold [74]. Kwok et al. presented a design optimization framework for using AM to fabricate flat origami structures that can be self-folded into a target 3D shape [75]. Felton, Tolley et al. conjointly developed a novel method of self-folding hinges and models to rapidly fabricate origami using shape-memory composites and predict the final geometry of the folding state and the overall folding torque (Figure 9B) [76, 77]. A model was also successfully used to predict the bending characteristics, e.g., bending curvature and bending angle, of a series of 3D-printed hydrogel-based inks capable of reversible shape deformation in response to hydration and temperature [78].



A B

Figure 9. 4D-printed special patterns made of rigid plastic and active expandable polymer materials which expands when exposed to water (A) [9], and origami-inspired self-folding structure using current as a stimulus (trought the related heating Joule effect) (B) [76].

While such structural designs have not been yet fully exploited through solid freeform fabrication technology due to the difficulty of implementing multiple materials in a single geometry, SLA has probably been the primary technology focus on creating multi-material structures [79]. Although this technique would not typically be considered a strong candidate for using multiple materials, as it would require the management of possible contamination between multiple viscous resins, it still offers the highest resolution and accuracy with a variety of materials options and easy access to the building chamber. Strategies for building multi-material structures were then conceived to have finally been the focus of recent researches [80-83]. During these developments,

others 3D printing techniques such as direct inks writing or even hybrid manufacturing systems were exploited to build multi-material parts [84, 85]. They are myriad issues, ranging from the processing of different materials to the combined performance of the materials in the final object, that are still challenging with the building of multiple materials in AM but it probably offers novel ways to fabricate, assemble, and morph structures in the right spatial arrangement.

3.2. Material Design

Designing novel active materials having configuration-changing abilities given environmental conditions has been widely used in 4D printing. Shape-morphing is probably one of its main descendant, allowing for a global deformation, which can stretch, fold and bend given environmental/external changes. Stimuli-wise, 4D printing can be categorized as induced by temperature, humidity, pH, light or magnetism [86].

3.2.1. Temperature

An advantageous activation method for 4D printing is the use of heat to trigger the "smart material" for shape-change purposes. So far, the most extensively investigated group of thermo-responsive materials are SMPs, which can revert its shape from a temporary to a permanent one by absorbing thermal energy. In this respect, Choong et al. used a thermally responsive network based on a dual-component phase switching mechanism to build parts of complex geometries having shape-memory behavior using SLA technology (Figure 10A) [87]. In additional research, SMPs fibers were precisely printed into an elastomeric matrix by Ge et al. in order to create an active composite capable of origami folding patterns [47, 48]. Other examples by Ge et al. included the use of a family of photo-curable methacrylate based copolymer networks to demonstrate a new 4D-printing approach that can create high resolution multi-material SMP architectures (Figure 10B) [88]. Liu et al. used 3D-printed thermally responsive SMPs to create actively deployable tensegrities that respond to environmental stimuli in a sequential fashion [89]. Mao et al. also created sequential self-folding structures by 3D-printing hinges with different digital SMPs into components [90]. The latter rapidly self-folds to specified shapes in controlled changing sequences when subjected to a uniform temperature. Multi-shape active composites consisting of families of SMP fibers with different T_g were printed by Wu et al. to control the transformation of the structure [91]. As a result, after being programmed into a temporary shape by a simple thermal-mechanical training program, the printed composite is able to change into multiple geometries and then recover the flat permanent state when stimulated by temperature. Conventional thermo-responsive SMPs can also result in heat-shrinkage. In this respect, Zhang et al. exploited uniform internal strain stored in printed material to fabricate heat-shrinkable polymer, which possesses controllable thermo-structural response and spontaneous pattern transformation under heating [64, 65]. Adaptive structures capable of

self-expanding and self-shrinking by means of four-dimensional printing technology were further developed by Bodaghi et al. [92]. Bakarich et al. here described relatively fast and reversible skeletal muscle-like linear actuation in 3D-printed hydrogels that are both mechanically robust and thermally actuated for their incorporation into a smart valve [93]. To that purpose, they used a thermally responsive covalent crosslinked network of poly(*N*-isopropylacrylamide) to function as both - the toughening agent and the provider of actuation through reversible volume transitions.

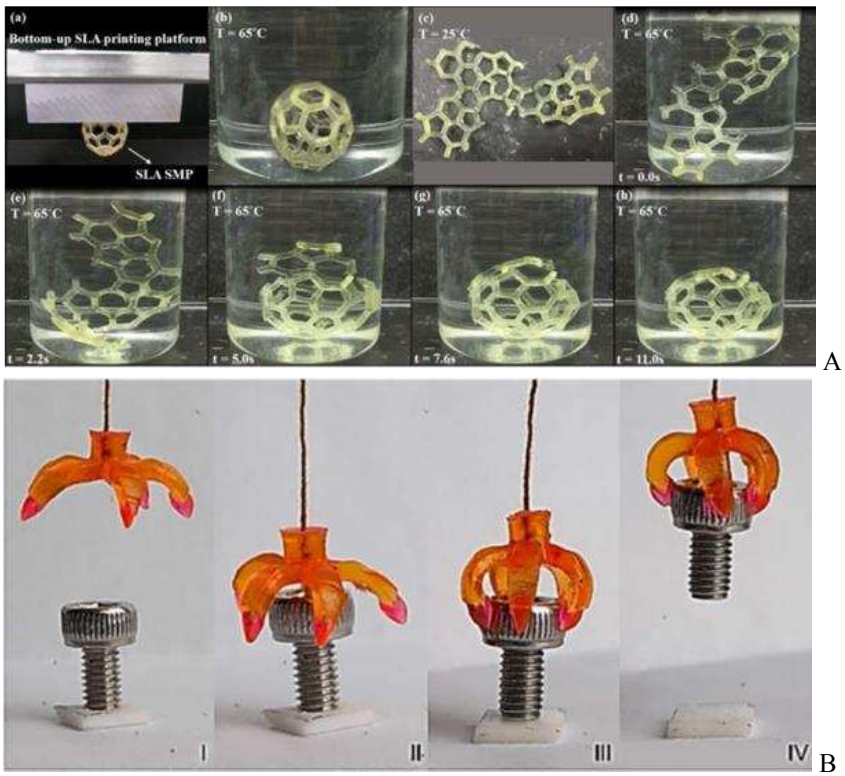
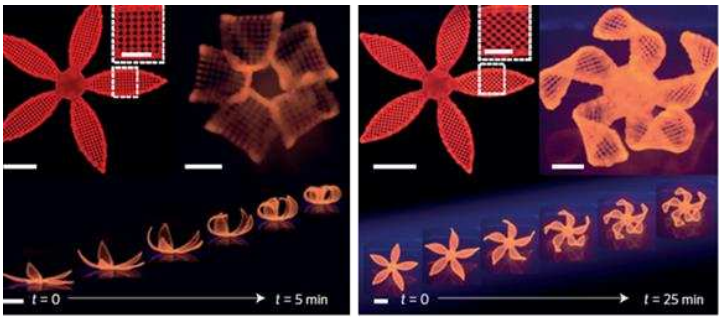


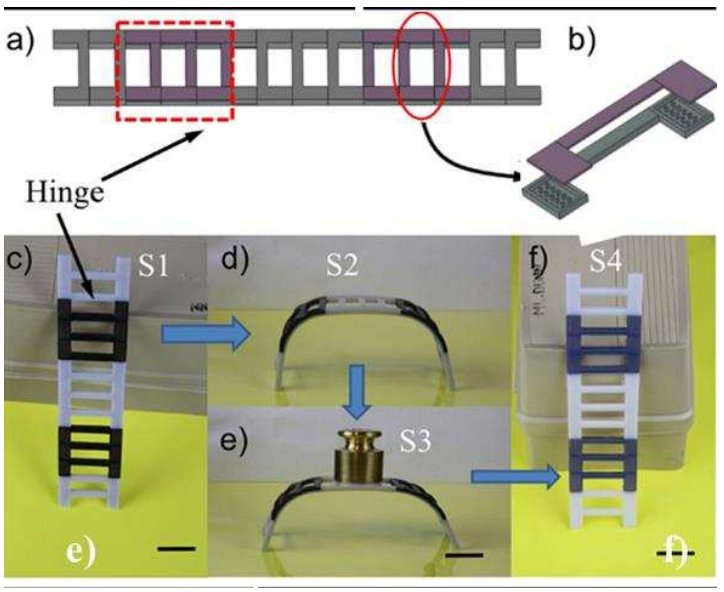
Figure 10. Folding/unfolding cycle for 4D-printed thermally-responsive buckminsterfullerene SMP (A) [87] and SMP gripper that reversibly grabes and releases the objects (B) [88].

3.2.2. Humidity

Hydrogels that swell when solvent molecules diffuse into polymer network is probably the second mainly used system to realize 4D-printing. Tibbits et al. described 3D-printed "smart materials" that expand to induce the transformation when exposed to moisture [8, 9, 67, 70]. His group even controlled the bending angle and direction of the expanding materials by placing rigid components in select areas that prevent the hygroscopic material from expanding in unintended directions. For instance, Tibbits et al. addressed the challenge of designing active printed materials for complex self-evolving deformations by utilizing hydrophilic materials that expand when submerged in water to



A



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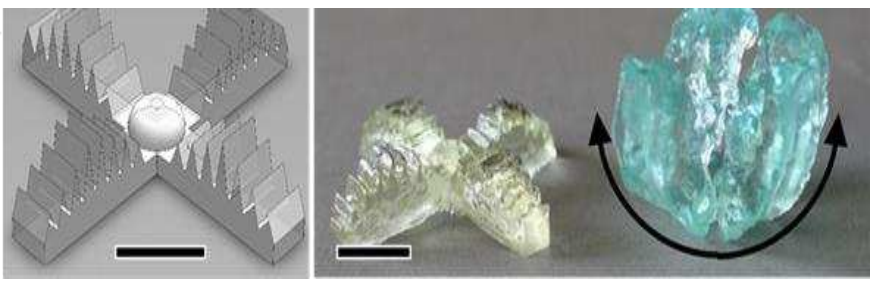

C

Figure 11. Complex flower morphologies generated by printing bilayers architectures that morph into given target shapes on immersion in water (A) [66], exemple of active ladder capable of two-way actuation upon the swelling of hydrogel hinges and the heating of SMP hinges (B) [95] and ionic hydrogel composite-based multi-armed gripper, as designed, and printed to rapidly swell from initially flat and open to curved and enclosed when immerged in water (C) [97].

induce various programmed shape changes [70]. Inspired by biomimetics, Gladman et al. created a 4D printing system composed of stiff cellulose fibrils embedded in a soft acrylamide hydrogel ink to programmably fabricate plant-inspired architectures that change shape on immersion in water (Figure 11A) [66]. Huang et al. recently reported ultrafast digital printing of multi-dimensional responsive polymers including hydrogels and SMPs having variable degree of monomer conversion and cross-linking density [94]. In essence, the subsequent immersion in water induced differential swelling in the pixelated polymer networks, turning the 2D polymer films into a 3D object. Active materials capable of two-way actuation were further demonstrated by Mao et al. upon the combination of SMPs and hydrogels in 3D-printed architectures [95]. This approach used the swelling of a hydrogel for the shape change and the temperature-dependent modulus of a SMP to drive the shape-change in a prescribe way (Figure 11B). Duigou et al. used the hygroscopicity of natural wood fibres for the production of original self-bending devices that actuate in a moisture gradient [96]. By controlling the orientation of particles in materials during printing using an external magnetic force, Kokkinis et al. managed to align fused silica particles into the materials to fabricate shape-changing objects [84]. Finally, Odent et al. demonstrated novel 3D-printed ionic composite hydrogels that allowed for fast diffusive swelling for practical implantation of large osmotically driven actuators [97].

3.2.3. Other Stimuli-Responsiveness

While the most common activation method for 4D-printing utilizes temperature and water to trigger shape change, other stimuli such as pH, light and magnetism, although still poorly exploited, have been recently considered in 4D-printing and present new opportunities for designing smart devices. For instance, Nadgorny et al. 3D-printed poly(2-vinylpyridine) objects that exhibited dynamic and reversible pH-dependent swelling. The printed hydrogels also acted as flow-regulating valves, controlling the flow rate depending on the pH [98]. The key to their formulation is the pyridine chemistry combined to a post-printing functionalization approach, which provide a fine-tuning of the degree of swelling by a precise choice of quaternizing reagents and their stoichiometry. Focusing on materials that could be reconfigured multiple times into different shapes with the use of different stimuli, Kuksenok et al. designed a composite that integrates functionalized photo-responsive fibers with thermo-responsive gels [99]. In particular, the single composite can display multiple functionalities as the application of light and heat produces distinctly different responses in these gel-fiber composites. In a new investigation, the sequential folding behavior of polystyrene sheets using the degree of transparency of line pattern was studied by Liu et al. as well as Lee et al. for their use in the design and manufacture of self-folding origami structures [100, 101]. This approach to self-folding then employed localized absorption of light on an otherwise compositionally homogeneous substrate into a hinging response (Figure 12A). Finally,

and in order to ensure optimal part design for potential magnetic applications, Bollig et al. investigated the effects of common 3D-printed structural features on the magnetic properties of the final printed object constructed from a magnetic iron-thermoplastic composite [102]. Magnetic iron oxide III nanoparticles were further employed by Ji et al. to develop digital light processing 3D printing resin, which enabled the free-assembly manufacturing of soft actuators with complex architectures [103]. As proof of concept, a flexible gripper allowing for remote control of gripping and transferring cargo in the presence of magnetic field was demonstrated.

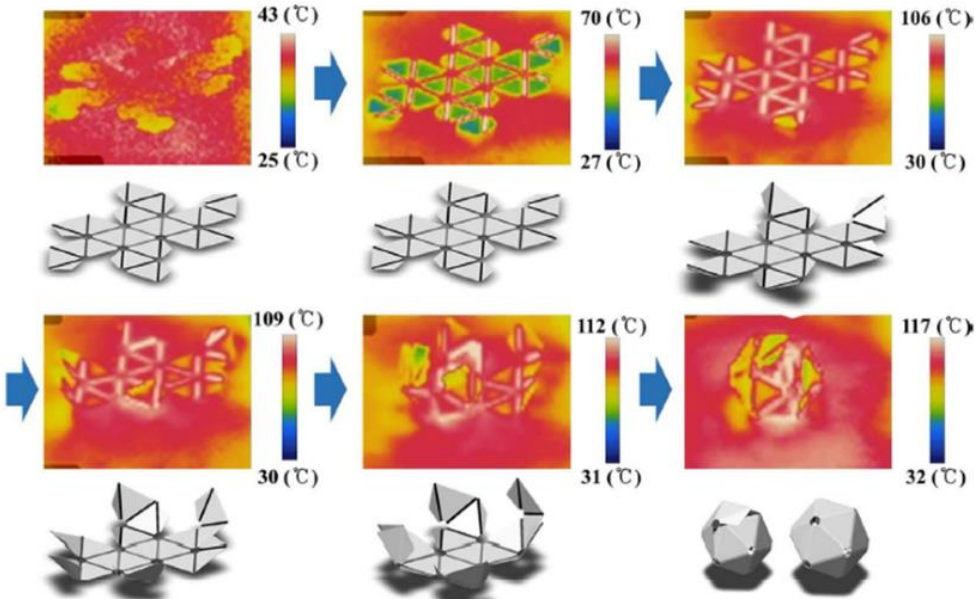

Figure 12. Icosahedral shape deformation of polystyrene sheets using sequential folding behavior (A) [101].

PERSPECTIVES AND CONCLUSION

Over the last years, 3D printing technology has been leading a revolution in the materials science research and manufacturing in term of object design with complex geometry and composition, as well as the fabrication of smart polymer systems with astonishing properties and rapid prototyping. Based on the technological progress, it is now possible to combine different methods such as FDM or SLA with the goal of achieving unique material properties and functionalities. Despite the great advantages of the here listed approaches and the promising application of the produced devices, major challenges in the 3D prototyping are still remaining:

FDM Challenges

1) Except for the commercially available polymer filaments based on PLA, ABS, PET and others, the production of new polymer (or composite) filaments is challenging due to the relatively low quantity of the synthesized polymers and the homogeneous dispersion of the nanofillers. In addition to this, new demands on the reactive extrusion processing were defined such as: facilities for filaments fabrication with precise diameter (1.75 mm), their collecting during the cooling step and eventual surface coating.
2) FDM faces some problems regarding the large-scale fabrication of mechanically robust 3D-printed parts along with some difficulties related to the slow speed and single material printing. New trend in this aspect is the manufacturing of 3D printers with multiple nozzles while filaments with different composition are used.
3) As discussed in this chapter, the problem with the anisotropic mechanical properties of the printed parts needs quick solutions. A potential solution is a post treatment of the surface (plasma, coating, solvent vapor exposure). The materials' surface morphology (roughness and distance between the deposited filaments) affecting directly the device properties can be additionally controlled by the use of printing nozzles with different diameter: the smaller is the diameter, the greater should be the resolution of process. Another set of challenges with an effect on the multi-axial mechanical loads of FDM printed parts are the presence of residual stress (warping and delamination of the printed components when an appropriate post processing steps are not taken) and dimensional errors (the parts are no longer meeting the dimensional specifications).

SLA Challenges

1) Despite the possibility to produce polymer devices by SLA from a great range of photo-sensible polymers, initiators and cross-linking agents, one main limitation of this technique is related to the poor mechanical properties of the final parts. Therefore, the major obstacle here would concern the reinforcement of the materials *via* incorporation of nanofillers or additional generation of supramolecular structures. This imposes the development of new types of liquid resins and photo-sensitive low molecular weight polymers suitable for SLA with desired functionalities to fit specific applications.
2) Even if the resolution of the SLA technique is superior to the one of the FDM (100 nm compared to 0.1 mm, respectively), the main way to prepare the monomers is in solution. This restricts the fabrication to soft materials, limiting

the exploration of new horizons for thermoplastic polymers (mostly soluble in organic solvents). A possible solution could be found in more complex solvent mixtures, but the risk of the printer damaging (solvent vapors) and the question of work security are unsolved.

3) Today as part of the AM techniques, 4D-printing has several unique advantages over 3D-printing that may lead to widespread implementation. Depending on the potential application dual-, triple- or multi-responsive materials can be designed. The main difficulty in this field is the speed and degree of responsiveness of the "smart materials". Some of them can sense stimulus but only provide minimal actuation or only respond after a very long time.

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