Future of Additive Manufacturing: Overview of 4D and 3D Printed Smart and Advanced Materials and their Applications

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Abstract

4D printing is an emerging field in additive manufacturing of time responsive programmable materials. The combination of 3D printing technologies with materials that can transform and possess shape memory and self-healing capabilities means the potential to manufacture dynamic structures readily for a myriad of applications. The benefits of using multifunctional materials in 4D printing create opportunities for solutions in demanding environments including outer space, and extreme weather conditions where human intervention is not possible. The current progress of 4D Printable smart materials and their stimuli-responsive capabilities are overviewed in this paper, including the discussion of shape-memory materials, metamaterials, and self-healing materials and their responses to thermal, pH, moisture, light, magnetic and electrical exposures. Potential applications of such systems have been explored to include advancements in health monitoring, electrical devices, deployable structures, soft robotics and tuneable metamaterials.

1.0 Introduction

Additive manufacturing (AM) or 3D printing allows one to fabricate structures with complex geometries that cannot be achieved through traditional methods.[1] Over recent years, 3D printing has moved towards printing functional components that can be used in a variety of applications including electronics[2] [3], electrochemistry & energy storage[4] [5], catalysts[6], thermal management[7], aerospace[8], healthcare monitoring[9] [10] [11], food industry[12], sensors and robotics[13],[14], with custom parts being draw easily using computer-aided design (CAD). Conventional 3D printing technologies include stereolithography (SLA)[15], fuse deposition modelling (FDM)[16] [17] filament extrusion-based system, selective laser sintering (SLS)[18] laser sintered powder materials, direct ink writing (DIW)[19] extruded colloidal suspension and ink-jet printing[20] [21] deposition of droplets of material. Generally, 3D printing produces parts with restricted functionalities limiting their final applications.[22] [23] However, the addition of functional fillers dispersed within a polymer matrix can provide a solution for manufacturing multi-functional parts that are mechanically robust with superior chemical, electrical and thermal properties. Such fillers include 2D materials graphene[24], Graphene Oxide (GO)[25], Boron Nitride (BN)[26], Molybdenum Disulfide (MoS_2)[27], Black Phosphorous (BP)[28], Mxenes[29], etc.[30] [31] [32] [33]

The emergence of smart materials or programmable materials that can transform through external stimuli offers an exciting new opportunity for 3D printing technologies. This combination has led to the new field known as 4D printing, the fourth dimension referring to time. This technology was first introduced by Skylar Tibbit in collaboration with Stratasys™ as a printed material that is programmed to change over time in response to an external stimulus.[34] [35] Although many reports on 4D printing are focused on the use of printing with smart materials, 4D printing can also be accomplished with the use of ‘general’ materials. These materials can transform over time due to predefined stresses created during the printing process generated by the chemical reactions and resin diffusion between the printed layers.[36][37] Smart materials require environmental changes such as moisture and heat for transformations, this environment can have a detrimental effect on some applications such as electronics. Therefore, controllable folding with engineered stresses at multiple positions can offer an alternative to achieve transformations without the use of smart materials.[36]

Smart materials are materials that respond to changes to their environment and as a result, go through a material property change. Smart materials include shape-memory materials and self-healing materials. Metamaterials are an interesting class of materials that appear as smart material from their complex carefully created structural design however, the material properties itself are not responsive more so the structural arrangement. These self-transforming materials respond overtime to assemble into new compositions via twisting, bending, shrinking and spreading. They respond to external stimuli including temperature changes, water, pH, UV radiation, electrical and magnetic fields. The dynamic functions of smart materials coupled with the complex geometries of 3D printed parts can be used in a variety of applications including soft robotics, self-folding packaging, biomedical applications, smart textiles, deployable structures, sensors and aerospace applications. This paper overviews the stimulus responses and applications of functional and smart materials for 4D printing applications (Figure 1).

The printing technologies used in 4D printing are the same as 3D printing as the fourth dimension refers to the nature of the materials printed rather than the technology. 4D printable inks usually consist of monomers, initiators, fillers and binders. Each ink formulation is required to meet the physical and chemical demands of the AM technology including photo and thermal sensitivities, operational rheological properties, contact angles and surface tension restrictions.[38] To date, the majority of reports on 4D printing has focused around using SLA, FDM and DIW technologies.[39] [40] [41] [42] [43] [44] [45] However, there have been significant strides with using SLM and ink-jet printing to manufacture dynamic materials that respond to external stimuli.[46] [47]

2.0 Smart & Complex Materials for 4D Printing

For printed parts to be considered 4D printed, the component is required to adapt and change over time. These classes of materials are known as smart materials and can be further divided into the subgroups including shape-memory materials (SMM) thermodynamic changes, self-healing materials supramolecular changes and metamaterials engineered changes.

2.1 Shape Memory Materials (SMM)

Shape memory materials are smart materials that can morph and transform shape over time as a response to an external stimulus. Shape memory materials include shape memory polymers (SMPs), shape memory alloys (SMAs), shape memory ceramics (SMCrs), shape memory composites (SMCs) and shape memory hybrids (SMHs). SMPs respond through physical and chemical cross-links related to temperature transitions such as glass transition temperature T_g and melting temperature T_m. The materials are often processed and shaped at temperatures above their T_g creating their 'original shape', the parts are then cooled down to below their T_g where their shape is deformed and fixed into position.[48] In the case of SMAs, the shape memory effect is related to the two crystal structures present in the alloys the martensite phase (low temperatures) and austenite phase (high temperatures). The SMA is deformed in the martensite phase then as the temperature increases to the austenite phase the structure recovers back to its original shape. Similar to SMAs shape memory ceramics SMCrs exhibit either superelasticity with the ability to deform to large strains and recover, or exhibit the shape memory effect where they can transform between states that have been predefined with the aid of an external stimulus.[49] Some brittle ceramics go through martensitic transformations and therefore can experience shape memory effects similar to that of SMAs, however one of the main concerns with SMCrs in their brittle nature that can lead to large amounts of cracking.

Beyond the commonly used SMMs, SMPs SMAs and SMCrs, are shape memory hybrids and composites (SMHs, SMCs). Here, shape-memory composites refer to a multiphase material that can include a filler and matrix phase and are combined at the macro level. Whilst shape memory hybrids refer to two materials combined at the molecular or nanometre level. The transformations exhibited by SMHs and SMCs are related to the material component that has the ability for shape memory, for example, an SMA wire used in a polymer matrix would go through martensitic changes whilst an SMH with different polymer phases would go through physical and chemical cross-links related to temperature transitions.

SMM is constantly in a metastable state switching

from a temporary state to a stable one.[50] This switching behaviour can also be induced by exposures to changes in electromagnetic radiation[51], moisture[52], pH levels[53] and electrical[54] and magnetic fields[55].

2.1.1 Shape Memory Polymers (SMPs)

Shape memory polymers are ideal for 4D printing applications, as they possess versatile processing abilities required for a range of AM technologies. Polymers that display elastic behaviours are particularly suited to the manipulations of geometries involved in 4D printing.

They can withstand large amounts of deformation strain over a range of temperatures, for radical and impressive transformations. [56] Polymeric materials are often used in AM due to their excellent processing capabilities, providing a smooth transition into 4D printing applications. SMPs can be easily tuned to their environments/applications by controlling the crystalline content of the polymer, which can be used to programme transition temperatures such as the T_g and T_m.[57] [58]

Ge *et al.* developed a multi-material system to print shape-memory polymers using micro-stereolithography. The inks were made up of methacrylate-based monomers, photoinitiator Phenylbis(2,4,6-trimethyl benzoyl)phosphine oxide (BAPO), Sudan I (0.05 wt. %) and Rhodamine B (1 wt. %).[59] The percentage of PEGDMA, BPA, DEGMA and BMA were refined to tailor the T_g's to control fixity at 43 °C and 56 °C. This allowed the bloom motion of the printed flower to occur by heating above the T_g's in two phases (

Figure ***2*** (i)). However, SLA resins and photopolymers tend to have high cross-link density, which means that they are more brittle. [60] This can be a challenge when designing 4D printable inks for SLA. One method to maximise the degree of shape change is by 3D printing shape-changing materials in strips or fibres that run through the polymer.[46] This enables control of the morphing properties and reduces the amount of SMM used. Wu *et al.* demonstrated this by using fibre-like regions made up alternating sheets of PNIPAm/PAMPS (Figure 2 (ii)).[61] PAMPS being the responsive material with shape-changing capabilities and PNIPAm the unresponsive material, both of which were manufactured using photopatterning. Another technique to improve the degree of transformation is by 4D printing meshes to allow large degrees of freedom to morph and close without putting large amounts of strain on the printed component. Gladman *et al.* demonstrated this using an SMP poly (N-isopropyl acrylamide).[43] In this work, the printed flower closes due to swelling from water exposure. The flowers were printed in a mesh formation based on a simple curved surface angled at 0° and 90° fabricated using DIW (

Figure *2* (iii)). Sun *et al.* developed a shape memory hybrid filament for FDM printing, the filament consisted of PLA and PEG acting as a plasticiser.[62] The shape memory effect was achieved through thermal transitions (T_g), the temperature of which could be altered by varying the plasticiser content. The group printed functionally graded layers with localised recovery by varying the percentage of plasticiser in each layer producing multi-shape actuators.

Recent reports of cross-linked liquid crystalline polymers (LCPs) and liquid crystal elastomers (LCE) describe the 4D printing of actuators and soft-robotics using DIW.[63] [64] LCE's are anisotropic and are controlled by their molecular orientation that is tuned upon different temperatures.[65] They have remarkable shape orientations and can be programmed to form cones, paraboloids and even origami folds.[66] The mechanical responses of LCE's are triggered by heat, light and electrical fields. The motion of LCE's is controlled by the orientation and organisation of the rigid molecules called mesogens and can be tuned upon different temperatures. The LCE transforms from an ordered state (anisotropic properties) to a disordered one (isotropic properties) at a transition temperature known as the isotropic transition temperature (T_i or T_m).[67] Lopez-Valdeolivas *et al.* printed thermo-actuators using LCE's and extrusion-based printer. In this case, the extrusion process aligned the polymer chains building up orientational order of the mesogens in the direction of the printers moving needle. Replacing the traditional methods of using heat to orientate the mesogens in LCE's through the T_i. They reported a 50 % contraction of their printed parts when heated to 90 °C and a rapid recovery back to their original length on cooling.[68] A key advantage of using LCE's is their rapid recovery rates that are not seen in the swelling of hydrogels. Yang *et al.* used IR light (808 nm) in the fabrication, repair and assembling of CNT and xLCEs for soft robotic actuators in low-temperature environments.[69] The xLCE can be used to self-heal micro-cracks through photo healing and is recyclable for long and efficient life cycle of the material. The CNT-xLCE's were manufactured through transesterification at temperatures above 180 °C.

So far, many of the SMPs mentioned have been thermoplastic as they can recover their shape through temperature transition involving the glass transition temperature (T_g) and melting temperature (T_m) that creates the transformations observed in 4D printing. Thermoplastics have good recyclability whilst maintaining their network integrity, however, are not as robust as thermoset plastics. The strong chemical covalent cross-links of thermosets permit their applications in demanding environments because of their excellent chemical and thermal stabilities. Where human interactions are required but not possible due to extreme and harsh environments, it would be advantageous for the production of self-actuating robotic systems that are chemically and thermally stable. Typically, this would mean thermosets are chosen for the desired application, however, a class of polymers known as Vitrimers have been developed which behave like thermosets at ambient temperatures however at raised temperatures the polymer goes through dynamic exchanges of its cross-links. [70] Vitrimer polymers come under the umbrella term of LCEs and are used to create shape memory polymers with morphing structures. [65] Vitrimers are recyclable and can transform and morph similar to thermoplastics, however, maintain the robustness of a thermoset for engineering applications in aerospace, automotive industry and electronics.[71] [72] Jin *et al.* designed a soft robotic made from a programmable crystalline shape memory polymer Vitrimer (Figure 3 (i)).[73] The SMP displayed both thermal and photo-reversible bonds for actuation and morphing applications. The designs were fabricated using a photo-masked pattern producing regions with morphing abilities. Shi *et al.* reported on a Vitrimer epoxy that could be recycled and printed using DIW up to four cycles which is a promising outlook for the development of sustainable and reusable materials in 4D printing.[74]

There have been reports of the use of SMPs in the form of hydrogels for 4D printing applications, here a hydrogel classified as a network of polymer chains that are hydrophilic which allow them to hold large amounts of water in their 3D network.[75] Hydrogels have been widely used in 4D printing applications due to their excellent processing abilities and their capacity to change volume as a response to their environment. Many reports have described their applications in DIW and SLA technologies for a whole host of applications from biomedical applications through to electronic devices. They are particularly good for 4D printing applications as they can respond to changes in temperature, moisture and pH to accommodate large amounts of swelling for hinged mechanisms and switches.

However, the main drawback of using hydrogels in 4D printing applications is the slow processing times for reversing back into the original shape usually *via* drying and heating and cooling approaches. Bakarich *et al.* demonstrated the use of alginate and poly (N-isopropyl acrylamide) IPN for thermally responsive actuators to control water flow. The extrusion printed actuators displayed a reversible length change of 41 % - 49 %.[76] Another approach of using hydrogels in 4D printing is through multi-material printing. Here, one polymer is printed for structural purposes while a second polymer is printed for responsive purposes i.e. swelling hinges. The two inks can be printed simultaneously to manufacture foldable structures. This has been demonstrated by Naficy *et al.* where poly (*N*-isopropyl acrylamide) (poly (NIPAM)) was used as the thermo-sensitive components and poly (2-hydroxyethyl methacrylate) (poly (HEMA)) was used as a structural component. Poly(NIPAM) was used to print hinges that would swell above 32 °C causing the part to contract and close (Figure 3 (ii)).[77] Hu *et al.* developed a 4D printable hydrogel that responded to changes in pH and was used to print structures that could morph to encapsulate a secondary component for drug delivery applications (Figure 4 (i)). [78]

Table 1 provides an overview of responsive 4D printed smart materials and their associated technologies and applications. Although these materials are commonly referred to as 4D printing, metamaterials and self-healing materials also can adapt and change over time using different techniques which will now be discussed.

2.1.2 Shape Memory Alloys (SMAs)

Shape memory alloys have been around for many years, a Swedish metallurgist first reported SMAs back in 1932, where they found their gold-cadmium alloy displayed a rubber-like behaviour now known as pseudo-elasticity. [79] SMAs are metallic alloys that go through solid-to-solid phase transformation.[80] The key mechanisms of shape memory alloys are associated with phase changes from the austenite or high-temperature phase to the martensite or low-temperature phase, resulting in macro-scale effect due to changes in the crystallographic structure of the alloy.[81] Many of the reports on shape memory alloys discuss the additive manufacture of Ni-Ti, Ti-Ni-Cu, Cu-Al-Ni, Fe-Mn-Al-Ni alloys using SLS and SLM. [82] [83] [84][85] SMAs are usually associated with SLS and SLM techniques as traditionally these methods of 3D printing are particularly good and printing metallic structures at high loadings with good strength properties. Akbari *et al.* used ink-jet printing to fabricate an SMA gripper that responded through joule heating *via* an electric current (Figure 4 (ii)). [86] The group printed and embedded a nickel-titanium alloy wire (diameter 0.25 mm) in a 'soft' matrix that contained hard phases for the dynamic movement of the griper without causing breakage. Umedachi *et al.* designed and printed a bioinspired soft robotic structure they named Softworm (Figure 5 (i-ii))[87] The movement of the Softworm was created via resistive heating to the

SMA when a current was applied; the temperature-induced changes in linear wire stain are transformed to large displacements, mimicking muscle tetanus of worms.[88] The body of the worm-like design was printed using a polyjet printer (Objet, Connex 500), an SMA coil (BMX-100, Toki Corp. Tokyo, Japan) was then threaded through the design to act like tendons that actuated. Caputo *et al.* 4D printed Ni-Mn-Ga magnetic shape memory alloys using powder bed binder jetting.[89] In general, binder jetting manufactures parts with high porosities that can be controlled through particle size distribution and packing densities, here Caputo *et al.* reported porosities as high as 70.43 % for the SMA. Thermo-magneto mechanically programmed materials that displayed reversible martensitic phase changes during heating and cooling processes controlled the shape memory effect reported.

Dadbakhsh *et al.* 4D printed NiTi shape memory alloys using the 4D printing technique SLM. The group investigated the effects of changing the laser's power and speed during printing on the properties of the alloys. It was concluded that when printing at high power and speed the alloy had improved overall strength and an increased pseudoelastic behaviour due to austenite present at room temperatures. Whereas the SMA printed at low, power and speeds displayed martensitic phases.[90] 4D printing of $Ni_{50.1}Ti_{49.9}$ SMAs using SLM was also reported by Andani *et al.* In their work they studied the mechanical and shape memory effects when the porosity and density of the alloys were adjusted. Andani *et al.* found that the more dense alloys had a higher elastic modulus and higher transformation temperatures (an increase of 10-14 °C) than the porous alloys. The SMA went through cyclic compression tests and showed a 5 % recoverable strain and partial recovery of the superelastic response. The porous alloys displayed a decrease in the elastic modulus by 86 % whilst retaining shape memory effects, showing that these lightweight 4D printed structures could be used as biomedical implants such as bone constructs.[91]

Applications of SMAs include temperature-controlled systems (opening valves), actuators, biomedicine (active implants), soft actuators and aerospace.[92,93] A key advantage in SMAs over the use of many SMPs is their enhanced thermal and mechanical properties allowing them to be utilised in demanding environments.

2.1.3 Shape Memory Ceramics (SMCrs)

Although mainly SMPs and SMAs are used for morphing properties and self-healing polymers are used for healing mechanisms in 4D printing applications. There have been some reports in the literature on more uncommon material selections including shape memory ceramics (SMCrs). Typically, ceramics are thought to be brittle and unable to bend, stretch, and deform without causing catastrophic damage. However, Lai *et al.* achieved this by modifying the ceramic polycrystalline zirconia with ceria or yttria the results of which could withstand strains over 7 % and cycled up to 50 times.[49] Zhang *et al.* developed a self-healing shape memory ceramic using yttria-stabilised tetragonal zirconia (YSTZ) nanopillars.[94] Liu *et al.* used a combination of 40 wt. % ZrO_2 nano-platelets dispersed within a PDMS resin to create an elastomeric derived ceramic EDC (Figure 5 (iii-vi)). They then threaded either an iron or copper wire through the DIW printed lattice to assist in the folding of their origami structures for 4D printing effect. The printed EDC structures then went through heat processes and chemical etching to remove the wires and leave a ceramic component.[95] The applications of SMCrs has the potential to become a desirable field for high-temperature actuators and robotics for space exploration and high temperature micro-electrical mechanical systems.

2.2 Metamaterials

Metamaterials were first introduced by Victor Veselago in 1968, they are engineered materials that can attain properties that are not usually found in natural materials, appearing as smart materials.[96] 3D printing can be used to manufacture metamaterials with curved structures and patterns that can display unique electromagnetic properties and functionalities.[97] [98] Metamaterials are based on arrays of specially designed individual unit cells to perform a function that is not intrinsic to the material. Because of this, these unit cells tend to be complex and intricate meaning high resolutions are needed to achieve such fine details.[99] [100] This can be a challenge for many AM technologies especially as most operate between 200-50 µm, and some metamaterial features may only function in the nm range. However, recently there have been advancements in micro-stereolithography with resolutions as high as 40 nm.[101] The main applications of metamaterials include sensors, absorbers, acoustic cloaks and antennas. AM can fabricate complex designs that cannot be achieved through traditional manufacturing methods this coupled with advancements in AM technologies improving resolutions means the realisation of complex metamaterials is a very realistic goal in near the future.[99]

Qiao *et al.* demonstrated the 3D printing of a nylon-based metamaterial using SLS, to produce lenses with meta-surface reflectors.[102]Wagner *et al.* reported on their auxetic metamaterial design to 4D print thermo-responsive materials using ink-jet printing (Figure 6 (i)).[103] The combination of metamaterial design with responsive smart materials means that the structures have a large range of movement and transformation whilst maintaining structural integrity. Most reports on the additive manufacture of metamaterials have been applied to dynamic mechanical systems.[104] [105] Providing the example of the door handle designed by Ion *et al.* the polymers intrinsic properties would fracture when torque is applied, however, careful placement of the individual unit cells means that the door handle can function without the use of hinges (Figure 6 (ii)).[106]

Rafsanjani *et al.* used SLS to design a snapping metamaterial with controllable tensile behaviours by tuning the snapping segments mimicking that of a soft spring system. The tuneable snapping metamaterial has applications for morphing, adaptable and deployable structures due to its sequential snaps from the initial wavy pattern until full extension has been reached when pulled along they-axis.[107] 4D printed metamaterials have also been used to develop magnetic field responsive mechanical metamaterials. Work by Jackson *et al.* used large area projection micro stereolithography (μSLA) to manufacture controllable architectures that have reversible responses when a magnetic field is applied. The responsive metamaterials could have applications in rapidly adaptive helmets, soft robotics and smart wearables with vibration-cancelling behaviours.[108]

2.2.1 Tuneable Metamaterials

Printable metamaterials coupled with shape memory polymers can be used to manufacture multi-functional lightweight designs with tunable mechanical, acoustic and thermal properties (Figure 6 (iii)).[104] Yang *et al.* reported on printing robust metamaterials for mechanical applications using acrylic acid AA and bisphenol A ethoxylate dimethacrylate. Boley *et al.* designed a frequency-shifting antenna using complex geometries and metamaterial designs. The metamaterial designs can be applied to control largely in plane-growth gradients by controlling Gaussian curvatures (Figure 6 (iv)).[109] The carefully constructed lattice arrays in metamaterials combined with shape memory properties mean that structures can be deformed without the need of an elastic phase in the matrix of the material. Lei *et al.* demonstrated this by printing mesh curvatures which were then programmed to achieve shape memory effects to tune rotation of mesh joints and the mechanical properties of the metamaterial.[110] This pairing can be applied to advanced applications that could not be achieved via many SMMs due to inherently poor mechanical and chemical properties.

2.3 Self-healing Polymeric Materials

Self-healing materials offer unique functionality to 4D printing; these materials can adapt and change over time to increase the longevity of printed components, in a variety of applications including electronics, and health care monitoring. Self-healing materials can reform and restore there chemical and physical functionalities. These are an attractive group of materials to increase longevity for safer and more reliable materials. To classify a material as self-healing the material must spontaneously begin repair once a defect occurs. Through the filling of a void caused by the defect such as a crack or scratch etc. with new matter. An ideal self-healing material will fully restore the original mechanical and chemical properties of the virgin material. [111]

Self-healing materials usually fall into two main categories based on their healing mechanisms, autonomous and non-autonomous. Non-autonomous materials require external stimuli to trigger the healing process such as UV light, heat or mechanical stimulus.[112] Autonomous materials, however, will begin to heal immediately upon damage through the presence of reversible hydrogen bonds and non-covalent bonds, or *via* a self-healing material embedded in the host material, which is released upon damage.

2.3.1 Microvascular Self-healing Mechanism

Vascular-based healing mechanisms consist of a network of channels filled with a repairing agent running throughout the matrix of the material. Once the network ruptures, capillary action causes the healing agent to be released into the site of the damage, which is then polymerised to fill the crack. Arteries found in a natural system have inspired vascular-based healing mechanism.[113] [114]

Li *et al.* developed a novel method biomimetic 3D vascular design inspired by nature fo self-healing cementitious systems (Figure 7 (i-ii)).[115] The 3D printed design consisted of polylactic acid (PLA) vascular network printed on an Ultimaker® 3D-printer (FDM), this structure housed the healing agent sodium silicate. Upon crack formation, in the cement matrix, the vascular design followed Murray's law for circulatory blood volume transfer as the healing system. Wu. *et al.* created a microvascular network using a fugitive ink and hydrogel reservoir to create a self-healing printed material for uses in health care microvascular devices.[116]

2.3.2 Encapsulation Self-healing Mechanisms

Capsule based self-repairing mechanism utilise micro or nano-sized particles filled usually with a healing agent such as a polymer or catalyst. Each capsule is protected by a case or coating made from an inert material so it does not interfere with the bulk material. This ensures the healing mechanism will only begin once damage occurs and not before. The 'shell' of the capsule should be weak to allow for easy rupture once damaged. These capsules are embedded throughout the matrix of the material, to ensure a rapid release of the healing agent upon rupture. The healing agent inside the capsules must have a low viscosity to allow for capillary action into the damage site. For an efficient healing process, the healing agent should be able to polymerise quickly at room temperature with no shrinkage.[117] Davami *et al.* used SLA 3D printing to fabricate structures entrapping the photocurable resin inside unit cells to act as a self-healing agent. Upon damage, the self-healing 'agent' flows out of the cell using capillary action to the site of damage where it is then cured using UV light. Here Davami *et al.* reported a healing efficiency of 52 % based on fracture toughness.[118]

2.3.3 Autonomous Self-healing Polymers: Supramolecular Polymers

Most polymers cannot self-repair autonomously without the addition of a host network containing a self-healing agent described by capsule and vascular-based mechanisms. However, supramolecular polymers are a class of material that consists of reversible non-covalent bonds which allow the bonds to reform and repair after cleavage.[119] The self-healing properties are therefore intrinsic to the polymer and are fully repeatable without the concern of depleting a host-healing agent. Supramolecular polymers are often described as 'solid-liquids,' they are made up of associated groups which are typically covalently bonded to chain ends or side chains of a polymer.[119] These chains join liquid-like polymers into a network of non-covalently cross-linked polymers displaying plastic behaviours.[119] Non-covalent crosslinks which are used in the reversible reforming process of supramolecular polymers include π-π staking, hydrogen bonds, host-guest interactions, ionic interactions and metal coordinations. To test the effectiveness of the restoration of the self-healing material several properties can be examined before and after healing including mechanical, electrical and thermal properties. This is known as the healing efficiency and is calculated using a ratio of the properties (p) before and after healing[120]:

$$\eta = \frac{P_{healed} - P_{damaged}}{P_{pristine - P_{damaged}}} \qquad (1)$$

Supramolecular polymers unlike SMM and hydrogels previously mentioned can reform without the need of an external stimulus. Wu *et al.* synthesised polyborosiloxane (PBS) a supramolecular polymer that can reform at room temperature due to hydrogen bonding. They further incorporated 5 vol. % graphene within the PBS matrix for printed gas sensors.[121] Shi *et al.* developed a self-healing hybrid gel made from a supramolecular polymer gel and electrically conductive polypyrrole. The hybrid gel was formed using freeze casting to produce a self-healing material with conductivity as high as 12 Sm^{-1} and 10 Sm^{-1} after healing.[122] Other examples of electrically conductive self-healing materials have been reported by Han *et al.* who developed a PDA-pGO-Pam hydrogel that is electrically conductive with a healing efficiency of 95 %. The hydrogel required no external stimulus to begin the healing process as the self-healing capabilities are provided through hydrogen bonding and cation-π interactions from the PDA. The applications of the self-healing conductive hydrogel include bioelectronics, implantable electrodes and electrical stimulators.[123]

Reports of self-healing elastomeric materials have been used in applications including fashion, wearable technology and sensing. Yu *et al.* developed a photo elastomer ink for SLA applications. The printed elastomer is simultaneously photocurable and fully self-healing through carefully tuned disulfide and thiol groups. The self-healing component is provided by the reversible cross-links of the disulphide bond. The self-healing efficiency of the printed composites showed that 90-100 % of the tensile strength remained after 10 cycles of cutting and healing.[124] When developing printable inks with multi-functionalities there is always a fine ratio between the printability properties and the functional properties. In this case, thiol groups would interact with the photocuring process and the disulphide groups would interact with the self-healing properties. Yu *et al.* found that tuning the P.I: IBDA (Iodobenzene diacetate) to 2.6 wt. % the healing strength plateaued at 100 %; however, the increase in IDBA caused a decrease in the curing coefficient k. Li *et al.* also reported on printing a photocurable elastomeric material *via* DLP (Figure 7 (iii)).[125] The polyurethane acrylate contained disulphide bonds that enabled the intrinsic self-healing of the material comparable to Yu *et al*.[124] They reported a tensile healing efficiency of up to 95 % (original 3.39 ± 0.09 MPa, after healing 3.22 ± 0.40 MPa) when heated to 80°C for 13 hours.

Zhang *et al.* developed a shape memory hydrogel with self-healing capabilities for the use in anti-counterfeiting and multi-stage data encryptions. The self-healing abilities of the hydrogel were due to covalent borate ester bonds between PVA and borax. The shape memory polymer was fixed in a 3D origami construction and transformed due to pH changes, Zhang *et* *al.* also included a secret message on the hydrogel that could only be seen when illuminated by 365 and 254 nm UV light.[126]

Table 1 summarises some of the current literature reports of self-healing 4D printed materials and their applications. The reports show that DIW technology is dominant in the manufacture of 4D printed self-healing materials.

3.0 Stimuli for Responsive Smart Materials

Many 4D printed materials require an external stimulus to trigger the transformative properties of the material. Smart materials can transform through twisting and folding mechanisms when exposed to changes in pH, moisture, temperature, light, electric and magnetic fields. The stimulus can be carefully selected and tuned dependant on the application of the operating environment. Stimuli-responsive materials have been extensively reported on over the past decade; however, their applications in 4D printing are still in their infancy. The main stimuli responses will now be discussed in more detail.

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3.1 Mechanisms of Responsive Materials

Materials respond to external stimuli through different mechanisms. These mechanisms are either constrained or unconstrained. Constrained mechanisms are those where the materials cannot return to their original structures after deformation, whereas unconstrained mechanisms can recover back to their original state.[127] These mechanisms can further be defined to the triggers that implement shape memory, shape-changing or self-healing effects, which are discussed in more detail in the subsequent sections.

3.2 Thermo-Responsive

Temperature is arguably the most widely used stimulant in 4D printing applications. This is because smart materials such as shape memory polymers, alloys and composites have a transitional temperature, $T_{transition}$ which is usually the T_g or T_m of the material, it is this transitional property that enables the morphing of a part when exposed to different temperature gradients. In 4D printing, the materials are printed above their $T_{transition}$ then deformed below the $T_{transition}$ into their second phase geometry. When the printed part is exposed to heating or cooling through the $T_{transition}$ the fabricated part will morph from one state to the next due to shape memory effects. Hydrogels are often used as 4D printed SMM as their transition temperature can be altered easily through increased cross-link density or through the addition of filler materials. 4D printing of multi-materials means that a printed part can have multiple transitions for impressive shape-shifting over varying operating temperatures.[60] However, one of the main drawbacks of printing hydrogels and SMPs is their inherently low operating temperatures limiting their applications.[128] Poly (N-isopropyl acrylamide) (PNIPAAm) a thermally responsive polymer has been printed using micro-stereolithography for applications in soft robotics and microfluidic devices.[129] Song *et al.* reported their thermo-responsive polymer consisting of a double layer actuator with switchable active and passive layers (Figure 8 (i)).[130]

3.3 Electro-Responsive

Electric fields can be used as indirect stimulants to trigger shape memory transformations of materials. Electric fields are often used to induce heating effects to increase the operating temperature past a material $T_{transition}$ to mimic shape memory effects as previously discussed in thermo-responsive materials. Xu *et al.* recently demonstrated this effect with their POE/CNT polymer composite, the group used an induced current to heat their sample above $T_{transition}$ (~80°C) which controlled actuation of their robotic structure. Similar to thermo-responsive materials the actuating structure was set above the $T_{transition}$ and then cooled down to room temperature where it was deformed to its second geometric phase.[131] Work by Han *et al.* developed an electrically responsive hydrogel printed using micro-stereolithography (µ-SLA). The hydrogel consisted of PPA cross-linked with PEGDA, which induced swelling that resulted in bending towards the cathode once an electric field was applied (Figure 8 (ii)). [132] Most reports of electrically assisted actuating materials have been developed for applications in soft robotics and artificial muscles.[132] [133] [134]

3.4 Magneto-Responsive

Other ways in which researchers have used stimulants to trigger the transformation of shape memory and smart materials is with the use of magnetic fields. In this case, the materials must be magnetic to be effective. This is usually achieved by doping the material with magnetic particles such as iron oxide.[135] [136] There are two main methods in which materials respond in the presence of magnetic fields. Firstly through the alignment of material under a magnetic field[137] and the other is through magnetically-induced heating effects.[138] An example of materials that respond to magnetic fields includes the work published by Huang *et al.* on a supercapacitor made from a self-healing yarn consisting of PPy, Fe_3O_4, stainless steel yarns coated in carboxylated Polyurethane with PVA-H_3PO_4 gel used as a solid electrolyte. The strong magnetic forces from the electrodes resulted in beneficial reconnections of fibres to restore electrical conductivity.[139] The self-healing capabilities, in this case, were possible through the abundance of hydrogen bond acceptors and donors in the supramolecular polymer. Although only the supramolecular polymer is self-healing, the magnetically assisted forces help to reconnect the yarns. [139] Magnetically-induced heating was reported by Wei *et al*. they demonstrated a magnetically responsive ink for DIW made from iron oxide nanoparticles embedded within Polylactic Acid (PLA) polymer matrix.[140] The magnetically responsive material began to uncoil when a 30 kHz magnetic field was induced the shape-changing properties can be seen in Figure 8 (iii).

3.5 Light-Responsive

Light or photo-responsive materials transform when exposed to specific wavelengths within the electromagnetic spectrum. Like other stimuli, light can induce changes to bond strength, twisting and folding and trigger healing mechanisms.[141] Similarly, to magnetically responsive materials, light-responsive materials respond *via* two methodologies. Firstly through sensitivities of the material to light, a photochemical effect from the presence of light-sensitive moieties.[142] [143] The second is through a photothermal effect [144] [145] that can increase the temperature of the material above its transition temperatures such as T_g, this can be achieved through the use of filler materials that can absorb light and convert this energy into heat.[146] Photo-responsive materials transform in the presence of light due to the existence of chromophores e.g. azobenzenes and cinnamic acid on the polymer chain. Dependant on the type of chromophores present, the reaction can be reversible or irreversible. Barrett *et al.* reported their photo-responsive LCE containing azobenzenes that could morph in the presence of visible and UV light (Figure 8 (iii)).[147] Poly (N-isopropyl acrylamide) (PNIPAM) functionalized with spirobenzopyran was developed by Sumaru *et al.* to morph under blue light irradiation for applications in microfluidic devices.[148] Light irradiance can also be applied to materials with self-healing capabilities to trigger the healing process. Amamoto *et al.* demonstrated this with trithiocarbonate (TTC) where self-healing through radical reorganisation was triggered when exposed to a lamp with a wavelength of 330 nm.[149] Researchers Moniruzzaman and Kister reported on the self-healing capabilities of epoxy thermosets when exposed to UV light through cis and trans isomerisation of azobenzene chromophores.[150] Zolfagharian *et al.* reported a 4D printed (DIW) polymer actuator that transformed due to photothermal effects.[151] The group printed a self-bending actuator made from polystyrene as the panels with chitosan hydrogel hinges. The chitosan hinges (black) absorbed light in the infrared region and converted the light energy to heat, this caused temperature gradients across the hinges and PS panels above the polymers T_g resulting in actuation.

3.6 Chemo-Responsive

Chemo-responsive materials are a prominent field in shape-changing materials especially SMPs. They work similarly to that of thermos-responsive materials; however, instead of using heat to go through transitional temperatures, they lower the T_g.[152] This is achieved through three main mechanisms including swelling, softening and dissolving.[153] An example of how chemo-responsive materials shape-change is through the absorption of solvent molecules within the polymer network leading to swelling.[154] This causes a plasticizing effect between the polymer and solvent that reduces the T_g of the material therefore external heat is not needed for transitions to occur.[152] Chemo-responsive materials can further be characterised to include moisture-responsive and pH-responsive materials that have been discussed in more detail in the following sub-sections.

3.6.1 Moisture-Responsive

There are three main mechanisms associated with moisture-responsive materials. These include the plastic effect whereby the absorption of water can reduce the T_g of the material resulting in shape change.[155] Another methodology is the breaking and re-forming of hydrogen bonds.[156] In this mechanism, the hydrogen bonds between the polymer and water molecules cause a reduction in interactions between the polymers macromolecules. This not only leads to a reduction in the T_g but stored mechanical energy is released triggering shape change. The last mechanisms are associated with the swelling effect of hydrogels, in this case, the hydrogel can absorb a large amount of water molecules into the polymer network resulting in drastic volume changes that can be either anisotropic or isotropic leading to shape changing effects.[157]

Undoubtedly, hydrogels are the most effective class of materials to respond to changes in moisture. Their ability to swell rapidly in the presence of water can be carefully tuned to form structures that fold and open mimicking hinge-like systems in the presence of a second unresponsive material. A key characteristic of using moisture responsive materials is the degree of swelling that can be obtained for radical transformations. Researchers Mulakkal *et al.* used water actuation for their hydrogel composed of carboxymethyl cellulose (CMC) hydrocolloid for advanced applications of complex architectures and actuating mechanisms (Figure 9 (i)).[158] In this work, the introduction of water leads to plasticisation of the amorphous regions of the CMC. Zheng *et al.* reported on their moisture activated stress-driven compressive bilayer films made up of PVA and PDMS. The films had wrinkling mechanisms to mimic the wrinkling that occurs in the skin when immersed in water for a set period. One of the potential applications for this type of morphing mechanism can be applied to tuneable optical properties such as smart windows.[159] Polypyrrole (PPy) is an electroactive polymer that can change shape through the absorption of water, creating a dynamic actuator for applications as artificial muscles. The shape-shifting changes of the polymer are rapid and recoverable mimicking 'fast-twitch' muscle activity. Ma *et al.* synthesised their PPy-PEE (pentaerythritol ethoxylate) composite using electro-polymerisation. The hybrid composite consisted of an IPN with a hard phase polymer and a soft phase moisture responsive polymer. The hybrid converted chemical potential energy into mechanical work through varied water gradients for applications in sensors and switches.[160] Han *et al.* developed a moisture responsive graphene oxide and reduced graphene oxide (rGO) bilayer paper that could be applied for graphene-based actuators.[161] PEG-DA and rhodamine B have been used together to form a photocurable humidity responsive polymer that can transform and change colour for applications in humidity indicators and walking actuators. [162]

3.6.2 pH-Responsive

Some SMPs and hydrogels respond to changes in pH or ion concentration causing their geometries to alter after exposure.[163] The reversible cross-links that are present, occur due to electrostatic interactions. Hydrogels have been extensively used to respond to changes in pH for applications in biomedicine with drug-releasing properties and catalysts. Dutta *et al.* reported on a thermal and pH-responsive hydrogel made from methacrylate poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) (pluronic) printed using SLA. The responsive polymer displayed reversible cross-links with fluctuations in pH between pH 2.0 and 7.4.[164] The hydrogel absorbed large amounts of water at a pH of 7.4 and then contracted back into its original shape when the pH was reduced to 2.0. The suggested application of the responsive-hydrogel was in microfluidic devices. Poly(2-vinylpyridine) (P2VP) is another pH-responsive polymer that swells when exposed to an acidic solution then contracts back under alkaline solutions.[165]

4.0 Applications of 4D Printed Materials

4D printing is an advanced manufacturing process offering unique solutions to complex and everyday problems. However, the research of 4D printing is still in its infancy, with current literature describing the initial works of an idea rather than a final working application. Therefore, the applications described in this following section discusses the potential applications envisioned by researchers with this new emerging technology.

4.1 Health Monitoring Devices

There has been significant interest in the development of dynamic biomedical devices to deliver applications in drug delivery, electronic-skins, self-tightening staples, and biomimetic robots to mimic biological systems such as complex artificial muscles.[141][166][167][168] Researchers have used 4D printing for drug delivery systems that are programmed and controlled by encapsulating drugs or cells, which are released through thermal, or moisture stimulus to open up and release the content inside as functioning bioreactors.[167] Bio-printing heavily relies on the use of hydrogels and their associated good biocompatibilities and excellent processing properties for AM technologies. Jamal *et al.* demonstrated the application of responsive hydrogels in bio-origami structures for tissue engineering. The group used a photo-cross linkable PEG hydrogel to create bilayers that resulted in curvatures or hinge-like systems that expanded when exposed to moisture releasing the encapsulated insulin-secreting β-TC-6 cells.[166] One fascinating outlook of 4D bioprinting is the idea of printing bones to scale then deforming structures down into injectable sizes for implantation (Figure 9 (ii)). This advanced surgical procedure was reported by Zhang *et al.* where they developed a shape recovery using PLA/Fe_3O_4 composites for bone repair applications.[169] The printed parts recover to their original shape by applying a magnetic field, which raises the temperature of the composite to above the $T_{transition}$.

Senatov *et al.* reported an SMC PLA/15 wt. % hydroxyapatite (HA) porous scaffold printed *via* FFF. The ceramic-based material exhibited shape recovery and self-healing effects for advanced applications as self-fitting bone implants.[170] 4D printing of SMAs has gained much interest in biomedical device applications.[171] [172] [173] Gul *et al.* used FDM to print a composite consisting of an SMA, SMP and graphene filament, the shape memory effect of the composite were receptive to electrically induced heating. Gul *et al.* printed an Omnidirectional actuator that could be used for biomedical applications such as steerable catheters.[174]

4.2 Electrical Devices

Advancements in electrical devices have led to high output rates of systems with powerful processors on a miniature scale. The ability for these components to meet the demands of their applications can cause major challenges in electrical device designs. One way of combating this is an issue through spontaneous self-repairing systems to allow a device to heal reconnecting a broken circuit. A printed electronic switch using an SMP and SLA can be seen in Figure 9 (iii). Ink-jet printed silver nanoparticles electrical contacts were deposited onto the surface of the SMP switch. The device is in a temporary state until heated to above the T_m where the circuit closes.[60] Shape memory switches can be used to break circuits when a critical temperature has been reached to avoid short-circuiting and permanent damage to the device.

The application of SMAs has been

Another field that has been heavily investigated is the use of smart electronic devices for health monitoring applications such as wearable sensors.[175] Wearable technology also offers an exciting opportunity for customisable clothing. Self-healing tracks are printed onto textiles to create circuits for illuminations, sounds and sensing purposes. The rapid response to damage significantly increases the life span of the wearable devices that are subjected to rigours activities including large changes in strain.[176] Research has also focused on the manufacture of sustainable electrical power through, self-healing grids and solar cells, supercapacitor and lithium-ion batteries.[120][177][178]

4.3 Soft Robotics

Soft robotics has become one of the focus areas for 4D printing applications. The programmable properties of transformative shape-memory materials mean that materials can be printed with actuating capabilities. These materials can be applied to a myriad of applications from biomedical devices for drug release, to programmable robotics in extreme environments. Including in high altitudes, outer space and extreme weather conditions such as flooding, snow and inhabitable environments. Soft robotics draws on how living organisms adapt to their environment. The materials are highly compliant allowing them to mimic living organisms. Soft robotics can be categorised as soft actuators, sensors and soft controllers.[179] An example of 4D printed soft robotics has been reported by Breger *et al.* where photo patterning was employed to fabricate micro grippers made from thermo-magnetically responsive polymer. To attain the gripping motion of the micro grippers the grippers were closed or deformed at 4 °C they then opened up when submerged in a phosphate-buffered saline solution at 37 °C (Figure 10 (i)).[180] Yang *et al.* used IR light (808 nm) in the fabrication, repair and assembling of CNT and xLCEs, for soft robotic actuators in low-temperature environments.[69] The composite material can self-heal micro-cracks through photo healing and is recyclable for long and efficient life spans. Gul *et al.* created a soft robotic system that mimicked the locomotion of a spider fabricated from an SMA wire and urethane, epoxy body.[181] Their design was printed using a customized multi-head, multilateral UV-3D printing system and the shape memory effect was activated via external electrical signalling.

An exciting new field for 4D printing also has seen the manufacture of field-assisted metamaterials that can adapt a change form when exposed to a field such as a magnetic field. Jackson *et al.* demonstrated this with their 4D printed reversible metamaterial that they envisaged could be applied to soft robotics.[108]

4.4 Self-folding Packaging and Origami Structures

Printable origami structures for self-folding packaging has created a very diverse field of research as applications can be found in the biomedical field, electronics and self-deploying structures.[92] Shape memory materials often use bilayers or multilayer structures to mimic the hinge-like effect needed for self-folding packaging. This is particularly useful to apply to non-elastic materials as the shape memory 'hinges' can react to strain whilst the main structural material is left unaffected. Zhang *et al.* used ink-jet printing to design self-folding packaging using black ink on shrink paper. Once the paper was exposed to infrared light the hinge-like structures deformed to obtain the folding motion.[182] Ge *et al.* reported on their 4D printed self-folding packaging shown in Figure 10 (ii). They demonstrate the opening and closing of a box and pyramid upon heating through their transitional temperatures to mimic the opening and closing motion of self-folding packaging.[183] The researchers used the commercial resins Tango black and Verowhite for the hinges and panels respectively. There have also been suggestions of using SMAs in self-folding packaging systems and deployable structures.[184][185][186][187] Although, some of these have been manufacture *via* other methods the combination of 3D printing technologies and SMAs opens up future potential in 4D printing applications for complex actuating structures.

Su *et al.* demonstrated printable origami structures for foldable antennas using SLA technology. In this work, a commercial flexible resin was used to create compliant structures that used mechanical folding to tune the antenna (Figure 10 (iii)).[188] The researchers reported potential applications of their antenna for collapsible and portable radars. Whilst Liu *et al.* reported that their morphing elastomer-derived ceramic that was printed (DIW) with origami structures could have potential structural applications in aerospace propulsion components, space exploration and electronic devices.[95]

4.5 Other Applications

One of the key advantages of SMM and self-actuating soft robotics is their ability to operate without the need for human intervention. This means they can be used for applications in demanding environments such as space and aircraft.[95][87] Another field that has been explored for shape memory and superelastic ceramic-based materials has been actuation, energy-damping, and energy-harvesting applications, suggested by Lai *et al*.[189]

There have also been reports of 4D printing applications in the food industry. Describing food that can change colour when exposed to changes in pH.[190] [191] He *et al.* demonstrated the colour changing effects of 4D printed (DIW) mashed potato with a change in pH.[191] The appearance of the printed mash potato was pink for acidic (pH ≈2.5), purple for neutral (pH ≈6.5) and green for the alkaline (pH ≈7.8) mixture, all three compositions intensified in colour over time (3 hours). He *et al.* added 1 % citric acid and 1 % sodium alginate to a mixture of gelatinized potato flakes and water to achieve the desired pH. The change in colour was due to the presence of anthocyanins (small molecules) a water-soluble pigment that changes structure with pH. Furthermore, He *et al.* was able to use multi-material printing to fabricate structures showing a gradient of colour with changes to the pH.

5.0 Conclusions

4D printing combines advanced materials and additive manufacturing for the fabrication of programmable structures that can offer unique solutions in the fields of health care monitoring, electrical devices, soft robotics and deployable structures, to name a few. Materials that can adapt and respond to demanding environments results in improved functionalities, increased life spans and efficient working conditions. Where self-healing materials are used, the longevity of the 4D printed parts is increased, reducing the need for costly repairs or replacements. The additive manufacture of metamaterials can be used to fabricate fully functional mechanical components without the need for hinge mechanisms. These advancements in AM materials can offer an exciting solution to problems that would usually require human interventions, however, due to the use in extreme environments would not be possible, for example, components used in outer space.

The key factors to consider for 4D printing applications include the availability of external stimuli, number of cycles of healing and/or morphing required and general property requirements (mechanical, electrical, optical and thermal). Therefore, this can create a trade-off between properties and the printability of the materials due to limitations of the AM technology.

Recent developments of AM technologies has seen the implementation of multi-material printing, embedded printing and alignment of filler materials using magnetic fields and particles. This combined with adaptive materials means that 4D printing could be realised as a feasible solution for next-generation manufacturing methods. Many of the reports discussed throughout this review focus on proof of concepts and potential applications however, with continued advancements in both AM technologies and materials these concepts could soon be realised in the near future.

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Abbreviations

µSLA	Micro stereolithography
AM	Additive manufacturing
CAD	Computer aided design
CLIP	Continuous liquid interface production
CMC	Carboxymethyl cellulose
CNT	Carbon nanotubes
DIW	Direct Ink write
DLP	Digital light processing
EBAM	Electron beam additive manufacturing
EBM	Electron beam melting
EMI	Electrical magnetic interference
FDM	Fuse deposition modelling
IPN	Interpenetrating network
LCEs	Liquid crystalline elastomers
LENS	Laser engineering net shape
LOM	Laminated object manufacturing
PBS	Poly borosiloxane
PDMS	Polydimethylsiloxane
PEGDA	Poly(ethylene gylcol) diacrylate
PNIPAM	Poly(N-isopropyl acrylamide)
POE	Polyolefin elastomer
PPy	Polypyrrole
SLA	Stereolithography
SLM	Selective laser melting
SLS	Selective laser sintering

SMAs	Shape memory alloys
SMCs	Shape memory composite
SMCrs	Shape memory ceramics
SMHs	Shape memory hybrids
SMMs	Shape memory materials
SMPs	Shape memory polymers

6.0 References

[1] H. Yin, M. Qu, H. Zhang, Y. Lim, 3D Printing and Buildings: A Technology Review and Future Outlook, Technol. + Des. 2 (2018) 94–111. https://doi.org/10.1080/24751448.2018.1420968.

[2] B.-H. Lu, H.-B. Lan, H.-Z. Liu, Additive manufacturing frontier: 3D printing electronics, Opto-Electronic Adv. 1 (2018) 17000401–17000410. https://doi.org/10.29026/oea.2018.170004.

[3] B. Roberts, The Third Industrial Revolution: Implications for Planning Cities and Regions, Work. Pap. Urban Front. 1 (2015).

[4] M.D. Symes, P.J. Kitson, J. Yan, C.J. Richmond, G.J.T. Cooper, R.W. Bowman, T. Vilbrandt, L. Cronin, Integrated 3D-printed reactionware for chemical synthesis and analysis, Nat. Chem. 4 (2012) 349–354. https://doi.org/10.1038/nchem.1313.

[5] F. Zhang, M. Wei, V. V. Viswanathan, B. Swart, Y. Shao, G. Wu, C. Zhou, 3D printing technologies for electrochemical energy storage, Nano Energy. 40 (2017) 418–431. https://doi.org/10.1016/j.nanoen.2017.08.037.

[6] S. Rossi, A. Puglisi, M. Benaglia, Additive Manufacturing Technologies: 3D Printing in Organic Synthesis, ChemCatChem. 10 (2018) 1512–1525. https://doi.org/10.1002/cctc.201701619.

[7] D. Jafari, W.W. Wits, The utilization of selective laser melting technology on heat transfer devices for thermal energy conversion applications: A review, Renew. Sustain. Energy Rev. 91 (2018) 420–442. https://doi.org/10.1016/j.rser.2018.03.109.

[8] F.H. Froes, R. Boyer, Additive Manufacturing for the Aerospace Industry, Elsevier, 2019.

[9] Q. Yan, H. Dong, J. Su, J. Han, B. Song, Q. Wei, Y. Shi, A Review of 3D Printing Technology for Medical Applications, Engineering. 4 (2018) 729–742. https://doi.org/10.1016/j.eng.2018.07.021.

[10] L.K. Prasad, H. Smyth, 3D Printing technologies for drug delivery: a review, Drug Dev. Ind. Pharm. 42 (2016) 1019–1031. https://doi.org/10.3109/03639045.2015.1120743.

[11] A.J. Capel, R.P. Rimington, M.P. Lewis, S.D.R. Christie, 3D printing for chemical, pharmaceutical and biological applications, Nat. Rev. Chem. 2 (2018) 422–436. https://doi.org/10.1038/s41570-018-0058-y.

[12] C. Guo, M. Zhang, B. Bhandari, Model Building and Slicing in Food 3D Printing Processes: A Review, Compr. Rev. Food Sci. Food Saf. 18 (2019) 1052–1069. https://doi.org/10.1111/1541-4337.12443.

[13] Y. Ni, R. Ji, K. Long, T. Bu, K. Chen, S. Zhuang, A review of 3D-printed sensors, Appl. Spectrosc. Rev. 52 (2017) 623–652. https://doi.org/10.1080/05704928.2017.1287082.

[14] J.Z. Gul, M. Sajid, M.M. Rehman, G.U. Siddiqui, I. Shah, K.H. Kim, J.W. Lee, K.H. Choi, 3D printing for soft robotics–a review, Sci. Technol. Adv. Mater. 19 (2018) 243–262. https://doi.org/10.1080/14686996.2018.1431862.

[15] F.P.W. Melchels, J. Feijen, D.W. Grijpma, A review on stereolithography and its applications in biomedical engineering, Biomaterials. 31 (2010) 6121–6130. https://doi.org/10.1016/j.biomaterials.2010.04.050.

[16] H.N. Chia, B.M. Wu, Recent advances in 3D printing of biomaterials, J. Biol. Eng. 9 (2015) 4. https://doi.org/10.1186/s13036-015-0001-4.

[17] N. Mohan, P. Senthil, S. Vinodh, N. Jayanth, A review on composite materials and process parameters optimisation for the fused deposition modelling process, Virtual Phys. Prototyp. 12 (2017) 47–59. https://doi.org/10.1080/17452759.2016.1274490.

[18] S. Yuan, F. Shen, C.K. Chua, K. Zhou, Polymeric composites for powder-based additive manufacturing: Materials and applications, Prog. Polym. Sci. 91 (2019) 141–168. https://doi.org/10.1016/j.progpolymsci.2018.11.001.

[19] X. Tian, J. Jin, S. Yuan, C.K. Chua, S.B. Tor, K. Zhou, Emerging 3D-Printed Electrochemical Energy Storage Devices: A Critical Review, Adv. Energy Mater. 7 (2017). https://doi.org/10.1002/aenm.201700127.

[20] G. Cummins, M.P.Y. Desmulliez, Inkjet printing of conductive materials: A review, Circuit World. 38 (2012) 193–213. https://doi.org/10.1108/03056121211280413.

[21] S. Kholghi Eshkalak, A. Chinnappan, W.A.D.M. Jayathilaka, M. Khatibzadeh, E. Kowsari, S. Ramakrishna, A review on inkjet printing of CNT composites for smart applications, Appl. Mater. Today. 9 (2017) 372–386. https://doi.org/10.1016/j.apmt.2017.09.003.

[22] F. Lederle, F. Meyer, G.-P. Brunotte, C. Kaldun, E.G. Hübner, Improved mechanical properties of 3D-printed parts by fused deposition modeling processed under the exclusion of oxygen, Prog. Addit. Manuf. 1 (2016) 3–7. https://doi.org/10.1007/s40964-016-0010-y.

[23] A.C. Uzcategui, A. Muralidharan, V.L. Ferguson, S.J. Bryant, R.R. McLeod, Understanding and Improving Mechanical Properties in 3D printed Parts Using a Dual-Cure Acrylate-Based Resin for Stereolithography, Adv. Eng. Mater. 20 (2018) 1800876. https://doi.org/10.1002/adem.201800876.

[24] A.K. Geim, Graphene: Status and prospects, Science (80-.). 324 (2009) 1530–1534. https://doi.org/10.1126/science.1158877.

[25] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Graphene and graphene oxide: Synthesis, properties, and applications, Adv. Mater. 22 (2010) 3906–3924. https://doi.org/10.1002/adma.201001068.

[26] J. Wang, F. Ma, M. Sun, Graphene, hexagonal boron nitride, and their heterostructures: properties and applications, RSC Adv. 7 (2017) 16801–16822. https://doi.org/10.1039/c7ra00260b.

[27] X. Li, H. Zhu, Two-dimensional MoS2: Properties, preparation, and applications, J. Mater. 1 (2015) 33–44. https://doi.org/10.1016/j.jmat.2015.03.003.

[28] V. Eswaraiah, Q. Zeng, Y. Long, Z. Liu, Black Phosphorus Nanosheets: Synthesis, Characterization and Applications, Small. 12 (2016) 3480–3502. https://doi.org/10.1002/smll.201600032.

[29] M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, 25th anniversary article: MXenes: A new family of two-dimensional materials, Adv. Mater. 26 (2014) 992–1005. https://doi.org/10.1002/adma.201304138.

[30] H. Zhang, Ultrathin Two-Dimensional Nanomaterials, ACS Nano. 9 (2015) 9451–9469. https://doi.org/10.1021/acsnano.5b05040.

[31] K. Khan, A.K. Tareen, M. Aslam, R. Wang, Y. Zhang, A. Mahmood, Z. Ouyang, H. Zhang, Z. Guo, Recent developments in emerging two-dimensional materials and their applications, J. Mater. Chem. C. 8 (2020) 387–440. https://doi.org/10.1039/c9tc04187g.

[32] S.Z. Butler, S.M. Hollen, L. Cao, Y. Cui, J.A. Gupta, H.R. Gutiérrez, T.F. Heinz, S.S. Hong, J. Huang, A.F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R.D. Robinson, R.S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M.G. Spencer, M. Terrones, W. Windl, J.E. Goldberger, Progress, challenges, and opportunities in two-dimensional materials beyond graphene, ACS Nano. 7 (2013) 2898–2926. https://doi.org/10.1021/nn400280c.

[33] M. Xu, T. Liang, M. Shi, H. Chen, Graphene-like two-dimensional materials, Chem. Rev. 113 (2013) 3766–3798. https://doi.org/10.1021/cr300263a.

[34] S. Tibbits, 4D printing: Multi-material shape change, Archit. Des. 84 (2014) 116–121. https://doi.org/10.1002/ad.1710.

[35] Skylar Tibbits: The emergence of "4D printing" | TED Talk, (n.d.). https://www.ted.com/talks/skylar_tibbits_the_emergence_of_4d_printing?language=en (accessed October 24, 2019).

[36] S. Sundaram, D.S. Kim, M.A. Baldo, R.C. Hayward, W. Matusik, 3D-Printed Self-Folding Electronics, ACS Appl. Mater. Interfaces. 9 (2017) 32290–32298. https://doi.org/10.1021/acsami.7b10443.

[37] A.R. Studart, R.M. Erb, Bioinspired materials that self-shape through programmed microstructures, Soft Matter. 10 (2014) 1284–1294. https://doi.org/10.1039/c3sm51883c.

[38] M.R. Hartings, Z. Ahmed, Chemistry from 3D printed objects, Nat. Rev. Chem. 3 (2019) 305–314. https://doi.org/10.1038/s41570-019-0097-z.

[39] Y.Y.C. Choong, S. Maleksaeedi, H. Eng, J. Wei, P.C. Su, 4D printing of high performance shape memory polymer using stereolithography, Mater. Des. 126 (2017) 219–225. https://doi.org/10.1016/j.matdes.2017.04.049.

[40] D. Wu, J. Song, Z. Zhai, M. Hua, C. Kim, I. Frenkel, H. Jiang, X. He, Visualizing morphogenesis through instability formation in 4-D printing, ACS Appl. Mater. Interfaces. (2019) acsami.9b19730. https://doi.org/10.1021/acsami.9b19730.

[41] L. Kačergis, R. Mitkus, M. Sinapius, Influence of fused deposition modeling process parameters on the transformation of 4D printed morphing structures, Smart Mater. Struct. 28 (2019) 105042. https://doi.org/10.1088/1361-665x/ab3d18.

[42] Y. Pyo, M. Kang, J. young Jang, Y. Park, Y.H. Son, M.C. Choi, J. wan Ha, Y.W. Chang, C.S. Lee, Design of a shape memory composite(SMC) using 4D printing technology, Sensors Actuators, A Phys. 283 (2018) 187–195. https://doi.org/10.1016/j.sna.2018.08.049.

[43] A. Sydney Gladman, E.A. Matsumoto, R.G. Nuzzo, L. Mahadevan, J.A. Lewis, Biomimetic 4D printing, Nat. Mater. 15 (2016) 413–418. https://doi.org/10.1038/nmat4544.

[44] P. Zhu, W. Yang, R. Wang, S. Gao, B. Li, Q. Li, 4D Printing of Complex Structures with a Fast Response Time to Magnetic Stimulus, ACS Appl. Mater. Interfaces. 10 (2018) 36435–36442. https://doi.org/10.1021/acsami.8b12853.

[45] C. Zhang, X. Lu, G. Fei, Z. Wang, H. Xia, Y. Zhao, 4D Printing of a Liquid Crystal Elastomer with a Controllable Orientation Gradient, ACS Appl. Mater. Interfaces. (2019) acsami.9b18037. https://doi.org/10.1021/acsami.9b18037.

[46] Q. Ge, H.J. Qi, M.L. Dunn, Active materials by four-dimension printing, Appl. Phys. Lett. 103 (2013). https://doi.org/10.1063/1.4819837.

[47] Y. Liu, J.K. Boyles, J. Genzer, M.D. Dickey, Self-folding of polymer sheets using local light absorption, Soft Matter. 8 (2012) 1764–1769. https://doi.org/10.1039/c1sm06564e.

[48] S.A. Abdullah, A. Jumahat, N.R. Abdullah, L. Frormann, Determination of shape fixity and shape recovery rate of carbon nanotube-filled shape memory polymer nanocomposites, in: Procedia Eng., Elsevier Ltd, 2012: pp. 1641–1646. https://doi.org/10.1016/j.proeng.2012.07.362.

[49] A. Lai, Z. Du, C.L. Gan, C.A. Schuh, Shape memory and superelastic ceramics at small scales, Science (80-.). 341 (2013) 1505–1508. https://doi.org/10.1126/science.1239745.

[50] A.I. Salimon, F.S. Senatov, V.A. Kalyaev, A.M. Korsunsky, Shape memory polymer blends and composites for 3D and 4D printing applications, in: 3D 4D Print. Polym. Nanocomposite Mater., Elsevier, 2020: pp. 161–189. https://doi.org/10.1016/B978-0-12-816805-9.00006-5.

[51] A. Lendlein, H. Jiang, O. Jünger, R. Langer, Light-induced shape-memory polymers, Nature. 434 (2005) 879–882. https://doi.org/10.1038/nature03496.

[52] B. Yang, W.M. Huang, C. Li, L. Li, Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer, Polymer (Guildf). 47 (2006) 1348–1356. https://doi.org/10.1016/j.polymer.2005.12.051.

[53] T. Miyata, N. Asami, T. Uragani, A reversibly antigen-responsive hydrogen, Nature. 399 (1999) 766–768. https://doi.org/10.1038/21619.

[54] J.W. Cho, J.W. Kim, Y.C. Jung, N.S. Goo, Electroactive Shape-Memory Polyurethane Composites Incorporating Carbon Nanotubes, Macromol. Rapid Commun. 26 (2005) 412–416. https://doi.org/10.1002/marc.200400492.

[55] L. Mañosa, D. González-Alonso, A. Planes, E. Bonnot, M. Barrio, J.L. Tamarit, S. Aksoy, M. Acet, Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy, Nat. Mater. 9 (2010) 478–481. https://doi.org/10.1038/nmat2731.

[56] X. Kuang, D.J. Roach, J. Wu, C.M. Hamel, Z. Ding, T. Wang, M.L. Dunn, H.J. Qi, Advances in 4D Printing: Materials and Applications, Adv. Funct. Mater. 29 (2019). https://doi.org/10.1002/adfm.201805290.

[57] W. Peng, G. Zhang, J. Liu, S. Nie, Y. Wu, S. Deng, G. Fang, J. Zhou, J. Song, J. Qian, P. Pan, Q. Zhao, T. Xie, Light-Coded Digital Crystallinity Patterns Toward Bioinspired 4D Transformation of Shape-Memory Polymers, Adv. Funct. Mater. 30 (2020) 2000522. https://doi.org/10.1002/adfm.202000522.

[58] Y.S. Wong, S.S. Venkatraman, Recovery as a measure of oriented crystalline structure in poly(l-lactide) used as shape memory polymer, Acta Mater. 58 (2010) 49–58. https://doi.org/10.1016/j.actamat.2009.08.075.

[59] Q. Ge, A.H. Sakhaei, H. Lee, C.K. Dunn, N.X. Fang, M.L. Dunn, Multimaterial 4D Printing with Tailorable Shape Memory Polymers, Sci. Rep. 6 (2016) 31110. https://doi.org/10.1038/srep31110.

[60] M. Zarek, M. Layani, I. Cooperstein, E. Sachyani, D. Cohn, S. Magdassi, 3D Printing of Shape Memory Polymers for Flexible Electronic Devices, Adv. Mater. 28 (2016) 4449–4454. https://doi.org/10.1002/adma.201503132.

[61] Z.L. Wu, M. Moshe, J. Greener, H. Therien-Aubin, Z. Nie, E. Sharon, E. Kumacheva, Three-dimensional shape transformations of hydrogel sheets induced by small-scale modulation of internal stresses, Nat. Commun. 4 (2013). https://doi.org/10.1038/ncomms2549.

[62] Y.C. Sun, Y. Wan, R. Nam, M. Chu, H.E. Naguib, 4D-printed hybrids with localized shape memory behaviour: Implementation in a functionally graded structure, Sci. Rep. 9 (2019) 1–13. https://doi.org/10.1038/s41598-019-55298-1.

[63] D.J. Roach, X. Kuang, C. Yuan, K. Chen, H.J. Qi, Novel ink for ambient condition printing of liquid crystal elastomers for 4D printing, Smart Mater. Struct. 27 (2018). https://doi.org/10.1088/1361-665X/aae96f.

[64] C.P. Ambulo, J.J. Burroughs, J.M. Boothby, H. Kim, M.R. Shankar, T.H. Ware, Four-dimensional Printing of Liquid Crystal Elastomers, ACS Appl. Mater. Interfaces. 9 (2017) 37332–37339. https://doi.org/10.1021/acsami.7b11851.

[65] Z. Pei, Y. Yang, Q. Chen, E.M. Terentjev, Y. Wei, Y. Ji, Mouldable liquid-crystalline elastomer actuators with exchangeable covalent bonds, Nat. Mater. 13 (2014) 36–41. https://doi.org/10.1038/nmat3812.

[66] T. Guin, M.J. Settle, B.A. Kowalski, A.D. Auguste, R. V. Beblo, G.W. Reich, T.J. White, Layered liquid crystal elastomer actuators, Nat. Commun. 9 (2018). https://doi.org/10.1038/s41467-018-04911-4.

[67] J. Kirton, The Physics of Liquid Crystals, Opt. Acta Int. J. Opt. (1975). https://doi.org/10.1080/716099366a.

[68] M. López-Valdeolivas, D. Liu, D.J. Broer, C. Sánchez-Somolinos, 4D Printed Actuators with Soft-Robotic Functions, Macromol. Rapid Commun. 39 (2018). https://doi.org/10.1002/marc.201700710.

[69] Y. Yang, Z. Pei, Z. Li, Y. Wei, Y. Ji, Making and Remaking Dynamic 3D Structures by Shining Light on Flat Liquid Crystalline Vitrimer Films without a Mold, J. Am. Chem. Soc. 138 (2016) 2118–2121. https://doi.org/10.1021/jacs.5b12531.

[70] J.J. Lessard, L.F. Garcia, C.P. Easterling, M.B. Sims, K.C. Bentz, S. Arencibia, D.A. Savin, B.S. Sumerlin, Catalyst-Free Vitrimers from Vinyl Polymers, Macromolecules. 52 (2019) 2105–2111. https://doi.org/10.1021/acs.macromol.8b02477.

[71] B. Zhang, C. Yuan, W. Zhang, M.L. Dunn, H.J. Qi, Z. Liu, K. Yu, Q. Ge, Recycling of vitrimer blends with tunable thermomechanical properties, RSC Adv. 9 (2019) 5431–5437. https://doi.org/10.1039/c9ra00015a.

[72] W. Denissen, J.M. Winne, F.E. Du Prez, Vitrimers: Permanent organic networks with glass-like fluidity, Chem. Sci. 7 (2016) 30–38. https://doi.org/10.1039/c5sc02223a.

[73] B. Jin, H. Song, R. Jiang, J. Song, Q. Zhao, T. Xie, Programming a crystalline shape memory polymer network with thermo- and photo-reversible bonds toward a single-component soft robot, Sci. Adv. 4 (2018). https://doi.org/10.1126/sciadv.aao3865.

[74] Q. Shi, K. Yu, X. Kuang, X. Mu, C.K. Dunn, M.L. Dunn, T. Wang, H. Jerry Qi, Recyclable 3D printing of vitrimer epoxy, Mater. Horizons. 4 (2017) 598–607. https://doi.org/10.1039/c7mh00043j.

[75] E.M. Ahmed, Hydrogel: Preparation, characterization, and applications: A review, J. Adv. Res. 6 (2015) 105–121. https://doi.org/10.1016/j.jare.2013.07.006.

[76] S.E. Bakarich, R. Gorkin, M. In Het Panhuis, G.M. Spinks, 4D printing with mechanically robust, thermally actuating hydrogels, Macromol. Rapid Commun. 36 (2015) 1211–1217. https://doi.org/10.1002/marc.201500079.

[77] S. Naficy, R. Gately, R. Gorkin, H. Xin, G.M. Spinks, 4D Printing of Reversible Shape Morphing Hydrogel Structures, Macromol. Mater. Eng. 302 (2017). https://doi.org/10.1002/mame.201600212.

[78] Y. Hu, Z. Wang, D. Jin, C. Zhang, R. Sun, Z. Li, K. Hu, J. Ni, Z. Cai, D. Pan, X. Wang, W. Zhu, J. Li, D. Wu, L. Zhang, J. Chu, Botanical-Inspired 4D Printing of Hydrogel at the Microscale, Adv. Funct. Mater. n/a (2019) 1907377. https://doi.org/10.1002/adfm.201907377.

[79] S.M. Society, Shape Memory Alloys 104 . P S E U D O - E L A S T I C I T Y AND H Y S T E R E S I S, (1951). https://doi.org/10.1016/B978-008044019-4/50031-3.

[80] D.J. Hartl, D.C. Lagoudas, Aerospace applications of shape memory alloys, Proc. Inst. Mech. Eng. Part G J. Aerosp. Eng. 221 (2007) 535–552. https://doi.org/10.1243/09544100JAERO211.

[81] Titanium alloys for aerospace structures and engines, in: Introd. to Aerosp. Mater., Elsevier, 2012: pp. 202–223. https://doi.org/10.1533/9780857095152.202.

[82] H.Z. Lu, C. Yang, X. Luo, H.W. Ma, B. Song, Y.Y. Li, L.C. Zhang, Ultrahigh-performance TiNi shape memory alloy by 4D printing, Mater. Sci. Eng. A. 763 (2019) 138166. https://doi.org/10.1016/j.msea.2019.138166.

[83] Z.X. Khoo, J. An, C.K. Chua, Y.F. Shen, C.N. Kuo, Y. Liu, Effect of heat treatment on repetitively scanned SLM NiTi shape memory alloy, Materials (Basel). 12 (2019). https://doi.org/10.3390/ma12010077.

[84] Z.X. Khoo, Y. Liu, Z.H. Low, J. An, C.K. Chua, K.F. Leong, Fabrication of SLM NiTi Shape Memory Alloy via Repetitive Laser Scanning, Shape Mem. Superelasticity. (2018). https://doi.org/10.1007/s40830-017-0139-7.

[85] S. Dadbakhsh, M. Speirs, J.P. Kruth, J. Schrooten, J. Luyten, J. Van Humbeeck, Effect of SLM parameters on transformation temperatures of shape memory nickel titanium parts, Adv. Eng. Mater. 16 (2014) 1140–1146. https://doi.org/10.1002/adem.201300558.

[86] S. Akbari, A.H. Sakhaei, S. Panjwani, K. Kowsari, A. Serjourei, Q. Ge, Multimaterial 3D Printed Soft Actuators Powered by Shape Memory Alloy Wires, Sensors Actuators, A Phys. 290 (2019) 177–189. https://doi.org/10.1016/j.sna.2019.03.015.

[87] T. Umedachi, V. Vikas, B.A. Trimmer, Softworms: The design and control of non-pneumatic, 3D-printed, deformable robots, Bioinspiration and Biomimetics. (2016). https://doi.org/10.1088/1748-3190/11/2/025001.

[88] H.-T. Lin, G.G. Leisk, B. Trimmer, GoQBot: a caterpillar-inspired soft-bodied rolling robot, Bioinspir. Biomim. 6 (2011) 026007. https://doi.org/10.1088/1748-3182/6/2/026007.

[89] M.P. Caputo, A.E. Berkowitz, A. Armstrong, P. Müllner, C.V. Solomon, 4D printing of net shape parts made from Ni-Mn-Ga magnetic shape-memory alloys, Addit. Manuf. 21 (2018) 579–588. https://doi.org/10.1016/j.addma.2018.03.028.

[90] S. Dadbakhsh, M. Speirs, J.P. Kruth, J. Van Humbeeck, Influence of SLM on shape memory and compression behaviour of NiTi scaffolds, CIRP Ann. - Manuf. Technol. 64 (2015) 209–212. https://doi.org/10.1016/j.cirp.2015.04.039.

[91] M. Taheri Andani, S. Saedi, A.S. Turabi, M.R. Karamooz, C. Haberland, H.E. Karaca, M. Elahinia, Mechanical and shape memory properties of porous Ni50.1Ti49.9 alloys manufactured by selective laser melting, J. Mech. Behav. Biomed. Mater. 68 (2017) 224–231. https://doi.org/10.1016/j.jmbbm.2017.01.047.

[92] W. Wang, N.G. Kim, H. Rodrigue, S.H. Ahn, Modular assembly of soft deployable structures and robots, Mater. Horizons. 4 (2017) 367–376. https://doi.org/10.1039/c6mh00550k.

[93] W. Wang, C. Li, H. Rodrigue, F. Yuan, M.W. Han, M. Cho, S.H. Ahn, Kirigami/Origami-Based Soft Deployable Reflector for Optical Beam Steering, Adv. Funct. Mater. 27 (2017). https://doi.org/10.1002/adfm.201604214.

[94] N. Zhang, M. Asle Zaeem, Nanoscale self-healing mechanisms in shape memory ceramics, Npj Comput. Mater. 5 (2019). https://doi.org/10.1038/s41524-019-0194-z.

[95] G. Liu, Y. Zhao, G. Wu, J. Lu, Origami and 4D printing of elastomer-derived ceramic structures, Sci. Adv. 4 (2018). https://doi.org/10.1126/sciadv.aat0641.

[96] V.G. Veselago, THE ELECTRODYNAMICS OF SUBSTANCES WITH SIMULTANEOUSLY NEGATIVE VALUES OF ϵ AND μ, Sov. Phys. Uspekhi. 10 (1968) 509–514. https://doi.org/10.1070/pu1968v010n04abeh003699.

[97] A. Sadeqi, H. Rezaei Nejad, R.E. Owyeung, S. Sonkusale, Three dimensional printing of metamaterial embedded geometrical optics (MEGO), Microsystems Nanoeng. 5 (2019). https://doi.org/10.1038/s41378-019-0053-6.

[98] M. Bodaghi, A.R. Damanpack, G.F. Hu, W.H. Liao, Large deformations of soft metamaterials fabricated by 3D printing, Mater. Des. 131 (2017) 81–91. https://doi.org/10.1016/j.matdes.2017.06.002.

[99] X. Wu, Y. Su, J. Shi, Perspective of additive manufacturing for metamaterials development, Smart Mater. Struct. 28 (2019) 093001. https://doi.org/10.1088/1361-665x/ab2eb6.

[100] Y. Jiang, Q. Wang, Highly-stretchable 3D-architected Mechanical Metamaterials, Sci. Rep. 6 (2016). https://doi.org/10.1038/srep34147.

[101] N. Li, R.R. Gattass, E. Gershgoren, H. Hwang, J.T. Fourkas, Achieving 1/20 resolution by one-color initiation and deactivation of polymerization, Science (80-.). 324 (2009) 910–913. https://doi.org/10.1126/science.1168996.

[102] H. Qiao, H. Liu, J. Mou, X. Lv, A compact W-band quasi-optical detector packaged by meta-surface reflector and 3D-printed lens, Microw. Opt. Technol. Lett. (2019). https://doi.org/10.1002/mop.32062.

[103] M. Wagner, T. Chen, K. Shea, Large shape transforming 4D auxetic structures, 3D Print. Addit. Manuf. 4 (2017) 133–141. https://doi.org/10.1089/3dp.2017.0027.

[104] C. Yang, M. Boorugu, A. Dopp, J. Ren, R. Martin, D. Han, W. Choi, H. Lee, 4D printing reconfigurable, deployable and mechanically tunable metamaterials, Mater. Horizons. 6 (2019) 1244–1250. https://doi.org/10.1039/c9mh00302a.

[105] M. Bodaghi, W.H. Liao, 4D printed tunable mechanical metamaterials with shape memory operations, Smart Mater. Struct. 28 (2019). https://doi.org/10.1088/1361-665X/ab0b6b.

[106] A. Ion, J. Frohnhofen, L. Wall, R. Kovacs, M. Alistar, J. Lindsay, P. Lopes, T. Chen, P. Baudisch, Metamaterial Mechanisms, 2016. https://doi.org/10.1145/2984511.2984540.

[107] A. Rafsanjani, A. Akbarzadeh, D. Pasini, Snapping Mechanical Metamaterials under Tension, Adv. Mater. 27 (2015) 5931–5935. https://doi.org/10.1002/adma.201502809.

[108] J.A. Jackson, M.C. Messner, N.A. Dudukovic, W.L. Smith, L. Bekker, B. Moran, A.M. Golobic, A.J. Pascall, E.B. Duoss, K.J. Loh, C.M. Spadaccini, Field responsive mechanical metamaterials, Sci. Adv. 4 (2018) eaau6419. https://doi.org/10.1126/sciadv.aau6419.

[109] J.W. Boley, W.M. van Rees, C. Lissandrello, M.N. Horenstein, R.L. Truby, A. Kotikian, J.A. Lewis, L. Mahadevan, Shape-shifting structured lattices via multimaterial 4D printing, Proc. Natl. Acad. Sci. (2019) 201908806. https://doi.org/10.1073/pnas.1908806116.

[110] M. Lei, W. Hong, Z. Zhao, C. Hamel, M. Chen, H. Lu, H.J. Qi, 3D Printing of Auxetic Metamaterials with Digitally Reprogrammable Shape, ACS Appl. Mater. Interfaces. (2019). https://doi.org/10.1021/acsami.9b06081.

[111] S. van der Zwaag, Self Healing Materials An Alternative Approach to 20 Centuries of Materials Science, 2007. https://doi.org/10.1007/s13398-014-0173-7.2.

[112] B.J. Blaiszik, S.L.B. Kramer, S.C. Olugebefola, J.S. Moore, N.R. Sottos, S.R. White, Self-healing polymers and composites, Annu. Rev. Mater. Res. 40 (2010) 179–211.

[113] C. De Nardi, D. Gardner, A.D. Jefferson, Development of 3D printed networks in self-healing concrete, Materials (Basel). 13 (2020). https://doi.org/10.3390/ma13061328.

[114] G. Postiglione, M. Alberini, S. Leigh, M. Levi, S. Turri, Effect of 3D-Printed Microvascular Network Design on the Self-Healing Behavior of Cross-Linked Polymers, ACS Appl. Mater. Interfaces. 9 (2017) 14371–14378. https://doi.org/10.1021/acsami.7b01830.

[115] Z. Li, L.R. de Souza, C. Litina, A.E. Markaki, A. Al-Tabbaa, A novel biomimetic design of a 3D vascular structure for self-healing in cementitious materials using Murray's law, Mater. Des. 190 (2020) 108572. https://doi.org/10.1016/j.matdes.2020.108572.

[116] W. Wu, A. Deconinck, J.A. Lewis, Omnidirectional printing of 3D microvascular networks, Adv. Mater. 23 (2011). https://doi.org/10.1002/adma.201004625.

[117] S.K. Ghosh, Self-Healing Materials: Fundamentals, Design Strategies, and Applications, 2009. https://doi.org/10.1002/9783527625376.

[118] K. Davami, M. Mohsenizadeh, M. Mitcham, P. Damasus, Q. Williams, M. Munther, Additively Manufactured Self-Healing Structures with Embedded Healing Agent Reservoirs, Sci. Rep. 9 (2019). https://doi.org/10.1038/s41598-019-43883-3.

[119] Y. Yang, X. Ding, M.W. Urban, Chemical and physical aspects of self-healing materials, Prog. Polym. Sci. (2015). https://doi.org/10.1016/j.progpolymsci.2015.06.001.

[120] Y.J. Tan, J. Wu, H. Li, B.C.K. Tee, Self-Healing Electronic Materials for a Smart and Sustainable Future, ACS Appl. Mater. Interfaces. 10 (2018) 15331–15345. https://doi.org/10.1021/acsami.7b19511.

[121] T. Wu, E. Gray, B. Chen, A self-healing, adaptive and conductive polymer composite ink for 3D printing of gas sensors, J. Mater. Chem. C. 6 (2018) 6200–6207. https://doi.org/10.1039/c8tc01092g.

[122] Y. Shi, M. Wang, C. Ma, Y. Wang, X. Li, G. Yu, A Conductive Self-Healing Hybrid Gel Enabled by Metal-Ligand Supramolecule and Nanostructured Conductive Polymer, Nano Lett. 15 (2015) 6276–6281. https://doi.org/10.1021/acs.nanolett.5b03069.

[123] L. Han, X. Lu, M. Wang, D. Gan, W. Deng, K. Wang, L. Fang, K. Liu, C.W. Chan, Y. Tang, L.T. Weng, H. Yuan, A Mussel-Inspired Conductive, Self-Adhesive, and Self-Healable Tough Hydrogel as Cell Stimulators and Implantable Bioelectronics, Small. 13 (2017). https://doi.org/10.1002/smll.201601916.

[124] K. Yu, A. Xin, H. Du, Y. Li, Q. Wang, Additive manufacturing of self-healing elastomers, NPG Asia Mater. 11 (2019). https://doi.org/10.1038/s41427-019-0109-y.

[125] X. Li, R. Yu, Y. He, Y. Zhang, X. Yang, X. Zhao, W. Huang, Self-Healing Polyurethane Elastomers Based on a Disulfide Bond by Digital Light Processing 3D Printing, ACS Macro Lett. (2019). https://doi.org/10.1021/acsmacrolett.9b00766.

[126] Y. Zhang, X. Le, Y. Jian, W. Lu, J. Zhang, T. Chen, 3D Fluorescent Hydrogel Origami for Multistage Data Security Protection, Adv. Funct. Mater. 29 (2019) 1905514. https://doi.org/10.1002/adfm.201905514.

[127] H. Ding, X. Zhang, Y. Liu, S. Ramakrishna, Review of mechanisms and deformation behaviors in 4D printing, Int. J. Adv. Manuf. Technol. 105 (2019) 4633–4649. https://doi.org/10.1007/s00170-019-03871-3.

[128] S.K. Leist, J. Zhou, Current status of 4D printing technology and the potential of light-reactive smart materials as 4D printable materials, Virtual Phys. Prototyp. 11 (2016) 249–262. https://doi.org/10.1080/17452759.2016.1198630.

[129] D. Han, Z. Lu, S.A. Chester, H. Lee, Micro 3D Printing of a Temperature-Responsive Hydrogel Using Projection Micro-Stereolithography, Sci. Rep. 8 (2018). https://doi.org/10.1038/s41598-018-20385-2.

[130] J. Song, Y. Zhang, From two-dimensional to three-dimensional structures: A superior thermal-driven actuator with switchable deformation behavior, Chem. Eng. J. (2019) 680–685. https://doi.org/10.1016/j.cej.2018.12.026.

[131] Z. Xu, C. Ding, D.-W. Wei, R.-Y. Bao, K. Ke, Z. Liu, M.-B. Yang, W. Yang, Electro and Light-Active Actuators Based on Reversible Shape-Memory Polymer Composites with Segregated Conductive Networks, ACS Appl. Mater. Interfaces. 11 (2019) 30332–30340. https://doi.org/10.1021/acsami.9b10386.

[132] D. Han, C. Farino, C. Yang, T. Scott, D. Browe, W. Choi, J.W. Freeman, H. Lee, Soft Robotic Manipulation and Locomotion with a 3D Printed Electroactive Hydrogel, ACS Appl. Mater. Interfaces. 10 (2018) 17512–17518. https://doi.org/10.1021/acsami.8b04250.

[133] L. Migliorini, T. Santaniello, Y. Yan, C. Lenardi, P. Milani, Low-voltage electrically driven homeostatic hydrogel-based actuators for underwater soft robotics, Sensors Actuators, B Chem. 228 (2016) 758–766. https://doi.org/10.1016/j.snb.2016.01.110.

[134] T. Li, G. Li, Y. Liang, T. Cheng, J. Dai, X. Yang, B. Liu, Z. Zeng, Z. Huang, Y. Luo, T. Xie, W. Yang, Fast-moving soft electronic fish, Sci. Adv. 3 (2017). https://doi.org/10.1126/sciadv.1602045.

[135] J. Liang, Y. Huang, J. Oh, M. Kozlov, D. Sui, S. Fang, R.H. Baughman, Y. Ma, Y. Chen, Electromechanical actuators based on graphene and graphene/Fe 3O4 hybrid paper, Adv. Funct. Mater. 21 (2011) 3778–3784. https://doi.org/10.1002/adfm.201101072.

[136] B. Shen, W. Zhai, M. Tao, J. Ling, W. Zheng, Lightweight, multifunctional polyetherimide/graphene@Fe3O 4 composite foams for shielding of electromagnetic pollution, ACS Appl. Mater. Interfaces. 5 (2013) 11383–11391. https://doi.org/10.1021/am4036527.

[137] H. Lu, J. Gou, J. Leng, S. Du, Magnetically aligned carbon nanotube in nanopaper enabled shape-memory nanocomposite for high speed electrical actuation, Appl. Phys. Lett. 98 (2011) 174105. https://doi.org/10.1063/1.3585669.

[138] A.M. Schmidt, Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles, Macromol. Rapid Commun. 27 (2006) 1168–1172. https://doi.org/10.1002/marc.200600225.

[139] Y. Huang, Y. Huang, M. Zhu, W. Meng, Z. Pei, C. Liu, H. Hu, C. Zhi, Magnetic-Assisted, Self-Healable, Yarn-Based Supercapacitor, ACS Nano. 9 (2015) 6242–6251. https://doi.org/10.1021/acsnano.5b01602.

[140] H. Wei, Q. Zhang, Y. Yao, L. Liu, Y. Liu, J. Leng, Direct-write fabrication of 4D active shape-changing structures based on a shape memory polymer and its nanocomposite, ACS Appl. Mater. Interfaces. 9 (2017) 876–883. https://doi.org/10.1021/acsami.6b12824.

[141] D.G. Tamay, T.D. Usal, A.S. Alagoz, D. Yucel, N. Hasirci, V. Hasirci, 3D and 4D printing of polymers for tissue engineering applications, Front. Bioeng. Biotechnol. 7 (2019). https://doi.org/10.3389/fbioe.2019.00164.

[142] K.M. Lee, H. Koerner, R.A. Vaia, T.J. Bunning, T.J. White, Light-activated shape memory of glassy, azobenzene liquid crystalline polymer networks, Soft Matter. 7 (2011) 4318–4324. https://doi.org/10.1039/c1sm00004g.

[143] H. Jiang, S. Kelch, A. Lendlein, Polymers move in response to light, Adv. Mater. 18 (2006) 1471–1475. https://doi.org/10.1002/adma.200502266.

[144] W. Qian, Y. Song, D. Shi, W. Dong, X. Wang, H. Zhang, Photothermal-triggered shape memory polymer prepared by cross-linking porphyrin-loaded micellar particles, Materials (Basel). 12 (2019). https://doi.org/10.3390/ma12030496.

[145] K.C. Hribar, R.B. Metter, J.L. Ifkovits, T. Troxler, J.A. Burdick, Light-induced temperature transitions in biodegradable polymer and nanorod composites, Small. 5 (2009) 1830–1834. https://doi.org/10.1002/smll.200900395.

[146] J. Liang, Y. Xu, Y. Huang, L. Zhang, Y. Wang, Y. Ma, F. Li, T. Guo, Y. Chen, Infrared-triggered actuators from graphene-based nanocomposites, J. Phys. Chem. C. 113 (2009) 9921–9927. https://doi.org/10.1021/jp901284d.

[147] C.J. Barrett, J.I. Mamiya, K.G. Yager, T. Ikeda, Photo-mechanical effects in azobenzene-containing soft materials, Soft Matter. 3 (2007) 1249–1261. https://doi.org/10.1039/b705619b.

[148] * Kimio Sumaru, Katsuhide Ohi, Toshiyuki Takagi, and Toshiyuki Kanamori, T. Shinbo, Photoresponsive Properties of Poly(N-isopropylacrylamide) Hydrogel Partly Modified with Spirobenzopyran, (2006). https://doi.org/10.1021/LA052899+.

[149] Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, Repeatable photoinduced self-healing of covalently cross-linked polymers through reshuffling of trithiocarbonate units, Angew. Chemie - Int. Ed. 50 (2011) 1660–1663. https://doi.org/10.1002/anie.201003888.

[150] M. Moniruzzaman, P. Christogianni, G. Kister, Self-Healing in Epoxy Thermoset Polymer Films Triggered by UV Light, in: Procedia Eng., Elsevier Ltd, 2016: pp. 114–121. https://doi.org/10.1016/j.proeng.2016.06.472.

[151] A. Zolfagharian, A. Kaynak, S.Y. Khoo, A. Kouzani, Pattern-driven 4D printing, Sensors Actuators, A Phys. 274 (2018) 231–243. https://doi.org/10.1016/j.sna.2018.03.034.

[152] H.B. Lu, W.M. Huang, Y.T. Yao, Review of chemo-responsive shape change/memory polymers, Pigment Resin Technol. 42 (2013) 237–246. https://doi.org/10.1108/PRT-11-2012-0079.

[153] W.M. Huang, B. Yang, L. An, C. Li, Y.S. Chan, Water-driven programmable polyurethane shape memory polymer: Demonstration and mechanism, Appl. Phys. Lett. 86 (2005) 1–3. https://doi.org/10.1063/1.1880448.

[154] H. Lu, Y. Liu, J. Leng, S. Du, Qualitative separation of the physical swelling effect on the recovery behavior of shape memory polymer, Eur. Polym. J. 46 (2010) 1908–1914. https://doi.org/10.1016/j.eurpolymj.2010.06.013.

[155] H. Lu, J. Leng, S. Du, A phenomenological approach for the chemo-responsive shape memory effect in amorphous polymers, Soft Matter. 9 (2013) 3851–3858. https://doi.org/10.1039/c3sm27539f.

[156] H. Lu, W.M. Huang, Y.Q. Fu, J. Leng, Quantitative separation of the influence of hydrogen bonding of ethanol/water mixture on the shape recovery behavior of polyurethane shape memory polymer, Smart Mater. Struct. 23 (2014) 125041. https://doi.org/10.1088/0964-1726/23/12/125041.

[157] X. Peng, H. Wang, Shape changing hydrogels and their applications as soft actuators, J. Polym. Sci. Part B Polym. Phys. 56 (2018) 1314–1324. https://doi.org/10.1002/polb.24724.

[158] M.C. Mulakkal, R.S. Trask, V.P. Ting, A.M. Seddon, Responsive cellulose-hydrogel composite ink for 4D printing, Mater. Des. 160 (2018) 108–118. https://doi.org/10.1016/j.matdes.2018.09.009.

[159] S. Zeng, R. Li, S.G. Freire, V.M.M. Garbellotto, E.Y. Huang, A.T. Smith, C. Hu, W.R.T. Tait, Z. Bian, G. Zheng, D. Zhang, L. Sun, Moisture-Responsive Wrinkling Surfaces with Tunable Dynamics, Adv. Mater. 29 (2017). https://doi.org/10.1002/adma.201700828.

[160] M. Ma, L. Guo, D.G. Anderson, R. Langer, Bio-inspired polymer composite actuator and generator driven by water gradients, Science (80-.). 339 (2013) 186–189. https://doi.org/10.1126/science.1230262.

[161] D.D. Han, Y.L. Zhang, H.B. Jiang, H. Xia, J. Feng, Q.D. Chen, H.L. Xu, H.B. Sun, Moisture-responsive graphene paper prepared by self-controlled photoreduction, Adv. Mater. 27 (2015) 332–338. https://doi.org/10.1002/adma.201403587.

[162] C. Lv, H. Xia, Q. Shi, G. Wang, Y.S. Wang, Q.D. Chen, Y.L. Zhang, L.Q. Liu, H.B. Sun, Sensitively Humidity-Driven Actuator Based on Photopolymerizable PEG-DA Films, Adv. Mater. Interfaces. 4 (2017). https://doi.org/10.1002/admi.201601002.

[163] R.T. Shafranek, S.C. Millik, P.T. Smith, C.U. Lee, A.J. Boydston, A. Nelson, Stimuli-responsive materials in additive manufacturing, Prog. Polym. Sci. 93 (2019) 36–67. https://doi.org/10.1016/j.progpolymsci.2019.03.002.

[164] S. Dutta, D. Cohn, Temperature and pH responsive 3D printed scaffolds, J. Mater. Chem. B. 5 (2017) 9514–9521. https://doi.org/10.1039/c7tb02368e.

[165] M. Nadgorny, Z. Xiao, C. Chen, L.A. Connal, Three-Dimensional Printing of pH-Responsive and Functional Polymers on an Affordable Desktop Printer, ACS Appl. Mater. Interfaces. 8 (2016) 28946–28954. https://doi.org/10.1021/acsami.6b07388.

[166] M. Jamal, S.S. Kadam, R. Xiao, F. Jivan, T.M. Onn, R. Fernandes, T.D. Nguyen, D.H. Gracias, Bio-origami hydrogel scaffolds composed of photocrosslinked PEG bilayers, Adv. Healthc. Mater. 2 (2013) 1142–1150. https://doi.org/10.1002/adhm.201200458.

[167] B. Gao, Q. Yang, X. Zhao, G. Jin, Y. Ma, F. Xu, 4D Bioprinting for Biomedical Applications, Trends Biotechnol. 34 (2016) 746–756. https://doi.org/10.1016/j.tibtech.2016.03.004.

[168] M. Bodaghi, A.R. Damanpack, W.H. Liao, Triple shape memory polymers by 4D printing, Smart Mater. Struct. 27 (2018). https://doi.org/10.1088/1361-665X/aabc2a.

[169] F. Zhang, L. Wang, Z. Zheng, Y. Liu, J. Leng, Magnetic programming of 4D printed shape memory composite structures, Compos. Part A Appl. Sci. Manuf. 125 (2019) 105571. https://doi.org/10.1016/j.compositesa.2019.105571.

[170] F.S. Senatov, K. V. Niaza, M.Y. Zadorozhnyy, A. V. Maksimkin, S.D. Kaloshkin, Y.Z. Estrin, Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds, J. Mech. Behav. Biomed. Mater. 57 (2016) 139–148. https://doi.org/10.1016/j.jmbbm.2015.11.036.

[171] B. Vandenbroucke, J.P. Kruth, Selective laser melting of biocompatible metals for rapid manufacturing of medical parts, Rapid Prototyp. J. 13 (2007) 196–203. https://doi.org/10.1108/13552540710776142.

[172] I. Shishkovsky, I. Yadroitsev, I. Smurov, Direct Selective Laser Melting of Nitinol Powder, in: Phys. Procedia, Elsevier B.V., 2012: pp. 447–454. https://doi.org/10.1016/j.phpro.2012.10.060.

[173] M.H. Elahinia, M. Hashemi, M. Tabesh, S.B. Bhaduri, Manufacturing and processing of NiTi implants: A review, Prog. Mater. Sci. 57 (2012) 911–946. https://doi.org/10.1016/j.pmatsci.2011.11.001.

[174] J.Z. Gul, Y.J. Yang, K.Y. Su, K.H. Choi, Omni Directional Multimaterial Soft Cylindrical Actuator and Its Application as a Steerable Catheter, Soft Robot. 4 (2017) 224–240. https://doi.org/10.1089/soro.2016.0042.

[175] W. Su, Z. Wu, Y. Fang, R. Bahr, P.M. Raj, R. Tummala, M.M. Tentzeris, 3D printed wearable flexible SIW and microfluidics sensors for Internet of Things and smart health applications, in: IEEE MTT-S Int. Microw. Symp. Dig., Institute of Electrical and Electronics Engineers Inc., 2017: pp. 544–547. https://doi.org/10.1109/MWSYM.2017.8058621.

[176] S. Xia, S. Song, F. Jia, G. Gao, A flexible, adhesive and self-healable hydrogel-based wearable strain sensor for human motion and physiological signal monitoring, J. Mater. Chem. B. 7 (2019) 4638–4648. https://doi.org/10.1039/c9tb01039d.

[177] C. Wang, H. Wu, Z. Chen, M.T. Mcdowell, Y. Cui, Z. Bao, Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries, Nat. Chem. 5 (2013) 1042–1048. https://doi.org/10.1038/nchem.1802.

[178] J. Wang, F. Liu, F. Tao, Q. Pan, Rationally Designed Self-Healing Hydrogel Electrolyte toward a Smart and Sustainable Supercapacitor, ACS Appl. Mater. Interfaces. 9 (2017) 27745–27753. https://doi.org/10.1021/acsami.7b07836.

[179] A. Chen, R. Yin, L. Cao, C. Yuan, H.K. Ding, W.J. Zhang, Soft robotics: Definition and research issues, in: 2017 24th Int. Conf. Mechatronics Mach. Vis. Pract. M2VIP 2017,

Institute of Electrical and Electronics Engineers Inc., 2017: pp. 366–369. https://doi.org/10.1109/M2VIP.2017.8267170.

[180] J.C. Breger, C. Yoon, R. Xiao, H.R. Kwag, M.O. Wang, J.P. Fisher, T.D. Nguyen, D.H. Gracias, Self-folding thermo-magnetically responsive soft microgrippers, ACS Appl. Mater. Interfaces. 7 (2015) 3398–3405. https://doi.org/10.1021/am508621s.

[181] J.Z. Gul, B.-S. Yang, Y.J. Yang, D.E. Chang, K.H. Choi, In situ UV curable 3D printing of multi-material tri-legged soft bot with spider mimicked multi-step forward dynamic gait, Smart Mater. Struct. 25 (2016) 115009. https://doi.org/10.1088/0964-1726/25/11/115009.

[182] Q. Zhang, J. Wommer, C. O'Rourke, J. Teitelman, Y. Tang, J. Robison, G. Lin, J. Yin, Origami and kirigami inspired self-folding for programming three-dimensional shape shifting of polymer sheets with light, Extrem. Mech. Lett. 11 (2017) 111–120. https://doi.org/10.1016/j.eml.2016.08.004.

[183] Q. Ge, C.K. Dunn, J. Qi, M.L. Dunn, Active origami by 4D printing, (2014). https://doi.org/10.1088/0964-1726/23/9/094007.

[184] J. Koh, S. Kim, K. Cho, Self-Folding Origami Using Torsion Shape Memory Alloy Wire Actuators, in: ASME International, 2014. https://doi.org/10.1115/detc2014-34822.

[185] E. Peraza-Hernandez, D. Hartl, R. Malak, Simulation-based design of a self-folding smart material system, in: Proc. ASME Des. Eng. Tech. Conf., American Society of Mechanical Engineers, 2013. https://doi.org/10.1115/DETC2013-13439.

[186] E.L. Pollard, T.W. Murphey, Development of deployable elastic composite shape memory alloy reinforced (DECSMAR) structures, in: Collect. Tech. Pap. - AIAA/ASME/ASCE/AHS/ASC Struct. Struct. Dyn. Mater. Conf., 2006: pp. 1044–1061. https://doi.org/10.2514/6.2006-1681.

[187] E. Peraza-Hernandez, D. Hartl, E. Galvan, R. Malak, Design and optimization of a shape memory alloy-based self-folding sheet, J. Mech. Des. Trans. ASME. 135 (2013). https://doi.org/10.1115/1.4025382.

[188] W. Su, R. Bahr, S.A. Nauroze, M.M. Tentzeris, Novel 3D-printed "Chinese Fan" Bow-tie antennas for origami/shape-changing configurations, in: 2017 IEEE Antennas Propag. Soc. Int. Symp. Proc., Institute of Electrical and Electronics Engineers Inc., 2017: pp. 1245–1246. https://doi.org/10.1109/APUSNCURSINRSM.2017.8072665.

[189] A. Lai, Z. Du, C.L. Gan, C.A. Schuh, Shape memory and superelastic ceramics at small scales, Science (80-.). 341 (2013) 1505–1508. https://doi.org/10.1126/science.1239745.

[190] A.F. Ghazal, M. Zhang, Z. Liu, Spontaneous Color Change of 3D Printed Healthy Food Product over Time after Printing as a Novel Application for 4D Food Printing, Food Bioprocess Technol. 12 (2019) 1627–1645. https://doi.org/10.1007/s11947-019-02327-6.

[191] C. He, M. Zhang, C. Guo, 4D printing of mashed potato/purple sweet potato puree with spontaneous color change, Innov. Food Sci. Emerg. Technol. 59 (2020). https://doi.org/10.1016/j.ifset.2019.102250.

[192] A. Duan, Y. Li, B. Li, P. Zhu, 3D-printable thermochromic acrylic resin with excellent mechanical performance, J. Appl. Polym. Sci. 137 (2020) 48277. https://doi.org/10.1002/app.48277.

[193] Y. Li, S. Cao, T. Li, L. Wang, Harnessing 3D printed residual stress to design heat-shrinkable metamaterials, Results Phys. 11 (2018) 85–95. https://doi.org/10.1016/j.rinp.2018.08.034.

[194] H. Fang, S.-C.A. Chu, Y. Xia, K.-W. Wang, Programmable Self-Locking Origami Mechanical Metamaterials, Adv. Mater. 30 (2018) 1706311. https://doi.org/10.1002/adma.201706311.

[195] P. Mostafalu, W. Lenk, M.R. Dokmeci, B. Ziaie, A. Khademhosseini, S.R. Sonkusale, Wireless Flexible Smart Bandage for Continuous Monitoring of Wound Oxygenation, IEEE Trans. Biomed. Circuits Syst. 9 (2015) 670–677. https://doi.org/10.1109/TBCAS.2015.2488582.

[196] Y. Mao, K. Yu, M.S. Isakov, J. Wu, M.L. Dunn, H. Jerry Qi, Sequential Self-Folding Structures by 3D Printed Digital Shape Memory Polymers, Sci. Rep. 5 (2015). https://doi.org/10.1038/srep13616.

[197] D.C. Zuluaga, A. Menges, 3D printed hygroscopic programmable material systems, in: Mater. Res. Soc. Symp. Proc., Materials Research Society, 2015: pp. 24–31. https://doi.org/10.1557/opl.2015.644.

[198] B. Hao, Y. Li, X. Xiao, W. Dai, H. Chen, S. Chen, A facile photo-polymerization method for reconfigurable shape memory polymers, Mater. Lett. 254 (2019) 214–217. https://doi.org/10.1016/j.matlet.2019.07.071.

[199] T. Umedachi, V. Vikas, Softworm Robots Softworms: The Design and Control of Non-pneumatic, 3D-Printed, Deformable Robots, n.d.

[200] E. Carreño-Morelli, S. Martinerie, J.E. Bidaux, Three-dimensional printing of shape memory alloys, in: Mater. Sci. Forum, Trans Tech Publ, 2007: pp. 477–480.

[201] A. Mostafaei, P. Rodriguez De Vecchis, E.L. Stevens, M. Chmielus, Sintering regimes and resulting microstructure and properties of binder jet 3D printed Ni-Mn-Ga magnetic shape memory alloys, Acta Mater. 154 (2018) 355–364. https://doi.org/10.1016/j.actamat.2018.05.047.

[202] G.R. Donoso, M. Walczak, E.R. Moore, J.A. Ramos-Grez, Towards direct metal laser fabrication of Cu-based shape memory alloys, Rapid Prototyp. J. 23 (2017) 329–336. https://doi.org/10.1108/RPJ-02-2016-0017.

[203] J. Ma, B. Franco, G. Tapia, K. Karayagiz, L. Johnson, J. Liu, R. Arroyave, I. Karaman, A. Elwany, Spatial control of functional response in 4D-printed active metallic structures, Sci. Rep. 7 (2017) 1–8. https://doi.org/10.1038/srep46707.

[204] S. Kee, M.A. Haque, D. Corzo, H.N. Alshareef, D. Baran, Self-Healing and Stretchable 3D-Printed Organic Thermoelectrics, Adv. Funct. Mater. (2019) 1905426. https://doi.org/10.1002/adfm.201905426.

[205] N.G. Cheng, A. Gopinath, L. Wang, K. Iagnemma, A.E. Hosoi, Thermally Tunable, Self-Healing Composites for Soft Robotic Applications, Macromol. Mater. Eng. 299 (2014) 1279–1284. https://doi.org/10.1002/mame.201400017.

[206] M.A. Darabi, A. Khosrozadeh, R. Mbeleck, Y. Liu, Q. Chang, J. Jiang, J. Cai, Q. Wang, G. Luo, M. Xing, Skin-Inspired Multifunctional Autonomic-Intrinsic Conductive Self-Healing Hydrogels with Pressure Sensitivity, Stretchability, and 3D Printability, Adv. Mater. 29 (2017) 1700533. https://doi.org/10.1002/adma.201700533.

[207] S. Liu, L. Li, Ultrastretchable and Self-Healing Double-Network Hydrogel for 3D Printing and Strain Sensor, ACS Appl. Mater. Interfaces. 9 (2017) 26429–26437. https://doi.org/10.1021/acsami.7b07445.

[208] A.R. Hamilton, N.R. Sottos, S.R. White, Self-Healing of Internal Damage in Synthetic Vascular Materials, Adv. Mater. 22 (2010) 5159–5163. https://doi.org/10.1002/adma.201002561.

Figure 1 Schematic overview of 4D printing, including 4D printing technologies, materials and stimuli.

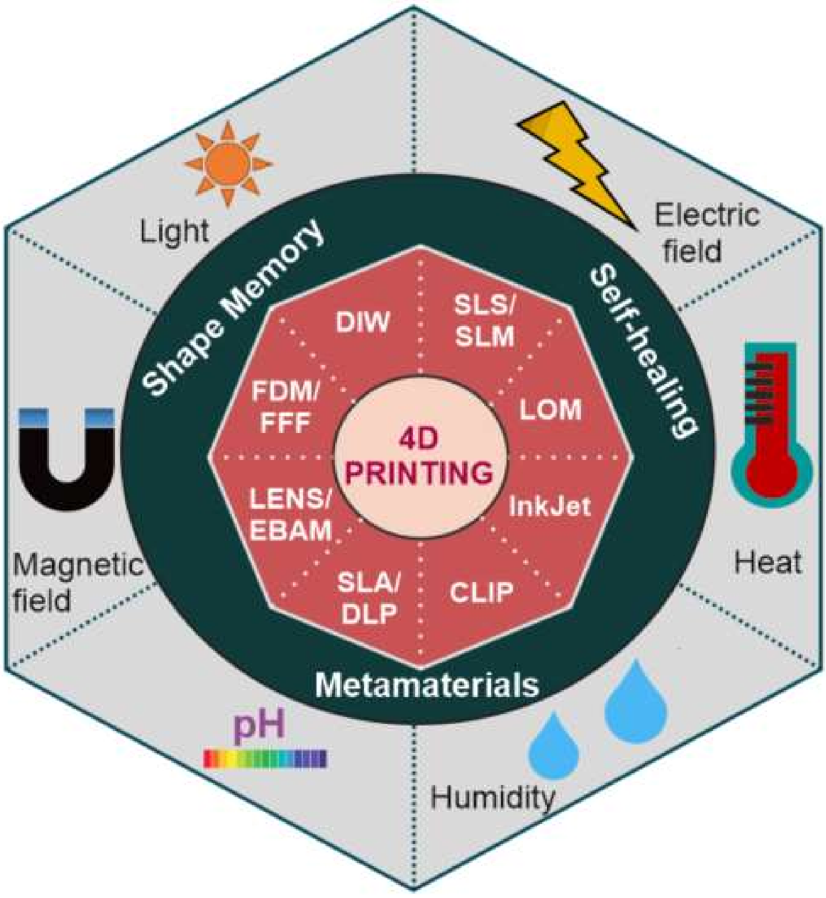

Figure 2 (i) μSLA printed SMM flower programmed to bloom over different temperature ranges. [59] (ii) Composite hydrogel patterned stripes. Scale bar = 1 cm.[61] (iii) Shape morphing flower constructed from a simple mesh grid at 0° and 90° printed using a composite ink made up of cellulose fibrils, N, N-dimethyl acrylamide, photoinitiator using DIW.[43]

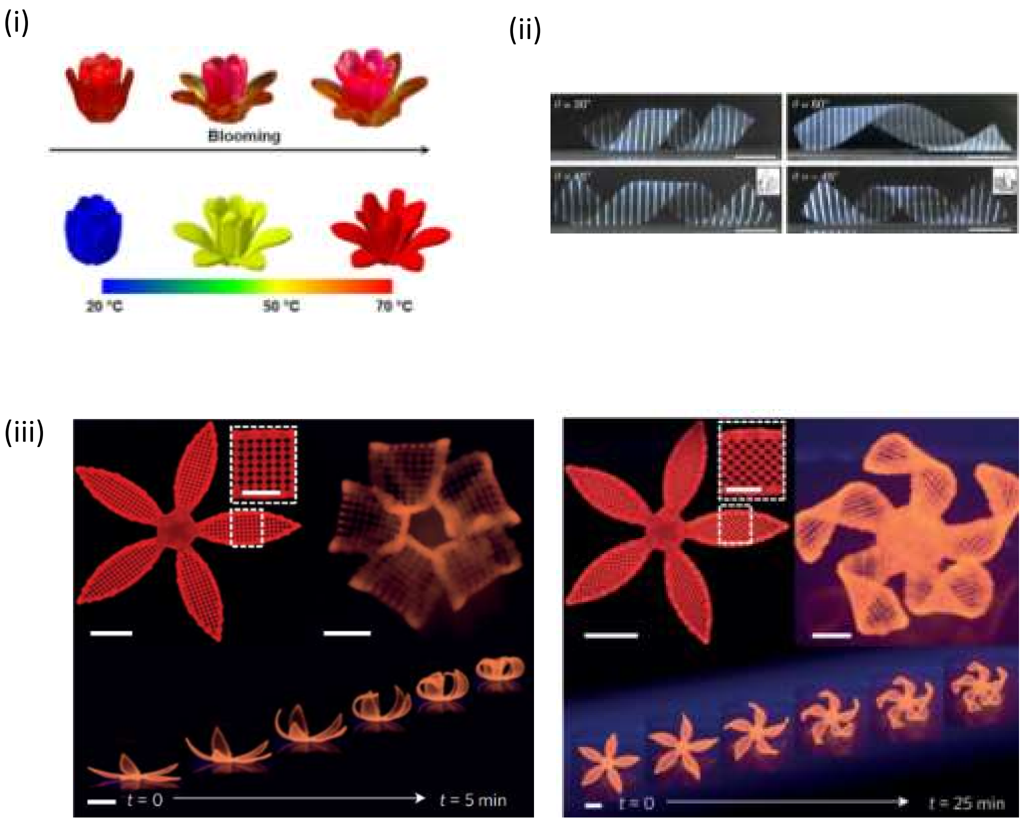

Figure 3 (i) Reversible shape morphing Vitrimer-based materials via exposure to UV and thermal changes.[73] (ii) 4D printed multi-material hydrogels for foldable structures. [77]

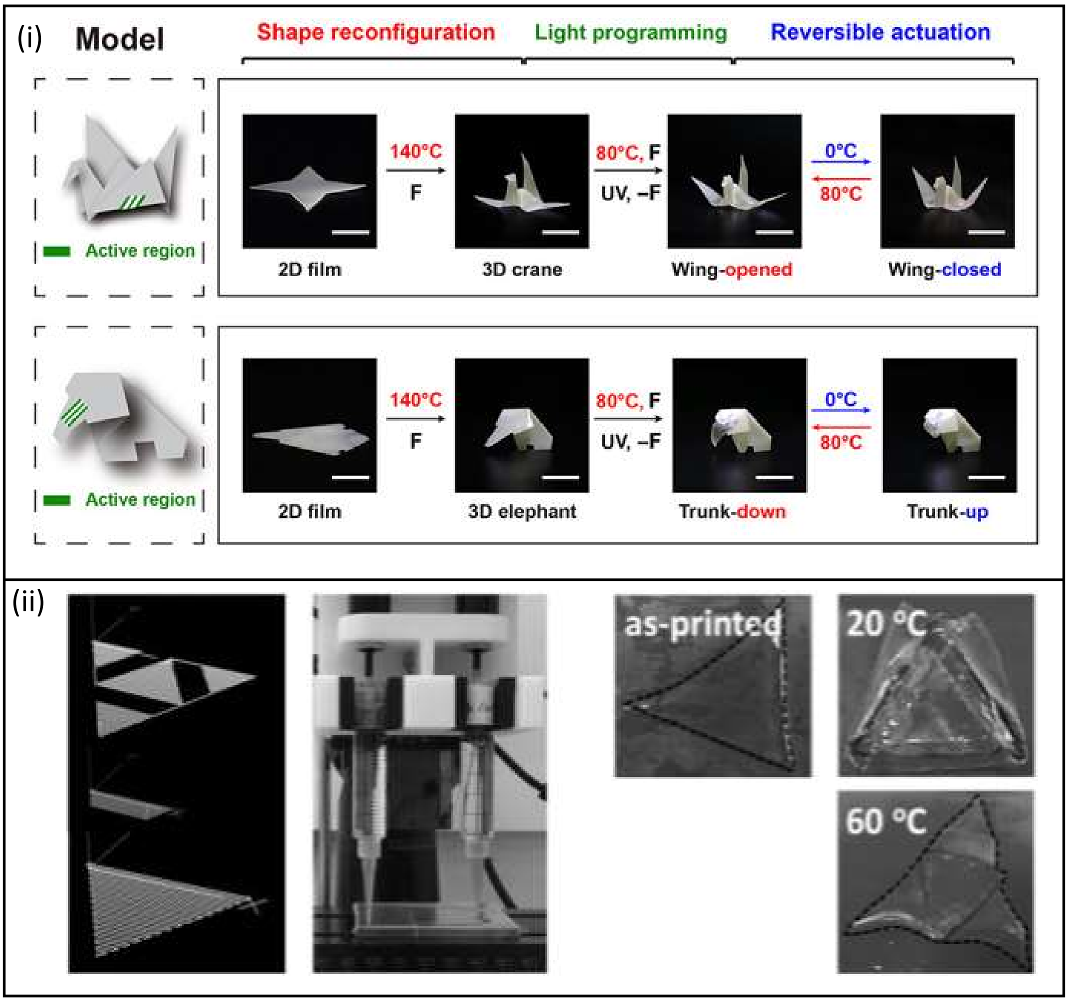

Figure 4 (i) Schematic diagram of the shape morphing particle capture process (top image). Experimental diagram showing the capture process including SEM images of the micro cage (left inset image (a) and right inset image (d)), scale bar 10 µm.[78] (ii) (ii) Ink-jet printed multi-material gripper using SMA. The photographs show the gripper picking up a 15 g cylindrical component over a 15 s period, the gripper is initiated *via* Joule heating.[86]

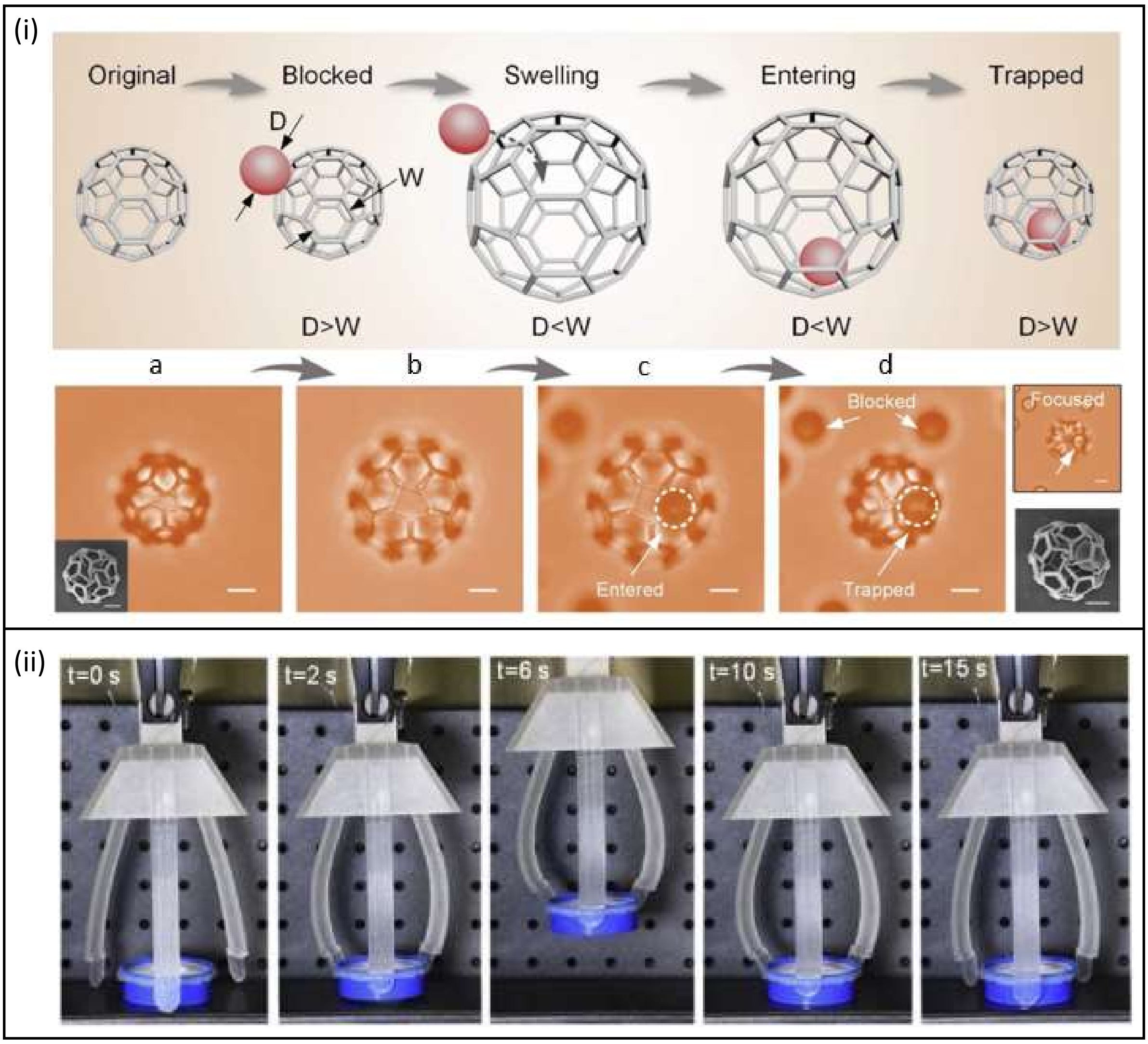

Figure 5 (i) Design of a SMA actuated soft worm robot, the body and feet have been printed using TangoPlus elastomer, whilst the surface and face are made from VeroClear. The yellow channels represent the SMA coils. (ii) Photographs showing a SMA activated worm structure crawling from left to right at 1 s intervals. [87] (iii-v) 4D printing (DIW) of elastomeric derived ceramics (EDC) ZrO_2 nanoplatelets and PDMS. The bending configuration is a result of printing programmed patterns on pre-streched precursor. (iii) helical ribbon (iv) saddle surface (v) important geometric parameters. (vi) Images representing 4D printed EDCs fully ceramics structures were obtain following a heat treatment of 1300°C in argon. [95]

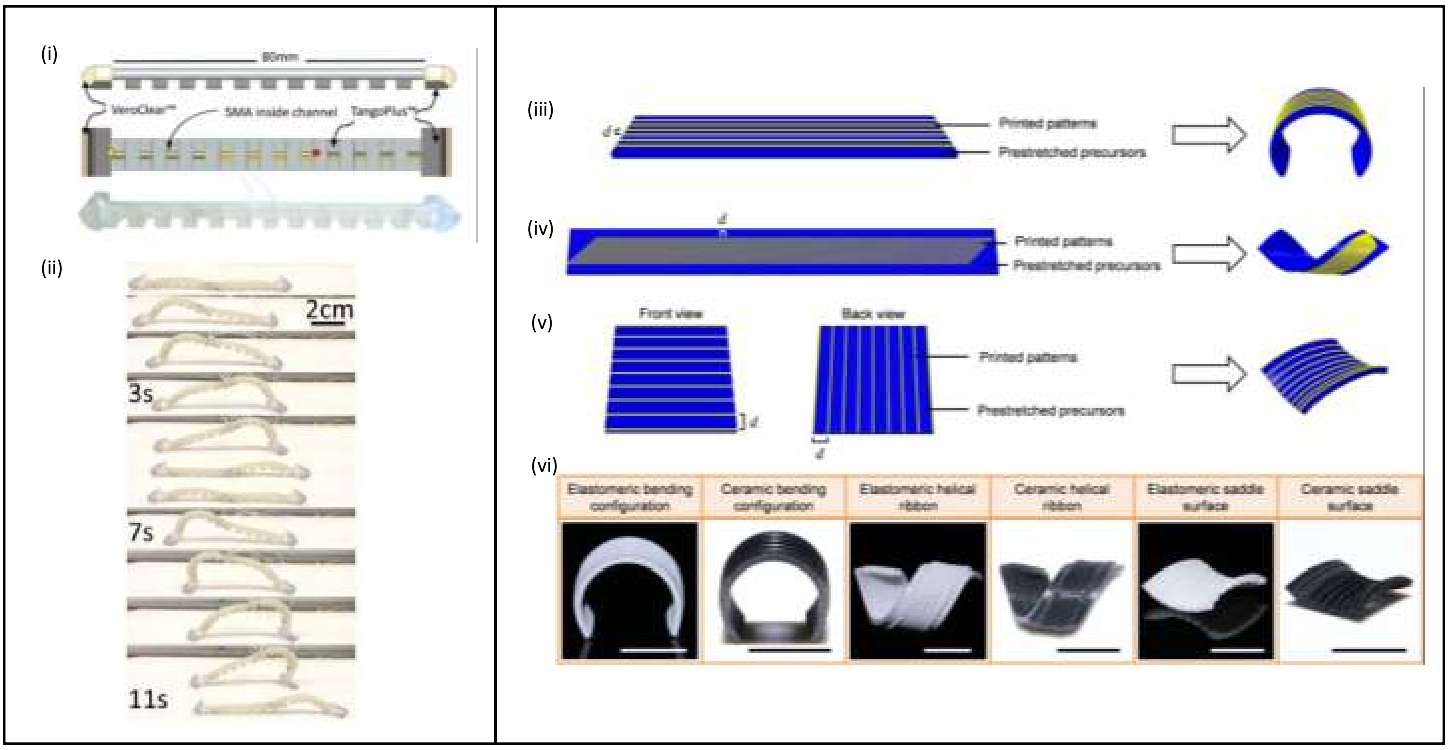

Figure 6 (i) 4D Printed auxetic metamaterials from left to right: programmed state, active state and permanent state. [103] Scale bar is 10 mm. (ii) Photograph of a mechanical metamaterial door handle in action. [106] (iii) (A) schematic of the AM process. (B) Photocurable reaction of SMP (C) DMA data showing the storage modulus, loss modulus and tan δ of SMP. (D) Photographs showing the deformation process of micro lattice.[104] (iv) PDMS shape-morphing structures using complex geometries and multi-material printings. [109]

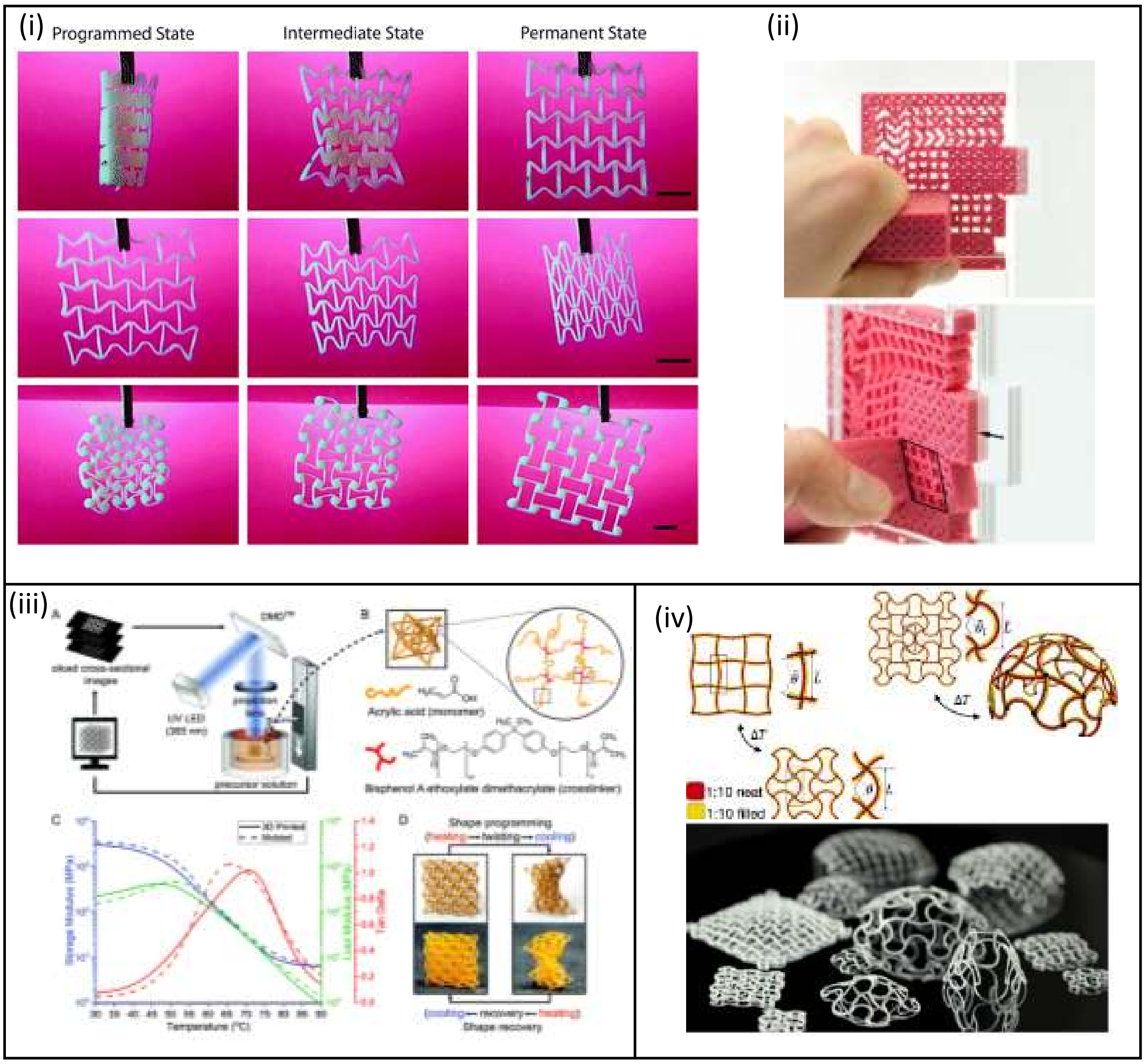

Figure 7(i) Photograph of vascular beam crack pattern and microscope images of the healing process after 4-point bend. [115] (ii) CT grey level image showing the concreate matrix, cracks, PLA vascular tubes and the sodium silicate self-healing agent. The 3D system has been reconstructed to show the vascular mechanisms, the yellow area represents the cement, violet sections represent the PLA vascular structure, blue section represents sodium silicate gel and the green area is the gel filled in cracks.

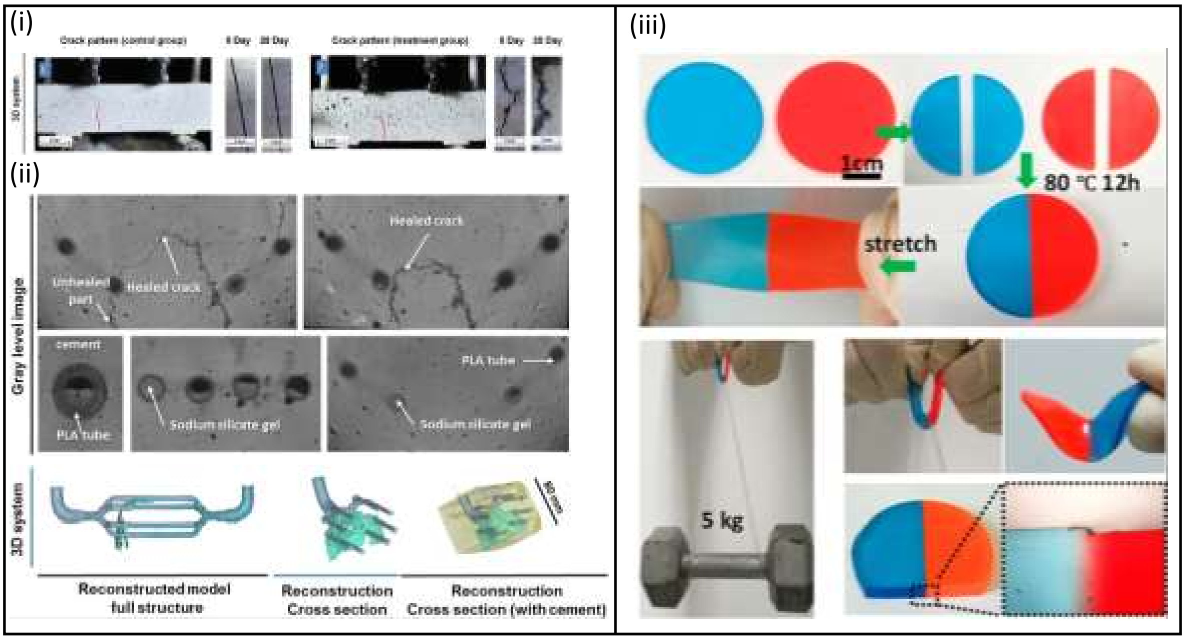

Figure 8 (i) Images of silicon actuators transforming from 2D to 3D at 120 and 170 °C. [130] (ii) 4D printed grippers using electrically responsive hydrogels. (a) Schematic of the action of the grippers with different beam widths. (b) Grippers gripping an object with assistance from an applied electric field. [132] (iii) Schematic of the shape recovery process (above),

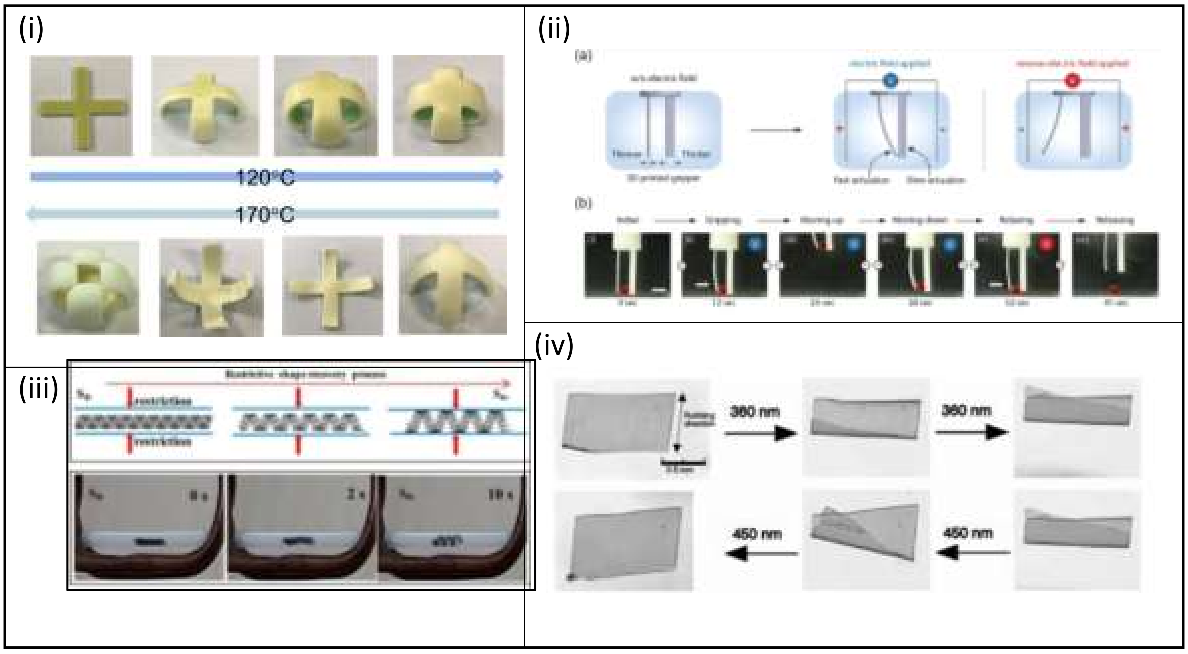

Figure 9 (i) 4D printed moisture responsive CMC. [158] (ii) (a) Photographs of the shape recovery process of bone repair structures deploying over time (b) Process of 4D printed injectable bone repair for tissue engineering applications. [169] (iii) Printed shape memory electronic device using SLA and ink-jet printing. [60]

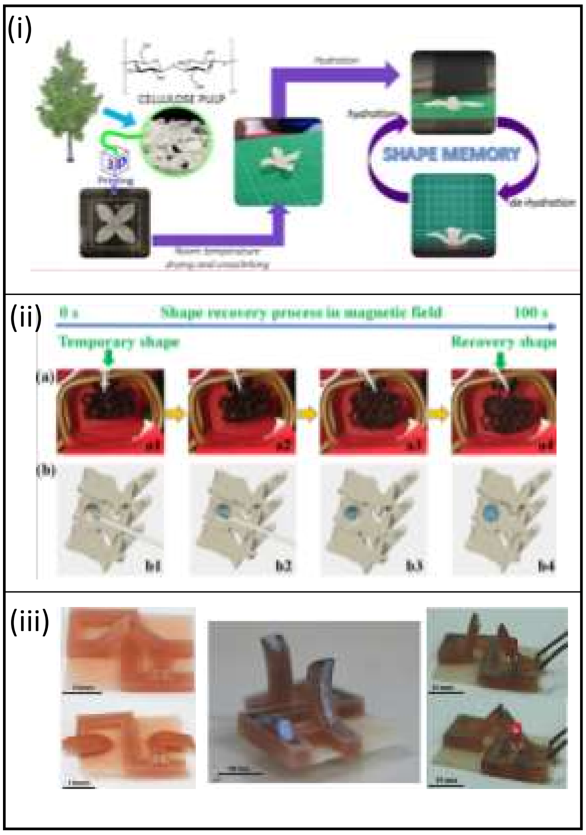

Figure 10 (i) Diagram of shape memory folding of thermally responsive materials. [180] (ii) Process of self-folding packaging, (a) opened box printed via SLA (b) closed box upon cooling below the transition temperature. (c) Open pyramid shape above the transition temperature. (d) closed pyramid structure upon cooling below the transition temperature. [183] (iii) SLA printed origami antenna. .[188]

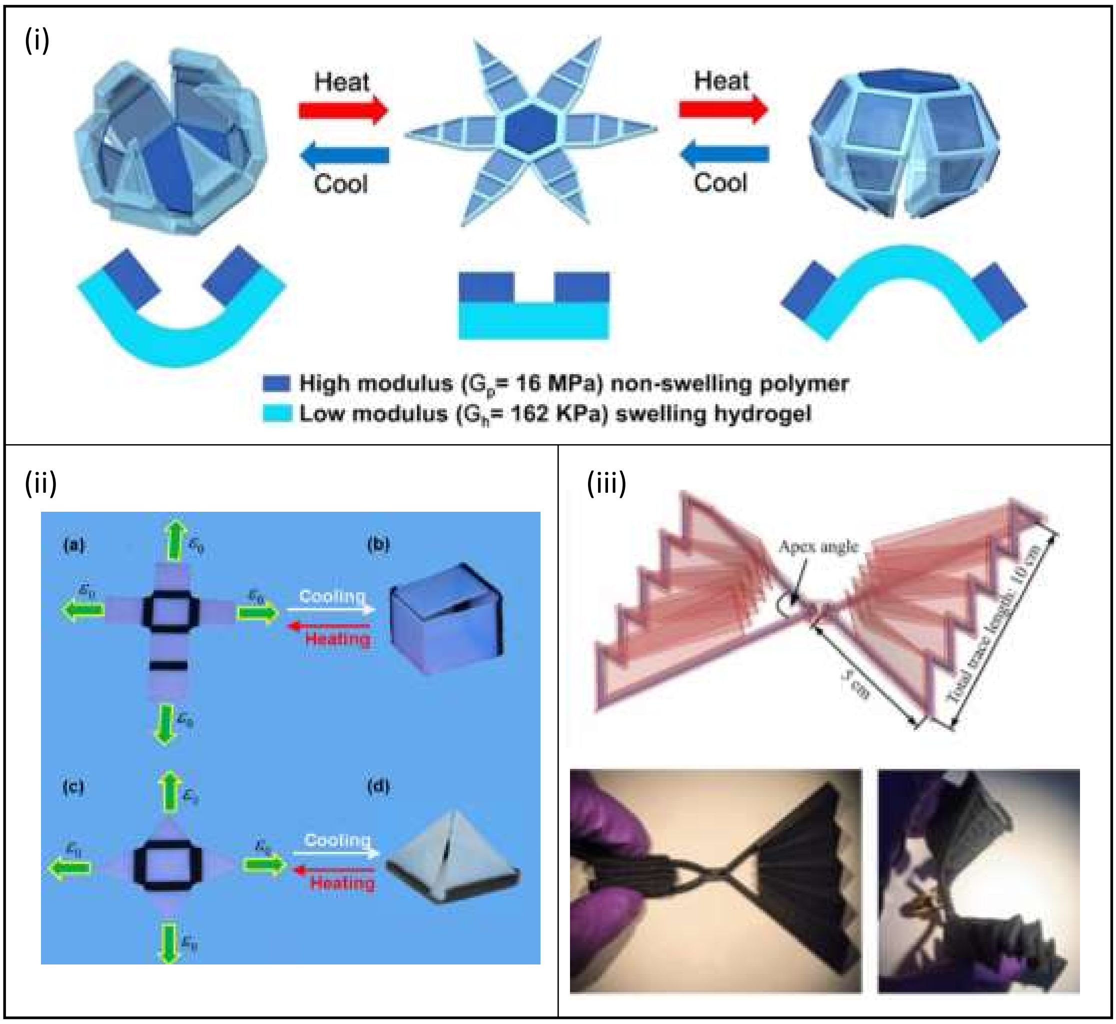

Table 1 4D printed smart materials and their associated stimulus for transformative properties and applications.

Material	Printing Technology	Stimulus	Applications	Ref.
PNIPAAm hydrogel	µSLA	Thermal	Soft robotics, microfluidic devices, drug delivery devices.	[129]
Poly(2-vinylpyridine)	FDM	pH	Membranes and photonic gels	[165]
Carboxymethyl cellulose (CMC) hydrocolloid	DIW	Moisture	Complex architectures and actuators	[158]
Poly(lactic acid) and iron oxide nanoparticles	DIW (UV cross-linked)	Magnetic field	Scaffold for an intravascular stent	[140]
PEO/CNT	µSLA	Electric field (induced heating)	Artificial muscles, soft robotics	[131]
Acrylic and modified thermochromic pigment	SLA	Thermal	Smart temperatures sensors, food and medicine packaging	[192]
Commercial resins VeroWhite and TangoPlus	Ink-jet	Thermal	Aerospace, coating protections, micro-robotics	[193]
CNTs layer deposited on top of PCL macromethacrylate	Ink-jet	Electric field (induced heating)	Shape-memory electrical devices	[60]
PDMS and ZrO2 nano-particles	DIW	Thermal	Aerospace propulsion, space exploration, electrical devices	[95]
Hydrogel, with large amounts of carboxyl groups in the side chain	Direct writing using femtosecond laser	Changes in pH	Single-cell analysis and drug delivery	[78]
Commercial resin	Ink-jet	Rearrangement of voxels due to kinetic energy	Replacement for mechanical hinges, pliers	[106]

Commercial flexible resin (Form-2)	SLA	Rearrangement of voxels due to kinetic energy	Self-locking mechanical metamaterials	[194]
Commercial resin (TangoPlus)	Ink-jet	Electronics	Smart Bandages (oxygen sensor)	[195]
Commercial multi-material (VeroWhite and Tangoblack)	Ink-jet	Thermal	Self-locking mechanisms	[196]
Wood veneer composite	FDM	Humidity	Weather responsive aperture mechanisms	[197]
hexamethylenediacrylate and 1,6-Hexanedithiol	SLA	Thermal	Ink for 4D printing applications	[198]
Nickel-Titanium alloy	Multimaterial inkjet 3D printing	Thermal	Soft robotic grippers	[86]
BMF-100 SMA, Urethane and Epoxy	Customized UV-3D printing	Electric field (induced heating)	Soft robotic devices, sensing, drug delivery, energy production, artificial synthetics.	[181]
SMA coils (BMX-100, Toki Corp., Tokyo, Japan), TangoPlus, VeroClear™	Polyjet (Objet, Connex 500)	Electric field (induced heating)	versatile deformable robots	[199]
Ti-50.5at%Ni pre-alloyed powder and a thermoplastic binder	InkJ-jet	Thermal	NiTi alloys –based 4D printing applications	[200]
Ni-Mn-Ga magnetic SMA	Binder jet 3D	Thermal	Energy applications, lightweight structures, magnets, and sensors	[201]
Cu-Al-Ni SMA	SLM	Thermal	SMA 4D printing applications, medical devices	[202]
Ni-Ti SMA	SLM	Thermal	Medicine and aerospace applications	[203]
(PLA)/15 wt% hydroxyapatite (HA)	FFF	Thermal	Self-fitting bone implants	[170]

Polycrystalline zirconia doped with ceria and yttria	Focused ion-beam milling	Thermal	Mechanical design, actuation, energy-damping, and energy-harvesting applications	[49]
ZrO_2 NPs and PDMS	DIW	Thermal	Aerospace propulsion, and bio-inspired tough ceramic/organic hybrid materials	[95]

Table 1 4D printable self-healing materials, properties and applications.

Material	**Printing Technology**	**Stimulus**	**Healing efficiency (%)**	**Healing mechanism**	**Applications**	**Ref.**
Photo elastomer	SLA	Thermal(60 °C)	90-100 (mechanical/tensile)	Reversible thiol groups	Self-healing shoe soles	[124]
DMSO-mixed PEDOT: PSS and Triton X-100 (healing agent)	DIW	Autonomous	>85 % of initial power output	hydrogen bonding	Wearable thermoelectric generators	[204]
Wax coated polyurethane foams	Ink-jet	Thermal (71 °C)	N/A	Melting and reforming of wax upon heating and cooling	Soft robotics	[205]
PPy and chitosan hydrogel	DIW	Autonomous	Complete mechanical recovery and 90 % electrical conductivity restored	Dynamic ionic interactions of carboxylic groups of PAA and ferric ions	Mimic human skin for sensing applications and wearable devices	[206]
K Carrageenan/ PAAm DN Hydrogel	DIW	Thermal (90 °C for 20 mins)	99.2 % (electrical conductivity)	Gel-sol-gel transition due to heating	Strain sensors for monitoring human body motions.	[207]

Epoxy	DIW	30 °C for 48h	86 % (mechanical, first cycle)	Vascular network of healing agent (capillary action)	Self-healing material to mimic natural mechanisms	[208]
Polyurethane	DLP	Thermal (80 °C 12 h)	95 % (mechanical/tensile strength)	Disulfide bonds	Flexible electronics, soft robotics and sensors.	[125]