4D printing of shape memory polymer composites: A review on fabrication techniques, applications, and future perspectives

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Abstract

In recent years, there has been rising interest in additively manufactured shape memory polymers (SMPs) and their multi-functional composites. Four-dimensional (4D) printing is an intriguing additive manufacturing field, which uses time-responsive programmable materials. Stimuli-responsive polymers present an ability to retain their original shapes from a programmed temporary shape upon exposure to different external stimuli including heat, light, electricity, humidity, or magnetism. In recent years, rapid technological developments have been made in the field of smart and multi-functional materials by integrating 4D printing (4DP) and shape memory polymer composites (SMPCs). 4DP of SMPCs helps in exploring the myriad engineering applications including automotive, soft robotics, food, smart textiles, biomedical devices, mechatronics, and wearable electronics. Herein, this review article presents important 4DP technologies in conjunction with the underlying functionalities of stimuli-responsive polymer composites. This review also elucidates the future opportunities of 4D-printed SMPCs in terms of preprogramming knowledge, multi-way SMPCs, multi-material printing, sustainability, and potential applications. Finally, based on the characteristics of the SMPCs employed for each technology illustrative examples of the principal applications are provided. It is anticipated that the insightful exploration of this novel field could support future advancements as well as spur innovations in the 4DP field.

Keywords: 3D printing, 4D printing, Shape memory polymers, Polymer composites, Stimuli-responsive polymers

List of abbreviations

2D	Two-dimensional
3D	Three-dimensional
4D	Four-dimensional
3DP	3D printing
4DP	4D printing
4DPC	4D printing of composites
β-CD	β-cyclodextrin
AA	Acrylic acid
ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
AFP	Automated fiber placement
AESO	Acrylated epoxidized soybean oil
Ag-NWs	Silver nanowires

BA	Butyl acrylate
BP	Black phosphorus
BPA	Bisphenol A ethoxylate dimethacrylate
CAD	Computer-aided design
CB	Carbon black
CCF	Continuous carbon fiber
CF	Carbon fiber
CFF	Continuous flax fiber
CMC	Carboxymethyl cellulose
CNF	Carbon nanofiber
CNT	Carbon nanotube
COVID-19	Coronavirus Disease 2019
EA	Ethyl acetate
EC	Ethyl cellulose
ECG	Electrocardiogram
EPOX	3,4-epoxycyclohexanecarboxylate
ESBO	Epoxidized soybean oil
DED	Direct energy deposition
DGEBA	Bisphenol A diglycidyl ether
DIW	Direct ink writing
DLP	Digital light processing
DLW	Direct laser writing
DMAEMA	2-(dimethylamino)ethyl Methacrylate
DMD	Digital micromirror device
FFF	Fused filament fabrication
FDM	Fused deposition modeling
GF	Glass fiber
GnPs	Graphene nanoplatelets
HEA	2-hydroxyethyl acrylate
HBCs	Hygromorph biocomposites
HUVECs	Human umbilical vein endothelial cells
IJP	Inkjet printing
IPA	Isopropyl alcohol
IPN	Interpenetrated polymer network
ITOP	Integrated tissue–organ printer
MA	Methacrylic anhydride
MWCNT	Multi-walled carbon nanotube
MJ	Material jetting
MSC	Mesenchymal stem cell
NF	Natural fiber
NIR	Near infrared
NPs	Nanoparticles
PA	Polyamide
PBS	Polybutylene Succinate
PC	Polycarbonate
PE	Polyethylene

PEMA	Poly(ethylene-co-methacrylic acid)
PEN	Polyethylene naphthalate
PET	Polyethene terephthalate
PCL	Polycaprolactone
PCLMA	Polycaprolactone methacrylate
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycols
PEGDA	Poly(ethylene glycol) diacrylate
PEGDMA	Poly (ethylene glycol) dimethacrylate
PEDOT	Poly(3,4 ethylenedioxythiophene)
PEEK	Polyetheretherketone
PLA	Polylactic acid
PLA-TMC	Poly(lactic acid-co-trimethylene carbonate)
PLMC	Poly (D,L-lactide-co-trimethylene carbonate)
PNIPAM	Poly(N-isopropylacrylamide)
PNVCL	Poly(N-Vinylcaprolactam)
PP	Polypropolene
PPSF	Polyphenylsulfone
PSS	Polystyrene sulfonate
PTFE	Polytetrafluoroethylene
PTMC	Poly (trimethylene carbonate)
PU	Polyurethane
PUA	Polyurethane acrylate
PUDA	Polyurethane diels−alder bond
PVC	Polyvinyl chloride
PμSL	Micro-stereolithography
SA	Sodium alginate
SCMs	Shape-changing materials
SCO	Spin-crossover
SEM	Scanning electron microscope
SLA	Stereolithography
SLM	Selective laser melting
SLS	Selective laser sintering
SMA	Shape-memory alloy
SMCr	Shape-memory ceramic
SME	Shape-memory effect
SMG	Shape-memory gel
SMH	Shape-memory hybrid
SMP	Shape-memory polymer
SMPC	Shape-memory polymer composite
SMM	Shape-memory materials
SPS	Strain perception strengthening
SRM	Stimuli-responsive material
RGO	Reduced graphene oxide
TCP	Tricalcium phosphate
TEGDMA	Triethylene glycol dimethacrylate

T_g	Glass transition temperature
THFM	Tetrahydrofurfuryl methacrylate
TPE	Thermoplastic elastomer
TPP	Two-photon polymerization
TPO	Diphenyl (2, 4, 6-trimethyl benzoyl) phosphine oxide
TPU	Thermoplastic polyurethane
UV	Ultraviolet
VP	Vat photopolymerization
WF	Wood fiber

1. Introduction

Additive manufacturing (AM) technology is extensively adopted for the digital and smart manufacturing of different materials [1]–[3]. In this technology, materials are created by adding layers in three dimensions (3D) with the help of computer-aided design (CAD) [4]–[6]. AM also refers as 3D printing (3DP), can be employed in the manufacturing of different materials including metals, polymers, ceramics, composites, cermets, and metamaterials [7]–[9]. 3DP offers a wide range of advantages that includes low cost, wide design spectrum, compact size, high adaptability, and ability to form precise and complex geometries [10]–[12]. The large-scale manufacturing of materials through 3DP is still limited in industries due to associated slow speed and an unbalanced trade-off between the quality and size of the printed part [13]–[16]. In addition to this, 3DP techniques generate static structures and cannot be employed for the development of the structures for dynamic applications [17]–[20]. With persistent progress in materials science, the 3DP has also gone through significant advancement and it has been upgraded to 4D printing (4DP) [21]–[23]. It is a novel technology that emerged in 2013, and it is programmed to transform the shape of the printed parts into artifacts [24]–[26]. 4DP envisages the self-assembly of the structure in the absence of conventional driving equipment, which also helps to simplify the manufacturing process [27]–[29]. It is the next-generation printing process that allows the smart or programmable materials to transform their shape with time due to the response of the external stimuli [30]–[32]. Additionally, 4DP technology has excellent perspectives in controlling the various factors including failure rate, minimizing the assembly time, and the overall cost [33]–[35]. The shape morphing pattern in 4DP is driven by programmed spatially controlled anisotropies produced from 3DP techniques [36], which usually involve the common multilayer shapes with various materials components, cross-link densities, percentage of weight, and alignment of different additives and fillers [37]–[39]. Additionally, the idea of self-assembly is already built in 4DP techniques, for instance, both raw materials and different assembling, are fed directly into the 4DP machine [40]–[42]. Shape memory polymers (SMPs) are those materials that have the ability to deform their shape and then recover to their original shapes upon exposure to external stimuli [43] including heat [44], electricity [45], light [46], magnetic field [47], thermal [48], moisture [49], and chemicals [50]. Owing to the dynamic functions and stimuli-responsive behavior, these materials are extensively used for the printing of smart textile, flexible electronic equipment, self-folding packaging, automotive parts, deployable architectures, tissue constructs, drug delivery devices, and adaptive wind turbine blades applications [51]–[53]. Figure 1 provides a detailed overview of 4DP technology.

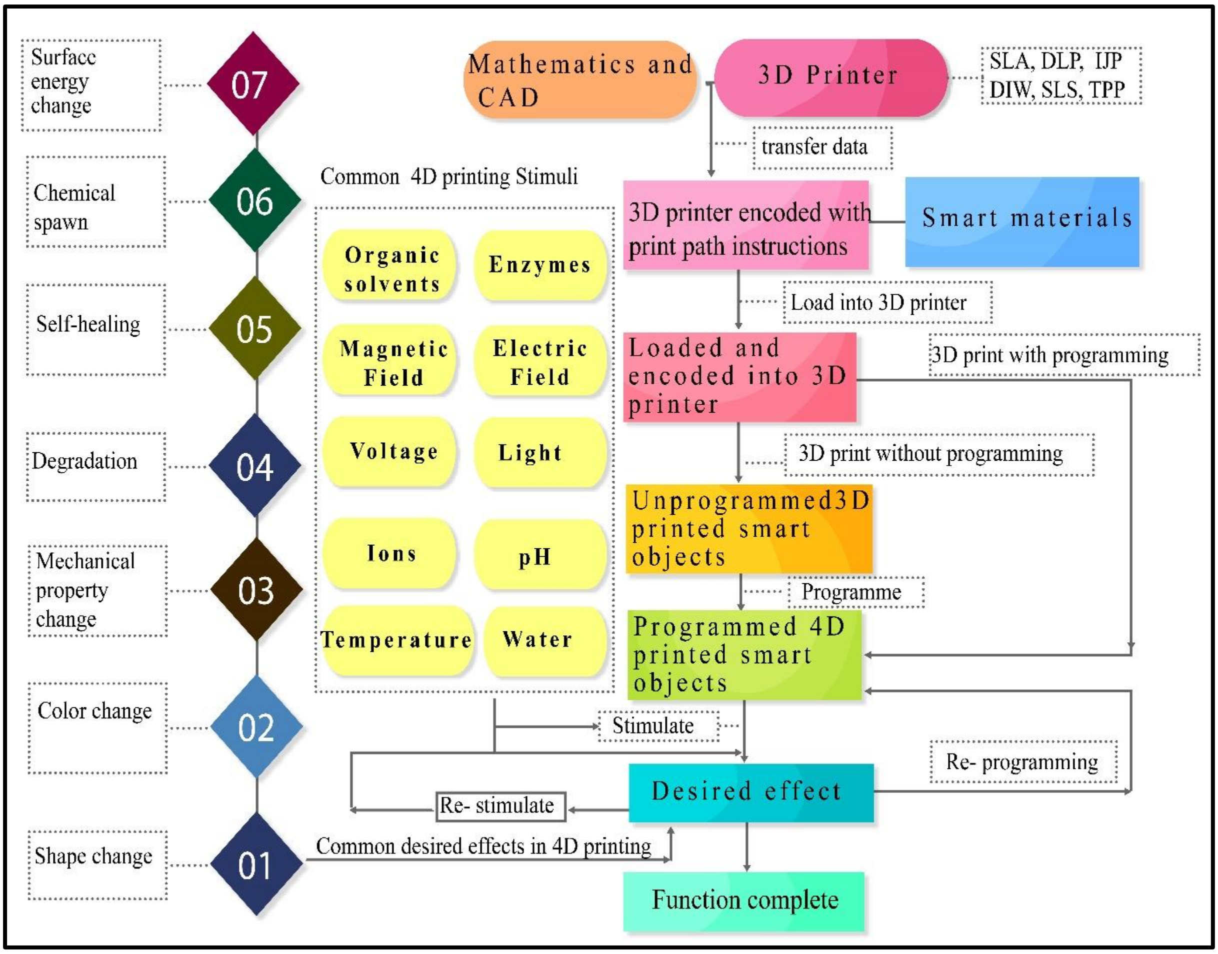

Figure 1. Flow diagram illustrating the evolution of 3DP technology to 4DP technology

1.1. Review Methodology

Since the inception of 4DP in 2013, the impact of 4DP technology has been continuously increasing in different engineering fields and requires up-to-date knowledge about 4DP techniques and novel stimuli-responsive materials (SRMs) to instigate the readers about this latest and futuristic rapid prototyping technology. The purpose of this review is to highlight and critically analyze seminal works of 4D-printed shape memory polymer composites (SMPCs). This review also elucidates different stimuli-responsive polymer composite mechanisms as well as illustrates biomedical (stents, tissue constructs, scaffolds), textile, soft robotics, and electronics applications. This review incorporates current findings, future perspective, and challenges in the designing of SMPCs through 4DP. It is envisioned that 4D-printed intricate and dynamic structures will be translated into different engineering applications by managing demands of key regulators.

2. Fundamentals of 4D printing technology

In the contemporary era, 4DP technology has intrigued engineers, designers, and scientists, due to cutting-edge results, which will be helpful in solving different industrial issues. It is a combination of intelligent materials, 3D printing, and a well-programmed design. This technology generates a variety of metamaterial structures under changing environments [54]. This section aims to elucidate key features of 4DP technology.

2.1. Shape transformation approaches

During 4DP of SRMs, the environmental stimuli enable transformation functions like twisting, bending, stretching, rolling, or swelling, as well as state and property changes depending upon the geometrical design. These transformations are mandatory for the development of smart devices and systems [55]. Furthermore, these changes in transformation functions with respect to time change the properties, states, forms, or functionalities of the SRMs to develop intricate mechanisms such as buckling, helixing, waving, or curling functions [56].

2.2. Stimuli-responsive materials in 4D printing

4DP is not a straightforward process rather it integrates printing techniques and intelligent materials to print shape-changing architectures upon exposure to external stimulus [57]. Intelligent materials possess the ability to change their properties with respect to time. These materials are highly sensitive to environmental stimuli and exhibit behaviors such as self-capability, self-healing, self-assembly, and shape-memory [58]. Some smart materials also exhibit shape as well as color-changing properties upon exposure to ultraviolet (UV) or visible light stimulus [59]. This subsection will illustrate 4DP behavior and different stimuli-responsive mechanisms of smart materials, especially SMPCs.

One of the distinct features of 4DP technology is the shape-changing behavior under the action of mechanical, chemical, or biological stimuli [60]. Smart materials can transform their geometry/shape, under the influence of environmental conditions [61]. Smart materials are classified into shape-changing materials (SCMs) and shape-memory materials (SMMs). SCMs are those materials in which different external stimuli including light, humidity, pH, current, thermal, electric, or magnetic field permits the transformation of shape in bending, folding, shrinkage, surface curling, twisting, or swelling form. These materials recover non-directionally and instantaneously and are mostly appears in the form of piezoelectric and electroactive polymers [62].

On the contrary, SMMs are multi-functional materials that possess the ability to remember their shapes and reconfigure them back to their original shapes even after temporary deformation. Additionally, these materials can recover directionally and consistently [63]. These materials are renowned due to systematic actuation, multi-stimuli sensitiveness, fixity properties, and shape recovery. These materials are further classified into hygroscopic, hygromorphic, non-programmable, programmable, piezoelectric, and thermo-responsive materials [64]–[66].

Programmable SMMs are novel smart materials, which can morph and undergo shape and function change through 4DP, based on the stimuli-response [67]. These materials are known by their feature of shape recovery from the quasi-plastic deformation under specific stimuli [68]. These materials do not require to change their shape, instead, the programming step is enough to permit substantially more complex and adaptable shape transformation [69]. SMMs usually incorporates shape-memory alloys (SMAs), shape-memory polymers (SMPs), shape-memory polymer composites (SMPCs), shape-memory gels (SMGs), shape-memory ceramics (SMCrs), and shape-memory hybrids (SMHs) [70]–[72], as illustrated in Figure 2.

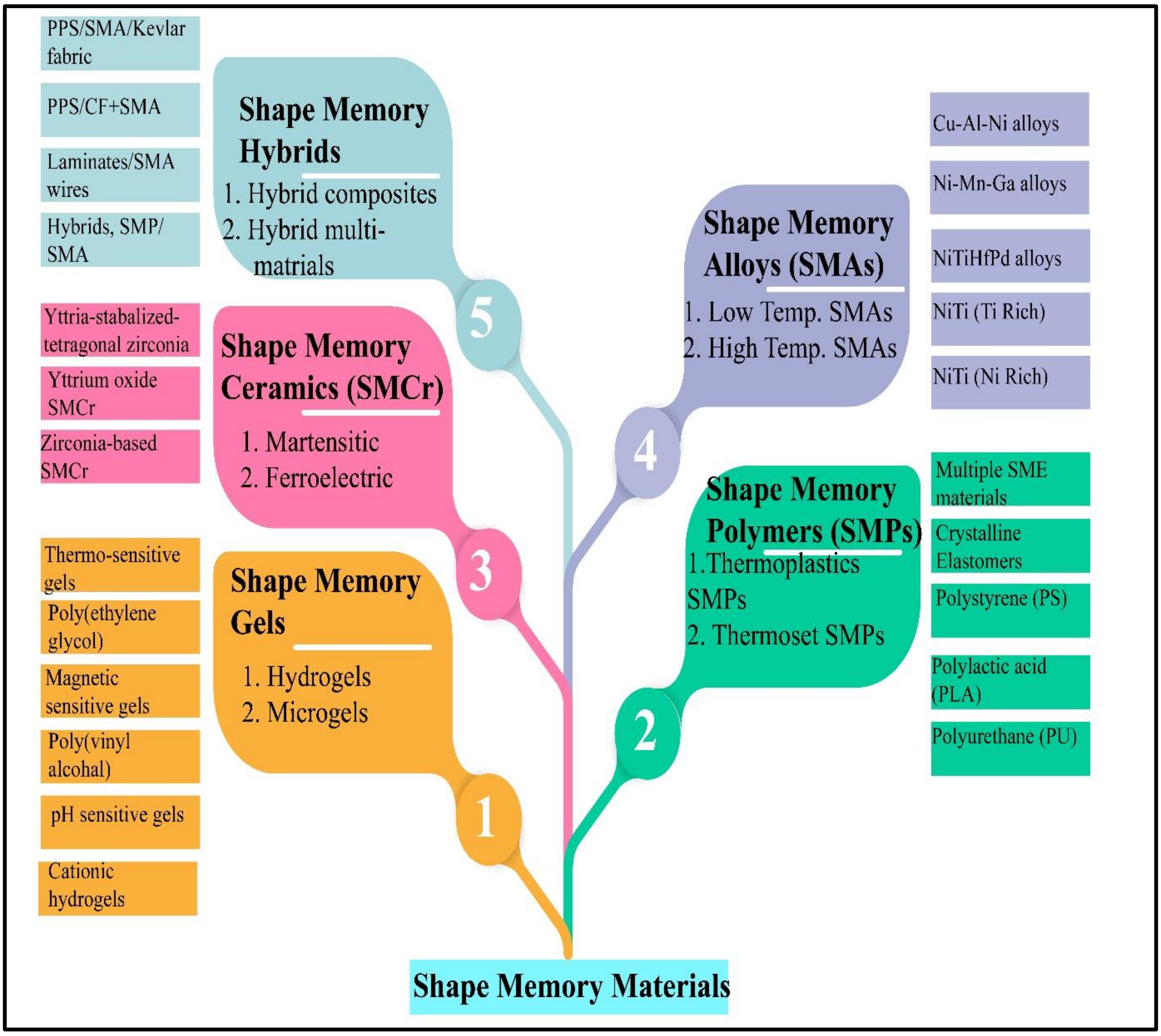

Figure 2. Classification of shape-memory materials

The most widely employed SMMs are SMAs and SMPs. Specific stimuli like heat, light, or humidity induce the shape-memory effect (SME) in SMMs [73]–[76]. SME occurs in SMA due to super-elasticity, whereas, in SMPs, it appears due to visco-elasticity [77]–[79]. SMPs are mostly formed by blending semicrystalline or amorphous polymers with mixtures of fibers and thermoplastic elastomers to develop copolymers of soft and hard segments [80]. In the recent past, SMPs and their composites have gained more attraction due to their high energy efficiency, low cost, excellent processability, and deformability [81].

SMP materials can be preprogrammed for providing predictable deformation upon exposing 3D-printed products to specific stimuli. Figure 3 illustrates the types of deformations that appeared in 4DP of SMPs. Based on the type of morphological transformations, SMPs are categorized into irreversible (one-way) SMPs and reversible (two-way and multiple-way) SMPs [82]. Irreversible SMPs are programmed into a particular shape upon a specific stimulus and these polymers remain in this new shape even after removing the stimulus, as illustrated in Figure 3(a_1). One-way shape memory effect (SME) is prominently observed in traditional cross-linked polymers [83]. These SMPs are commercially employed to develop low-end products like heat-shrinkable labels, tubes, and toys. Nowadays, high-tech research products such as smart medical devices and self-deployable hinges are developed by using these polymers [84].

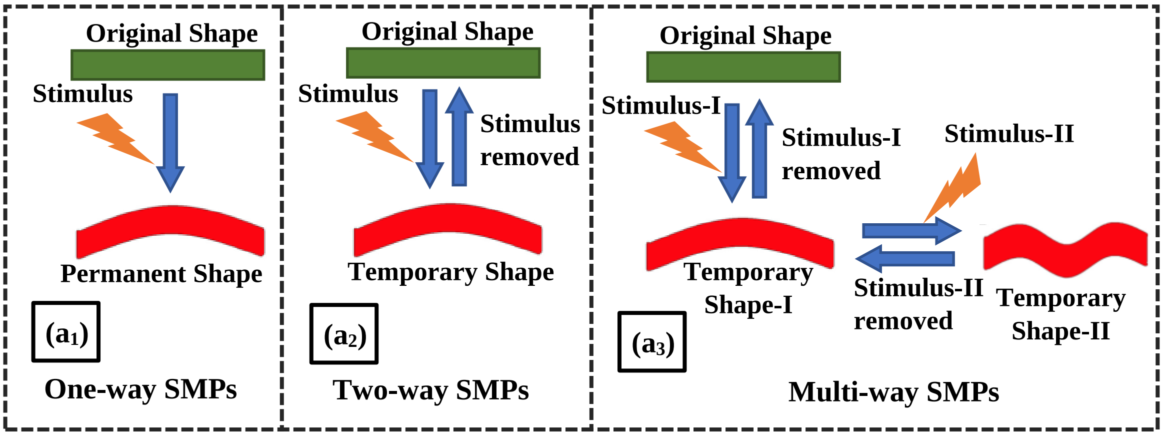

Figure 3. Schematic diagrams illustrating the SMEs of SMPs; **(a_1)** One-way SMPs; **(a_2)** Two-way SMPs; **(a_3)** Multi-way SMPs

Contrarily, two-way SMPs, also refer as reversible SMPs, morph between two distinct shapes through a switching stimulus to develop complex bimorph mechanisms [85]. In a two-way SME mechanism, molecular chains are directionally rearranged upon external stimulus and are mostly used to fabricate semicrystalline polymers and LCEs [86]. Additionally, SMPs capable of maintaining two or more than two temporary shapes are called multi-way SMPs, as illustrated in Figure 3(a_3). These polymers are co-polymer of a set of irreversible SMPs with diverse transition temperatures [87]. Furthermore, multiple SMEs permit the polymer to switch through different shapes by using appropriate programming techniques [88].

2.3. Stimuli for SMPs

4D-printed SMPCs require a specific stimulus for triggering the shape and morphological transformations. These composites use twisting, bending, and folding mechanisms in response to external [78]. The choice and tunning of stimulus depend upon the operating environment. This sub-section elucidates different types of stimuli-responses for SMP-based composites.

During 4DP, SMPCs recover their original shape in response to specific stimuli such as moisture, light, pH, heat, magnetic, and electric fields [89]. The elongation of structures, deformation difference among materials, electric current through heating, as well as expansion of printed parts usually triggers SME [90]. Figure 4 summarizes all possible stimuli employed for 4DP of SMPCs. However, this paper discusses only prominent stimuli used in 4DP of SMPCs.

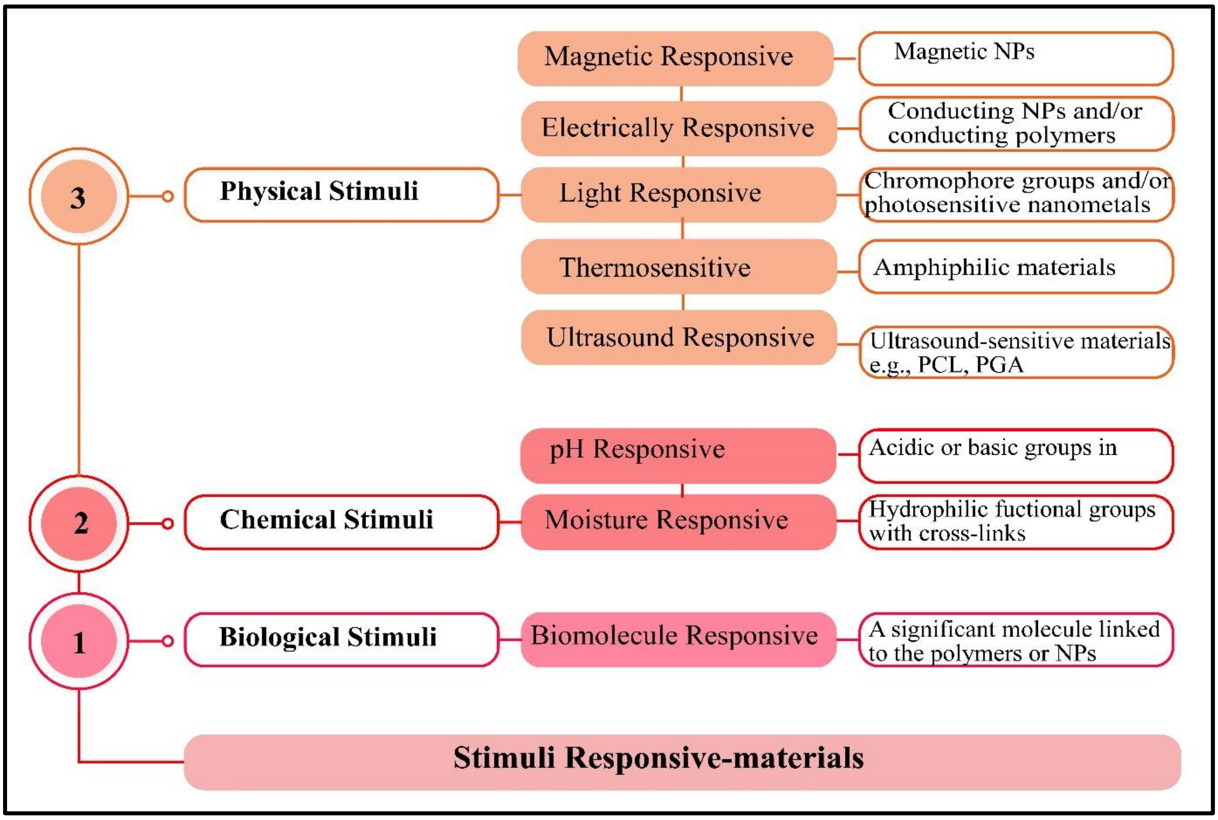

Figure 4. Types of stimuli for 4DP

2.3.1. Thermally-activated SMPs

Thermally-activated SMPs are most commonly observed in 4DP fields, due to the easiness and adaptability of a wide range of SMPs. These thermally-activated SMPs deformed by heating above glass transition temperature (Tg) and original shapes are restored due to the entropic elasticity effect [91]. Additionally, indirect thermal activation through photothermal effect, Joule heating effect, and hysteresis effect also enable actuation. Different researches focused on the exploration of temperature as a stimulant for SMPs. For instance, Wu et al. [92] studied the influence of thermally-activated bio-based shape memory copolymers fabricated through the 4DP technique. The results revealed that 3D-printed models including “Sanxingdui bronze mask” and protecting cover device exhibited excellent shape memory characteristics upon exposure to the thermal stimulus, as presented in Figure 5(a). Similarly, Jian et al. [93] investigated origami-based design models along with 3D support-free hollow structures in terms of two-dimensional (2D) printed origami precursor layouts. These origami-based models were capable of demonstrating the folding functions under heat stimulus and also exhibited the transformation of the 2D origami layout to 3D structures, as presented in Figure 5(b). The transition temperature of the hydrogels can be changed easily by increasing the cross-link density or by incorporating filler materials. Additionally, multi-material-based 4D-printed products possess impressive shape-shifting behavior due to multi-transition temperatures. However, the applications of SMPs and hydrogels are limited due to low operating temperatures. For instance, Solis et al. [94] explored the effect of the thermal stimulus on the DLP-printed poly(N-isopropylacrylamide (PNIPAM)-based hydrogels. The results indicated that these printed hydrogels have exhibited remarkable swelling properties at 5°C, as shown in Figure 5(c).

Bardakova et al. [95] proposed new photosensitive compositions using aromatic heterochain polymers and different post-curing methods were used. Furthermore, the 4D fabricated structures demonstrated excellent shape memory characteristics and gripping behavior, as presented in Figure 5(e), under temperature stimulus.

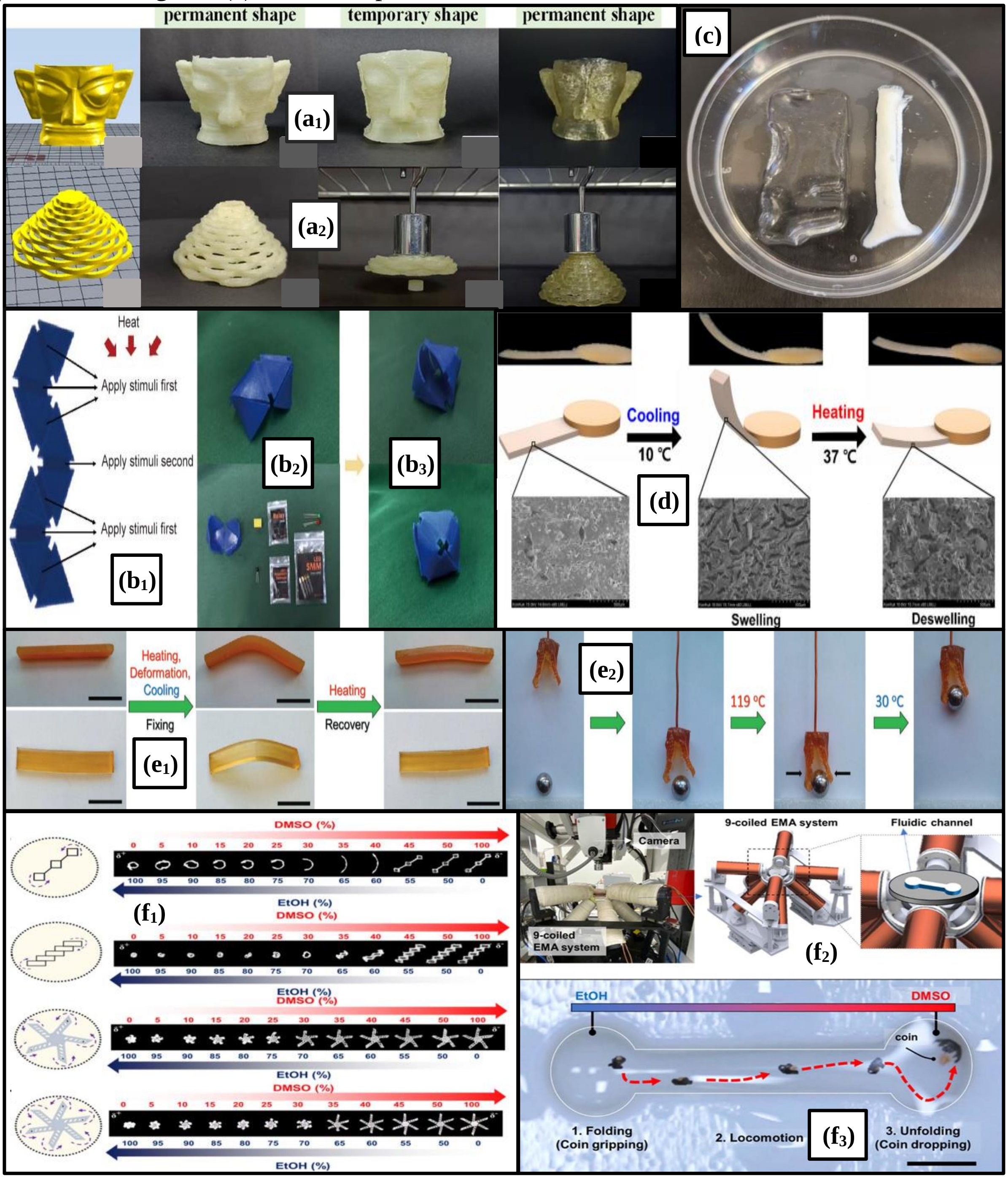

Figure 5. Shape memory behavior of different printed models; (a_1) CAD and actual model "Sanxingdui bronze mask"; (a_2) CAD and actual model "protecting cover device". Both models exhibited temporary shapes at room temperature and permanent shapes recovered at 90°C (adapted with permission from ref. [92]); (b_1) Printed structure with the same hinges; (b_2) First stimulation; (b_2) Second stimulation (adapted with permission from ref. [93]); (c) Printed hydrogel samples before and thermal stimulus (adapted with permission from ref. [94]); (d) SMP-based 4D-printed structure in which swelling stimulus produced actuation (adapted with permission from ref. [96]); (e_1) Shape memory behavior of 4D-fabricated SMP; (e_2) Demonstration of gripping behavior of crocodile shape gripper under

temperature stimulus (adapted with permission from ref. [95]); (f_1) Shape-morphing reversibility of various design models under protic and aprotic stimuli; (f_2) 3D-printed fluidic chip inside the nine-coiled EMA workspace; (f_3) Microrobot grabbed the coin under protic stimuli and steered through magnetic fields (red arrow) and finally released the coin under aprotic stimuli (adapted with permission from ref. [97]).

2.3.2. Humidity/solvent-activated SMPs

Humidity/solvent-driven materials transform their configuration temporally and spatially through differential swelling, deswelling, shrinkage, and stretching mechanisms [98]. These materials include hygromorph biocomposites (HBCs), hydrogels, nano-cellulosic materials, and polyurethane (PU)-based SMPs. Nowadays, humidity-activated SMPs are gaining great interest in actuators, tissue engineering, and drug delivery applications [99]. Swelling mechanism is considered a shape change reversible approach. It can be reversed upon loss of solvent due to environmental conditions [100]. The incorporation of photocurable SMPs into swellable hydrogel materials significantly induces the ability to retain the temporary shape, while swelling is diminished. This help in reverting to the original configuration through the actuation of SMPs. For instance, Seo et al. [96] integrated swellable materials and fabricated a dual-crosslinkable/temperature reversible chitosan-based product. The results indicated that SMP-based 4D-printed structures generated actuation due to swelling and reverted to their initial configuration at 37^{o}C, as shown in Figure 5(d).

The shape morphing mechanisms of 4D-printed grippers and actuators under protic or aprotic stimuli s evaluated by extortionate researchers. For instance, Li et al. [97] fabricated a solvent-responsive untethered micro-robotic gripper through a novel single-layer 4DP system. Different microrobots including helical-type, band-type, tube-type, and gripper-type exhibited responsive behavior, without any external energy source, as presented in Figure 5(f_1). Furthermore, 3D-printed fluidic chip was placed at the center of a nine-coiled electromagnetic actuation system and a five-arm microgripper inside the fluidic channel successfully demonstrate its folding and unfolding behavior under protic or aprotic stimuli, as presented in Figure 5(f_3).

Some SMPs and their composites respond to the changes in pH and transform their configurations upon exposure. SMPs with weak alkalinity and acidity are associated with pH-sensitivity, which encompasses the carboxyl or amino group [123]. The reversible cross-links appear due to electrostatic interactions. pH-responsive SMPs are vastly applied in biomedical fields to develop drug delivery systems [101].

2.3.3. Electrically-activated SMPs

Electric current is an efficient method to induce heat into SMPs for actuation purposes, however, this heat produced through electric current is considered independent from heat stimulus. Additionally, there is a difference between the actuation through electric stimulus and environmental heating. Mostly, dry SMPs are poor conductors of electricity and require the reinforcements of electrically active carbon-based nanoparticles (NPs) including graphite, graphene, and carbon nanotubes (CNTs). These fillers improve the electrical conductivity of SMPs, thus, promoting SME with the joule heating effect. For instance, Zhang et al. [102] developed polyurethane acrylate (PUA)-based SMPCs by incorporating multi-walled carbon nanotubes (MWCNTs) and by spraying silver nanowires (Ag-NWs). These SMPC-based architectures were fabricated by using the UV-curing 4DP technique. The authors observed excellent shape memory properties and improved mechanical properties of deployable and extendible bat wing-like structure imitating under the current stimulus, as presented in Figure

6(a). Extortionate researches show that the electrically-activated SMPs developed through 4DP are usually applied in soft robotics and actuating applications.

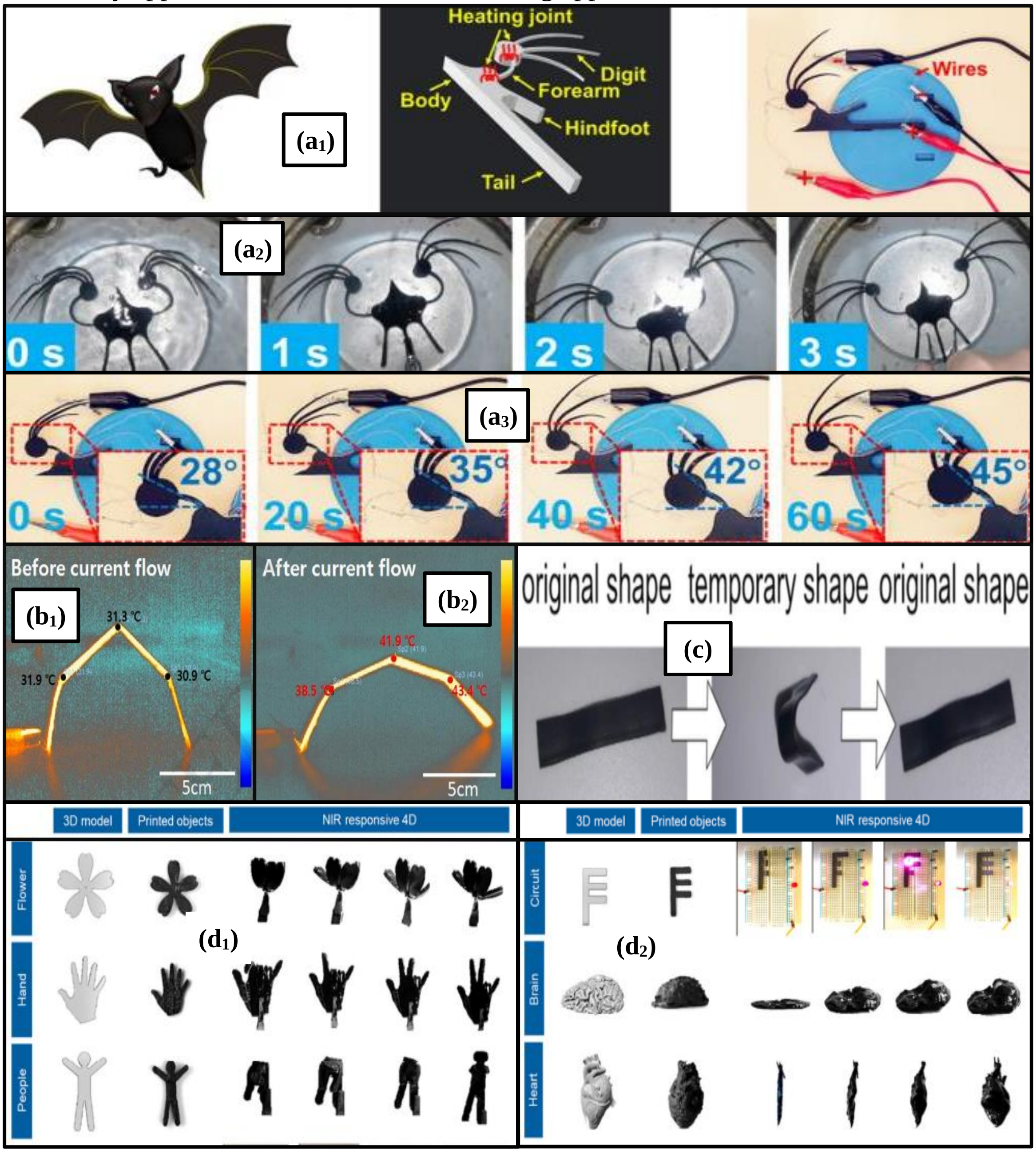

Figure 6. (a_1) Bat wing (one-half) was designed according to the principle of bionics and current was employed for the heating; (a_2- a_3) Images of the shape recovery process of the printed whole bat wing under the stimulus of (a_2) hot water (80 °C) (a_3) current (1.2 A) (adapted with permission from ref. [102]); (b_1-b_2) Reversible actuation mechanism of SMPC actuator under the current stimulus (adapted with permission from ref. [103]); (c) Shape changing behavior of 4D-printed CuS/PU-based composites under light stimulus (adapted with permission from ref. [104]); (d_1-d_2) Dynamically controlled light-responsive 4D-printed constructs including blooming flower, exerciser, hand gesture, electrical circuit, brain and dialted heart model (adapted with permission from ref. [105]).

Both types of SMMs (SMPs and SMAs) exhibit SMEs and return to their original shape after deformation [106]. However, there is a significant difference in the returning mechanisms. The crystallographic transformation from the austenite phase to the martensite phase produces SME in SMAs, which can be triggered by temperature, stress, or their combination [107]. On the other hand, SMEs in SMPs occur by a change in proportions of soft and hard segments near the T_g. SMP and SMA possess non-reversible actuation and low strength, respectively. Recently, the researchers have fabricated high strength, lightweight, and reversibly actuated SMPCs by integrating SMAs and SMPs, to address these issues [108]. These types of composites have shown their potential in valve controller and stent applications. For instance, Pyo et al. [103] used FDM technique to fabricate SMPC actuator by merging SMA with a Nylon 12-based SMP in the ratio 1:5 and achieved the maximum flexural modulus of 1180 MPa. Additionally, the developed actuator exhibited excellent response upon electrical stimulus, as illustrated in Figure 6(b).

2.3.4. Light-activated SMPs

SMPs can be effectively triggered through the non-contacting light stimulus of specific wavelengths and intensities within the electromagnetic spectrum to fabricate actuated smart structures. This stimulus induces folding, twisting, and bond strength as well as triggers a self-healing mechanism [109]. Additionally, light stimulus helps to develop high precise small-scaled components. The light stimulus enables a photothermal effect, which increases the temperature of SMPs above the T_g. Furthermore, the addition of filler materials also enhances the temperature by absorbing light energy and converting it into heat [110]. For instance, Vitola et al. [104] printed PU-based SMPCs and evaluated their shape memory behavior upon light activation. The results revealed that the 4D-printed composites maintained their original configuration after light stimulation, as illustrated in Figure 6(c). Likewise, Cui et al. [105] developed near-infrared (NIR) light-responsive SMPs and evaluated the shape transformation performance, as shown in Figure 6(d). These graphene-doped SMPCs exhibited excellent shape memory behavior and biocompatibility, as well as cell adhesion, differentiation, and growth. These nano-printed smart devices can be applied as bio-actuators, bio-sensors, and bio-robots to inspect the shape transformations of tissues and cells.

2.3.5. Magnetically-activated SMPs

Magnetism is another important stimulus, which can be used for the shape transformation of SMPs. This stimulus can trigger intricate structures which are unresponsive to direct heating [111]. SMPs are either triggered by aligning the materials under magnetic stimulus or through a magnetically-induced heating effect [112]. These magnetic-responsive polymers are fabricated by doping with magnetic NPs like Fe_2O_3 and NdFeB [113]–[115]. These magnetically-triggered SMPs have found their applications in the biomedical world and are used to develop drug-releasing devices and biorobotic architectures for minimally invasive procedures [116]. For instance, Lin et al. [117] 4D-printed remotely controllable and biodegradable PLA-based occluders by incorporating Fe_3O_4 magnetic particles. These magnetically responsive SMPCs exhibited excellent shape memory characteristics, as illustrated in Figure 7(a). Additionally, these biodegradable occluders exhibited excellent cell adhesion, growth, and proliferation, which facilitated rapid endothelialization. Similarly, Zhang et al. [118] printed polydimethylsiloxane (PDMS)-based magneto-responsive SMPCs by incorporating NdFeB-based magnetic NPs, as depicted in Figure 7(b). These origami structures exhibited programmable transformation, excellent shape memory characteristics, and controllable locomotion.

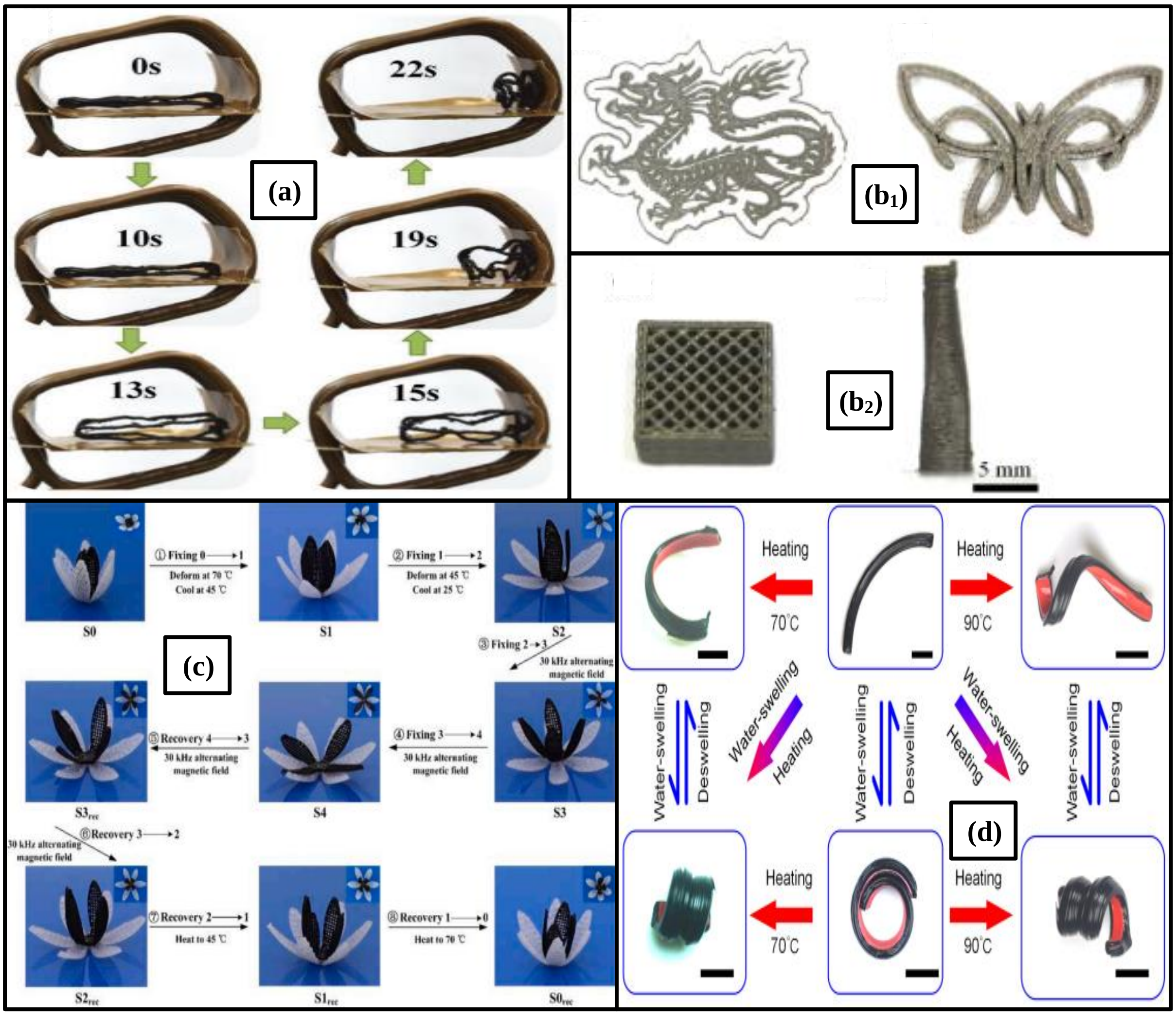

Figure 7. (a) 4D-printed magnetically-driven PLA/Fe_3O_4-based shape memory occluders (adapted with permission from ref. [117]); (b) PDMS/NdFeB-based 4D-printed SMPCs; (b_1) Chinese dragon and butterfly; (b_2) Porous cuboid and Shanghai Tower (adapted with permission from ref. [118]); (c) PTMC/PLMC/Fe_3O_4-based 4D-printed triple memory flower petals under magnetic field and temperature stimuli and later immersed in a water bath (adapted with permission from ref. [119]); (d) Deformation behavior of PU/PVA-based 4D-printed bilayer structure with a quadrant shape in response to both temperature and water stimuli (adapted with permission from ref. [120]).

2.3.6. Multi stimuli-activated SMPs

SMPC-based shape morphing architectures can be precisely controlled by using multiple stimuli. Multi-stimuli responsive SMPs undergo multiple shape configurations and are extensively applied in recent days to promote practical applications [121]. Multi-responsive SMPs are commonly developed by incorporating functional additives into SMPs, which makes them more sensitive compared to the original SMPs [122]. Furthermore, the addition of different NPs like Fe_3O_4 and CNTs also allows SMPCs to convert magnetism to heat, electricity to heat, or light to heat, thereby realizing multi-stimuli responsive 4DP. For instance, Wan et al. [119] printed poly (trimethylene carbonate) (PTMC)/poly (D,L-lactide-co-trimethylene carbonate) (PLMC)/Fe_3O_4-based triple memory SMPC structure, as shown in Figure 7(c). The results indicated that these printed structures exhibited excellent SME and biocompatibility, and transformed into complicated configurations. These triple memory SMPC demonstrate excellent potential in tissue engineering and drug delivery applications.

Multi-responsive SMPs can be developed by constructing a bilayer architecture incorporating two materials with different and versatile response properties. This approach is more suitable for producing more configurations upon deformation, which also enrich deformation modes of single architecture [123]. For instance, Ren et al. [120] developed a temperature-responsive and water-responsive SMP-based bilayer structure, as illustrated in Figure 7(d). The results revealed that the diversified PU/polyvinyl chloride (PVC)-based printing structure exhibited excellent structural changes under both stimuli.

2.4.Stimuli-responsive SMPCs

Stimuli-responsive features make SMP-based composites highly suitable for 4DP. SMPCs produced through 4DP are one of the emerging research areas and have drawn great interest. These materials can overcome the different issues generated in other types of SMMs [124]. For instance, these materials can easily maintain their shape even under the low effect stimuli, and secondly, their shape-changing modes are set with no or limited shape re-programmability [125]. SMP-based 4D-printed models can be reprogrammed to generate new SMP shapes [126]. However, the biggest hurdle in 4DP of SMPs is to attain the complex 3D model transformations, spatially fixed with mechanical loading conditions through the preprogramming of the models. The multi-layer composites help to manufacture reversibly deformable structures through 4DP by incorporating different fillers as well as fiber layers. Furthermore, these composites can be tailored to any available shape and properties through the wide range of available fillers/fibers [127]. Figure 8 depicts the 4D-printed SMPCs developed for versatile engineering applications. For instance, thermoplastic polyurethane (TPU)/PLA-based SMPCs are effectively produced through reversible bending architectures by Wang et al. [128]. The proposed design confirmed that the composite laminate structures deformed repeatably and had a fast response. Furthermore, different complex reversibly deformable structures can be flexibly printed with pre-programmed through simulation.

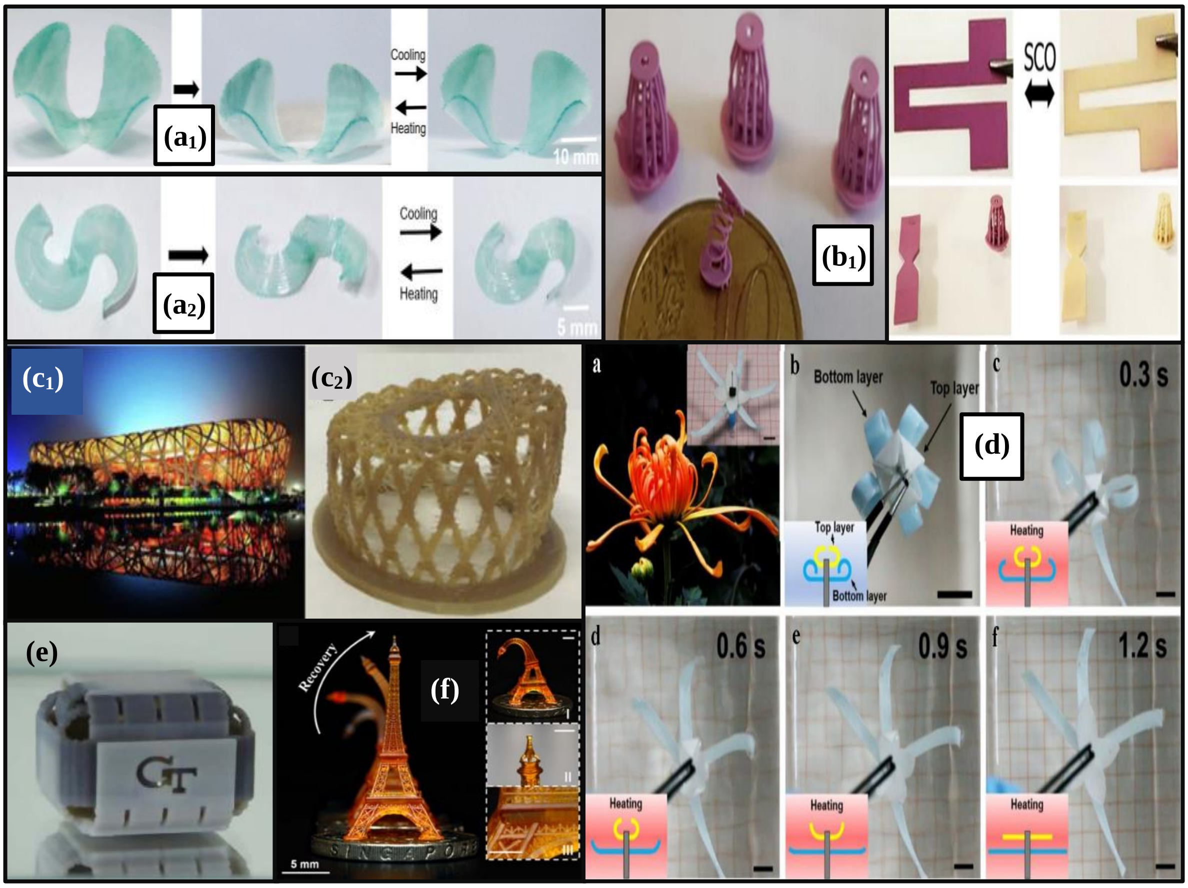

Figure 8. Expanded and original shapes of TPU/PLA-based reversible bending structures; (a$_1$) Butterfly model; (a$_2$) S-shaped ring model obtained during experiment (adapted with permission from ref. [128]); (b) 4D-printed SCO-polymer composite in which a reversible color change occurs between the low spin (violet) and high spin (light-yellow) conditions when heated above 80^{o}C (adapted with permission from ref. [129]); (c) Different prototypes developed through the 4DP of SMPCs; (c$_1$, c$_2$) Bird's Nest stadium original (on the left side) and prototype (on the right side) developed via 4DP (adapted with permission from ref. [130]); (d) PLA/PCL-based 4D-printed chrysanthemum under open state and closed temporary states (adapted with permission from ref. [131]); (e) Self-folded structure manufactured through 4DP (adapted with permission from ref. [29]); (f) Eiffel tower prototype printed on Singapore dollar by using SMPs which bent upon heating at 60^{o}C, subsequent cooling at 25^{o}C and return to its original shape by reheating at 60^{o}C (adapted with permission from ref. [76]).

The mechanical characteristics of the polymer composites can be improved through the incorporation of biopolymers [132]. Therefore, there is a developing interest in less dense bio-sourced reinforcing fillers [133]. For instance, Zhang et al. [134] developed NF-reinforced polymer composite through the pollen-based reinforcing fillers manufactured through photopolymerization. The results revealed that the addition of softer pine-pollen fibers into the poly(ethylene glycol) diacrylate (PEGDA) matrix provided better fracture resistance and swelling behavior.

Recently, a novel 4DP approach is developed by using the spin-crossover (SCO) phenomenon. It appears in some transition metal complexes and external stimulus reversibly changes the spin state from low-spin to high-spin. This SCO is associated with considerable changes in electrical, optical, magnetic, and mechanical properties. For instance, Piedrahita-Bello et al. [129] propose a novel approach to develop SCO/polymer-based nanocomposites. The results revealed that the printed model possessed good thermal and mechanical properties. This model can also offer reversible mechanical actuation generated by the volume change accompanying the SCO, as illustrated in Figure 8(b). The novel fabrication process proposed in this research is simple, versatile, and allows the creation of microfluidics parts, adaptive optics, drug delivery, and grippers.

3. 4D Printing technologies

The novel and the state of art different 3D printers are mainly employed in cutting-edge AM technologies [135]. The dynamic and multi-functional products in 4DP are developed through technical approaches. The integration of time-dependent components to 3DP yields 4D-printed products. To date, there are various AM technologies have been employed and these AM technologies have layup the foundation of advanced 4DP techniques [136]–[138]. 4DP is usually achieved through 3DP techniques and commonly employed 3DP techniques are extrusion-based processes (fused deposition modeling (FDM) direct ink writing (DIW)), light-based vat photopolymerization (VP) processes, selective laser sintering (SLS), material jetting (MJ)/inkjet printing (IJP), and selective laser melting (SLM) [139]–[141]. However, it is impossible to generate irreversible deformation in the 4D-printed structures using these 3DP technologies [142]–[144]. Additionally, manual pre-programming is applied prior to the model deforming, which makes this technology imprecise, cumbersome, and difficult to control [145]. To overcome this issue, 4D-printed reversible structures can be produced, due to the impulsive transformation of material features and shaped upon external stimuli [146]. Light-based and extrusion-based processes are most commonly applied for 4DP [147]. **Table 1** presents the consolidated data including the printing mechanisms, important features, disadvantages, and functional materials for all 4DP techniques.

Table 1. Comparison of different key features of printing processes and their adaptive materials

4DP technology	Resolution	Feed state	Illustration	Curing mechanism	Prominent stimuli resources	Features	Disadvantages	Applications	Materials	Ref.
FDM	100-700 µm	Solid	Layer-by-layer deposition of melted solid materials.	Unaided-cooling, extrusion	Humidity, temperature	Less investment cost, multi-material printing, highly available materials, and clean and fast printing environment due to the filament	Blockage of filament, low surface quality, and warpage	Stents, scaffolds, aerospace, and automotive	SMPCs, elastomers, thermoplastics including ABS, PA, PLA, and PE	[148]–[150]
DIW	100-600 µm	Liquid	Liquid polymer-based viscoelastic inks are solidified in a layer-by-layer manner.	Temperature-assisted, gel formation, and evaporation	Mechanical, temperature	High resolution, strong multi-material printing, thixotropic ink, and no supporting requirement for filaments	Material limitation, poor curing, high maintenance cost, low printing speed, and gel formation	Soft robotics and actuators	Ceramics, waxes, nano-composites, ferromagnetic SMPs, and viscoelastic inks	[151]–[153]
SLA	5-100 µm	Liquid	Layer-by-layer curing and hardening of liquid resin	Photopolymerization and crosslinking	Electric field	Excellent surface finish, high resolution, UV curing, and precise outline	High maintenance cost, low printing speed, expensive printing materials, and limited liquid resins	Aerospace, automotive, soft robotics, and microfluidics	Thermo-set polymers, SMPs, SMPCs, ceramics, and liquid photopolymers	[154]–[156]
DLP (SLA variant)	15-100 µm	Liquid	Liquid is solidified and deposited in a layered manner	Photopolymerization and crosslinking	Light, humidity, or temperature	No supporting requirement, projector light curing, and high printing speed	Materials limitation, high maintenance cost	Aerospace, automotive, microfluidics, and soft robotics	Metamaterials and elastomers	[157]–[159]

TPP	80-160 nm	Liquid	The femtosecond laser beam is focused on the photocurable resins to print structures with sub-micrometer resolution	Photopolymerization and crosslinking	Light, solvent, light, pH, or ions	No supporting requirement, fast printing speed, high resolution, and smooth finishing	Print only micro-scaled products	Micro-robotics, micro-grippers and micro-fluidics devices	Hydrogels, elastomers, and photocuring resins	[160]–[162]
SLM	30-150 µm	Powder	Previously melted metallic powder is sintered	Laser-assisted	Magnetic field	Complete melting, leftover powder can be reused, thermal stresses are relieved, anisotropic properties	Additional supporting requirement, large columnar grain structure, average surface quality, and second phase formation	Tissue engineering	Ceramics, composites, metals, and alloys including aluminum, Cr-Co alloys, and TiNi alloys	[163]–[165]
SLS	10-120 µm	Powder	Powder material is sintered upon heating	Laser-assisted	Magnetic field	Leftover powder can be reused, High printing speed, No additional supporting requirement, design freedom	High maintenance cost, poor surface quality, small build size, poor multi-material printing, expensive, and second phase formation	Scaffolds, bone, and cartilage tissue engineering	Metals, powdered polymers including nylon, and TPEs	[166]–[168]
IJP	20-200 µm	Powder	Material in powder form is sintered upon heating and solidified in layer-by-layer manner	UV-assisted	Ionic	No additional supporting requirement, multi-color printing, isotropic properties, equiaxed grain structure, high machine speed	Long printing time, high thermal stresses, poor surface quality, expensive, weak prototypes, less economic	Full-color products, prototypes, and medical models	Ceramics, SMPs, polymeric powders including starch and cellulose	[169]–[171]

3.1. Fused deposition modeling

FDM also known as fused filament fabrication (FFF) is commonly applied to fabricate polymeric composites-based smart materials through 4DP [172]–[174]. This programmable extrusion-based approach deposits layers of thermoplastic polymers via a nozzle on the platform or over the formerly printed layers [175]–[177]. Additionally, the printing head of the FDM moves in the x- and y-direction to deposit the layer while the built platform moves in the Z-direction [178]. This technique has several advantages over the other printing techniques that include lowering the production cost, minimizing the waste of the production, and shrinking the design-manufacturing circle [179]. Additionally, this technique has the ability to tune the mechanical properties as well as develop complex products for high-end engineering applications [180]–[182].

From the 4DP perspective, FDM technology is usually employed to print stimuli-responsive thermoplastics polymers including polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), PU, polycarbonate (PC), polycaprolactone (PCL), polyethylene (PE), polyphenylsulfone (PPSF), polyetheretherketone (PEEK), nylon, and polypropolene (PP) [183]–[187]. Whereas, thermosets are usually printed via other 4DP techniques including SLA and DIW techniques. This technology has limitation to 4D-print only thermoplastic SMPs. However, continuous developments in 4DP technology have helped the scientific community to develop printing products of shape memory polymer composites (SMPCs) [188]. These composites integrate SMPs with fillers including glass fibers (GFs), nanohydroxyapatite, carbon fibers (CFs), carbon black (CB), natural fibers (NFs), wood fibers (WFs), CNTs, ceramics, copper particles, and iron particles [189]–[192]. These fillers not only result in the reinforcement and strengthening of the SMPs but also behaves as an active medium for stimulating shape morphing ability [193]. Additionally, this processing of materials can further be reduced by using FDM technology to print SMP-based composites and laminated-object composites [194]. Laminated-object composites are manufactured through the subsequent stacking of preform and functional materials layers [195].

Cheng et al. [130] developed an elbow protector model based on PCL/PLA copolymer by utilizing the FDM process, as illustrated in Figure 9(a) and achieved maximum tensile stress and young’s modulus of 28.02 ± 2.21 MPa and 318.89 ± 17.04 MPa, respectively. Similarly, Chen et al. [196] employed the FDM technique to print the shape memory thermosets by incorporating the CNTs, as elaborated in Figure 9(b). The authors achieved the flexural modulus, flexural strength, tensile modulus, and tensile strength of 6 GPa, 135 MPa, 2 GPa, and 60 MPa, respectively.

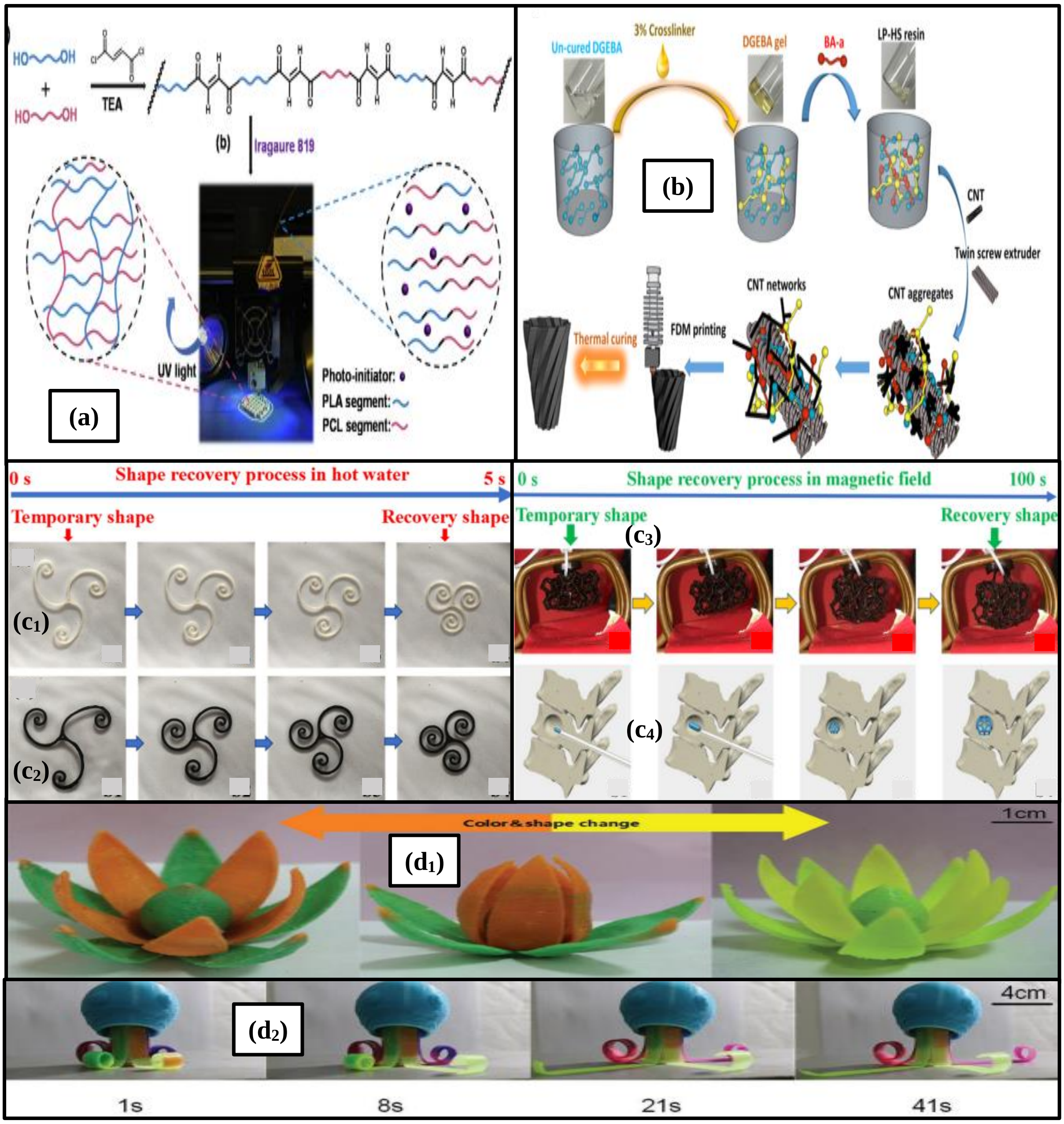

Figure 9. (a) Development of U-PLA/PCL-based copolymer through the synthetic route and 4DP through UV-assisted FDM technology (adapted with permission from ref. [130]) (b) Schmatic diagram depicting the development of high-performance thermoset by using FDM method (adapted with permission from ref. [196]); (c) 4D-printed deployable strucutures in hot water; (c_1) PLA; (c_2) Fe_3O_4/PLA; (c_3) Shape recovery behavior of Fe_3O_4/PLA-based FDM-fabricated composites under magnetism; (c_4) Simulation depicting 4D intricate acrhitectures as bone repairing medium (adapted with permission from ref. [197]); (d_1-d_2) PLA-based blooming and color shifting flower fabricated through FDM. Orange and green flowers transform from bud shape to yellow shape after blooming (adapted with permission from ref. [198]).

Liu et al. [199] analyzed the influence of carbon graphite (C) and silicon carbide (SiC) reinforcements on the recovery rate, training, and recovery force of the PLA-based composites. The results indicated that the incorporation of fillers decreased the training and recovery rate, and increased the recovery force. These results showed that the actuation ability of the SMP can be tailored through filler reinforcement. This actuating mechanism can be potentially employed for signaling or aesthetic functions. Likewise, Zhang et al. [197] developed the magnetoactive behavior of PLA-based composites through the reinforcement of iron oxide (Fe_3O_4), as illustrated in Figure 9(c_3). The results revealed that the presence of ferromagnetic media inside the polymer produced an induction heating effect. This effect generated shape recovery inside the PLA polymer.

FDM fabricated 4D-printed products usually undergo shape-changing behavior. However, this technique also possesses the potential to develop color-shape changing products. For instance, Wang et al. [198] introduced thermochromic pigments as filler material into the PLA composites manufactured via FDM technology, as demonstrated in Figure 9(d). The pigment has the ability to change its color upon thermal stimulus. The results revealed that thermochromic reinforced PLA-based 4D-printed products not only transformed their shape but also changed their color. This feature can be applied for aesthetic purposes or temperature signaling.

Thermoplastic polymers can be blended with the NFs through FDM technique to improve the shape morphing ability [200]. For instance, Le Duigou et al. [201] developed 4D-printed HBCs by introducing WFs in a PLA-based biopolymer matrix through the FDM technique. The presence of water inside the polymer matrix resulted in the swelling of WFs which transformed the shape. PU is another SMP that can be utilized to develop 4D-printed architectures. The chemical structure of PUs can be controlled by blending the semi-crystalline PU and glassy TPU for developing PU-based SMPCs [202]. Monzón et al. [203] examined the shape morphing ability of the TPU polymer manufactured through FFF technology. The results indicated that the recovery rate was better at a lower feed rate, which resulted in an excellent shape recovery ratio.

Some polymer composites exhibit excellent triple shape memory [204]. For instance, Ly et al. [205] investigated the MWCNTs reinforced TPU-based polymer composite prepared through the FDM technique. The authors used dimethylformamide to disperse MWCNTs along TPU-pellets and pellets were de-humidified upon combining solution. Additionally, the authors noted observed excellent shape recovery of SMPCs. Likewise, Wang et al. [128] developed the SMPC-based reversible deformable 4D-printed structure by using PLA and TPU-based elastomer material prepared through FDM technology. The preprogrammed simulation results revealed that structural and printing parameters considerably affected the deformation of the polymer composites. These reversible shape-change structures could be useful for different engineering applications including actuators, soft robots, and intelligent mechanisms.

3.2. Direct ink writing

DIW technology is an extrusion-based 3DP process where an under pressure nozzle is utilized to dispense the liquid ink or filament layer-by-layer, according to the instructions provided by CAD software until the final part is constructed [206]. High printing resolution can be achieved in the DIW process through the use of micro-nozzles. The thixotropic behavior of the extruded filament in DIW is helpful in printing bone scaffolds. Other materials including UV-cured polymers, polymer solutions, ceramic inks, and colloid suspensions can also be employed as feedstock for this approach. This process exhibits superiority over the other 4DP processes due to the minuscule number of raw materials, free options of materials, and viability for the printing of multi-materials [207]. This process is primarily applied in laboratories for the printing of nano-composites under varying content of nanoparticles (NPs) and nanofillers [208]–[210]. Contrary to SLA, SLS, and IJP techniques, DIW is extensively applied to print thermoplastic SMPs and ferromagnetic materials. However, this process exhibits low printing speed, high structural deformation, and low dimensions of the built part. Additionally, this technology has the ability to print metals, multi-materials, and ceramics. Furthermore, it is essential to carefully regulate the viscosity of ink to improve its rheological performance. The important rheological factors including compressive yield stress, shear stress, apparent viscosity, and viscoelastic properties are needed to be tuned [211]. Additionally, some additives are also applied to control the printing temperature and rheological performance. Owing to the advantages of the DIW process, it is extensively applied in 4DP of smart materials which have their potential in electronics, biomedical fields, smart actuators, and soft robotics [212]–[216]. This technique is frequently applied for the 4DP of SCMs and SMPCs [217]. Weng et al. [218] fabricated self-morphing structures that can be deformed under external stimuli using a multi-material DIW process. The mechanical testing was performed on the printed objects and the results revealed the maximum elastic modulus of ~4.8 GPa. Another study was performed by Mohan et. al. [219] who developed complex shape 3D structures using DIW that have the ability to change shape under external stimuli. The authors used cellulose as the main matrix and added graphene nanoplatelets (GnPs) to enhance their mechanical strength. The printed objects resulted in 20 % increase in tensile strength and 37 % increase in elastic modulus. In another study, Rodriguez et al. [220] 4D-printed structure of thermoset SMPCs with multi-material and complex architectures by using environmentally benign epoxidized soybean oil (ESBO) as a matrix. To improve the mass ratio and mechanical strength, bisphenol-F-diglycidyl ether (BFDGE) was incorporated into the polymer matrix. The results revealed that the incorporation of carbon nanofibers (CNFs) tuned the rheological characteristics and the 4D-printed origami structures were triggered through electrical stimulus, as illustrated in Figure 10(a). Thus, the ability of SMPCs to return their folded form upon external stimulus makes them suitable candidates for aerospace, robotics, and medical applications.

Chen et al. [221] developed the 4D-printed structure of SMPs through the UV-assisted DIW technique. The resin contained thermally curable epoxy and photocurable acrylates of weightage ratio 6:4. Furthermore, nano-particulates [SiO_2] were incorporated to regulate the viscosity. The results revealed excellent isotropic mechanical characteristics of the SMPs fabricated through UV-assisted mechanism and post-heating. This is due to the formation of cross-linked networks in acrylates upon UV-assisted approach, followed by polymerization of polymer matrix upon post-heated curing. The development of interpenetrated polymer network (IPN) due to the perfect locking of the cross-linked structures helped to successfully print lattice, swirl bow, gear wheel, and locked structures, as depicted in Figure 10(b).

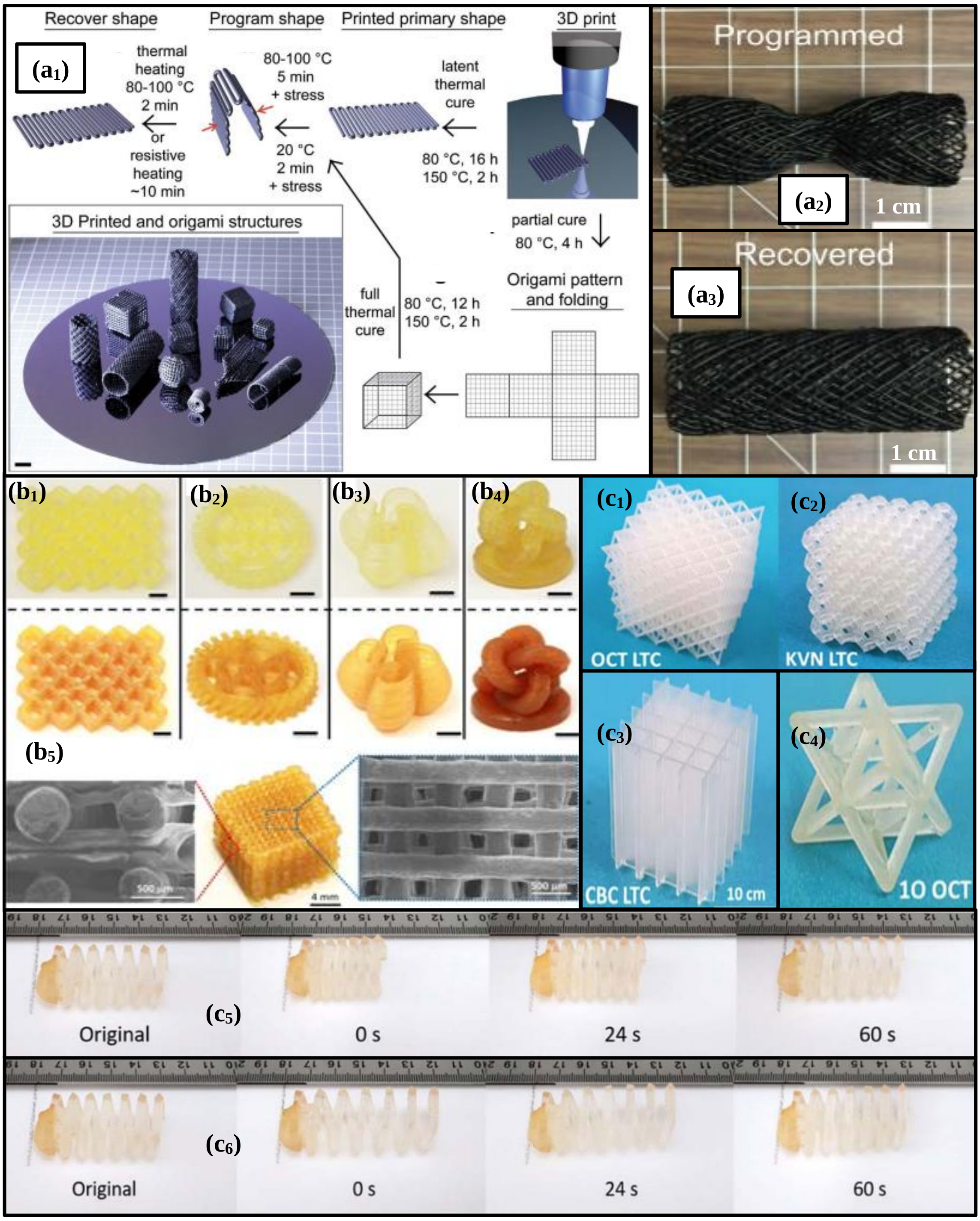

Figure 10. (a_1) EBSO/ BFDGE/CNF-based 4D-printed products developed through DIW; (a_2) Programmed stent which is transformed into dumbbell shape; (a_3) Recovered stent upon thermal stimulus [85°C] (adapted with permission from ref. [220]); Photographs of 4D-printed structures with photocurable resins manufactured through DIW process; (b_1) Lattice architectures; (b_2) Spiral gear; (b_3) Spiral swirl bowl; (b_4) Three-link product; (b_5) SEM micrographs depicting single-layered lattice structure which contains filament without any noticeable sagging. These structures transformed their shape at 104°C within 10 s. (adapted with permission from ref. [221]); (c_1) 3D-printed Octet micro-lattice structure; (c_2) 3D-printed Kelvin micro-lattice structure; (c_3) 3D-printed cubic micro-lattice structure; (c_4) 3D-printed 1st order octet-truss structure and Shape recovery mechanisms of SMP-based printed product; (c_5) Figure depicting shape recovery of hot compression programmed 4D-printed product; (c_6) Figure depicting shape recovery of hot tension programmed 4D-printed product upon heating (adapted with permission from ref. [222]).

3.3. Vat photopolymerization

VP is a well-known AM technology in which photo-sensitive material is polymerized through the UV light or laser beam which cures the materials in a controlled manner [223]–[225]. The layer thickness is controlled by the movement of the platform in the z-axis direction. This process is only applicable to those smart materials which are photo-sensitive to light [226]. These materials can be cured through different curing sources and this technique is extensively applied to print variety of metamaterials [227]. This technology is further categorized into different sub-processes including volumetric 3DP, stereolithography (SLA), digital light processing (DLP), two-photon polymerization (TPP), and micro-SLA (PμSL). These techniques are not only employed in 3DP but also used for the 4DP of polymers and composites [228]. Out of these techniques, SLA and DLP techniques have played a significant role in 4DP. VP approaches are differentiated on the basis of the arrangement of their elements including build platform, light source, resin tank, and curing direction [229].

3.3.1 Stereolithography

SLA employs a beam of visible or UV light emitted from the laser which is deflected to produce a highly intense single-spot laser beam. This light is concentrated on the photosensitive resin surface [230]. The highly intense UV beam selectively cured the photosensitive resin by initiating the photo-crosslinking reaction in ink materials [231]. The platform gets lower after the curing of one layer [232]. The repetition of this technique for the subsequent layer generates the printed product. This technique permits high-resolution printing and precise control and is extensively applied for the 4DP of SMPs [233]. Extortionate researchers have investigated the mechanical properties of the 4D-printed smart materials using the SLA technique. For instance, Li et al. [222] developed SMP-based 4D-printed structure using the SLA process, as illustrated in Figure 10(c) and examined its mechanical strength. The results noted maximum tensile strength and elastic modulus of 62 ± 2.8 MPa and 1.46 ± 0.07 GPa, respectively. Additionally, the compressive test was also performed to observe their strength under compression. The results depicted that the specimen showed the maximum compressive strength of 190.0 ± 7.7 MPa. These lightweight architectures can be potentially applied for load-carrying applications due to the mechanical properties comparable with metallic lattice structures. A similar study was performed by Zhao et al. [234] to observe the mechanical strength of SMPs. Specimens were 3D-printed using prepolymer PUA via the SLA process and mechanical testing was performed. The results showed the maximum tensile strength, flexible strength, flexible modulus, glass modulus, and rubbery modulus were 37.3 ± 3.0 MPa, 49.5 ± 1.1 MPa, 1267.1 ± 61.6 MPa, 1820.2 MPa, 7.2 MPa, respectively. Additionally, nozzle-free printing also helps in minimizing the clogging issues, which is extremely beneficial in the bioprinting approach. However, non-uniform mechanical characteristics, inability to use bioplastics, and high cost have limited the use of SLA technique in the biomedical field.

3.3.2 Micro-stereolithography

SLA and PμSL look similar from their names, however, these approaches are fundamentally different from each other. SLA uses a laser beam that follows the CAD pathway [235]. Whereas, PμSL, a high-resolution technique is derived from DLP and cross-links an entire layer of the product [236]. Ge et al. [76] employed the PμSL approach to develop SMP-based 4D-printed structures, which were thermally stimulated. This high-resolution technology provided energy for photo-curing a variety of bioinks and developed 4D products including springs and grippers. In another study, Chen et al. [237] fabricated thermochromic SMP-based 4D-printed intricate architectures through the high-resolution PμSL technique, as illustrated in

Figure 11(a). The study indicated that these polymers possessed excellent shape-color recovery behavior, thermochromic ability, and repeated response performance. These 4D-printed thermochromic SMPs can be potentially applied to develop bionic devices, soft robots, high-precision devices, safe data recording, and intelligent anti-counterfeiting.

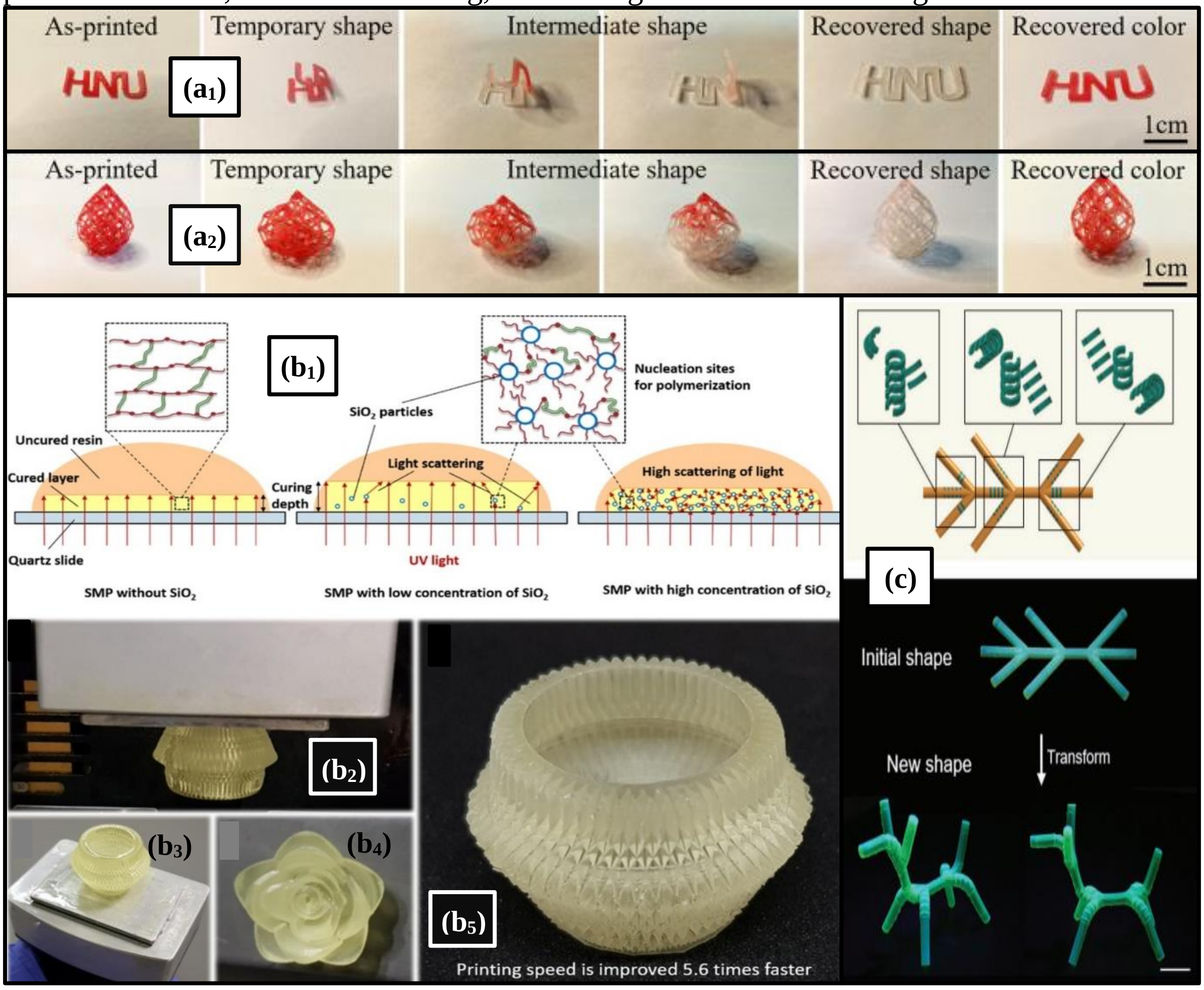

Figure 11. Thermochromic SMP-based products; (a$_1$) 4D-printed "HNU" letters; (a$_2$) 4D-printed hollow architecture with excellent recovery behavior (adapted with permission from ref. [237]); (b$_1$) A schematic representation of SiO_2-based NPs providing nucleation sites for polymerization process; (b$_2$-b$_3$) Nanosilica-reinforced SMPCs manufactured through DLP process; (b$_4$- b$_5$) Development of intricate architectures (adapted with permission from ref. [238]); (c) 4D-printed SMP-based dog-shaped tubular strucutre developed through thermo-pneumatic stimulus (adapted with permission from ref. [239]).

3.3.3 Digital Light Processing

DLP technology is extensively applied for the printing of photocurable polymers. This technique employs a dynamic mask known as a digital micromirror device (DMD), to obtain a 2D image [240]–[243]. In this process, the whole layer is cured simultaneously through DMD. DMD contains micrometer-sized mirrors that help in reflecting the light away or onto the polymer surface [244]–[246]. This generates the 2D pattern on the surface of the liquid resin followed by the subsequent layer deposition [247]–[249]. Additionally, this technique can be applied to tune the mechanical characteristics of the printed part by controlling the photocurable polymer formulations [250]. Different functional smart materials developed through the DLP process can be photopolymerized by using external stimuli. For instance, Choong et al. [238] employed the DLP process for developing nanosilica-reinforced SMPCs, as illustrated in Figure 11(b), which depicted excellent mechanical properties. Additionally, mechanical tests showed that tensile strength and Young's modulus of SiO_2-SMPs increased to 2.4–3.6 times and 8 times, respectively. These particulate-reinforced 4D-printed products possessed extraodinary shape recovery performance due to the cross-linking behavior of SiO_2. Another experimental study was performed by Zhang et al. [239] developed a pneumatic multi-material 4D printing approach to study the behavior of shape memory structures developed via the DLP technique. The results of mechanical strength of 4D-printed specimens showed the maximum weight reduction of 40 % along with young's modulus of value 708.6 MPa at 100% brightness level and room temperature. Thus, this approach can be applied to manufacture reconfigurable structures (as shown in Figure 11(c)), biomedical devices, and metamaterials, due to the lightweight features, complex structure programmability, and robust mechanical stiffness.

3.3.4 Two-photon polymerization

TPP also known as direct laser writing, offers spatial resolution and is generally used to produce intricate 3D nanostructures. It is a highly suitable technique for inducing selective polymerization in a variety of SRMs [251]. The non-linear excitation nature permits the photopolymerization process to occur in the focal point near-infrared laser beam without influencing other regions [252]. This process exhibits ultra-high resolution and freedom in structural designs [253]. In comparison to the DLP technique, this process offers high surface tension, and low surface roughness, as well as eliminates the need for supporting materials [254]. Therefore, this process fabricates micro-actuators for grasping, swimming, walking, and drug delivery devices [255]. For instance, Liu et al. [256] developed reversible and bidirectional self-assembly of ethyl acetate (EA)-, isopropyl alcohol (IPA)- and n-pentane-based liquid-responsive microstructures through the TPP technique, as shown in Figure 12(a). The results indicated that the 4D-printed micro-structures reversibly switched to a curved state with controlled curvature, thickness, and smooth morphology. These 4D-printed micro-structures can be potentially applied in biology and mechanics for micro-encapsulation, switchable wetting, reversible micro-patterns, and dynamic actuation of origami and micro-robots.

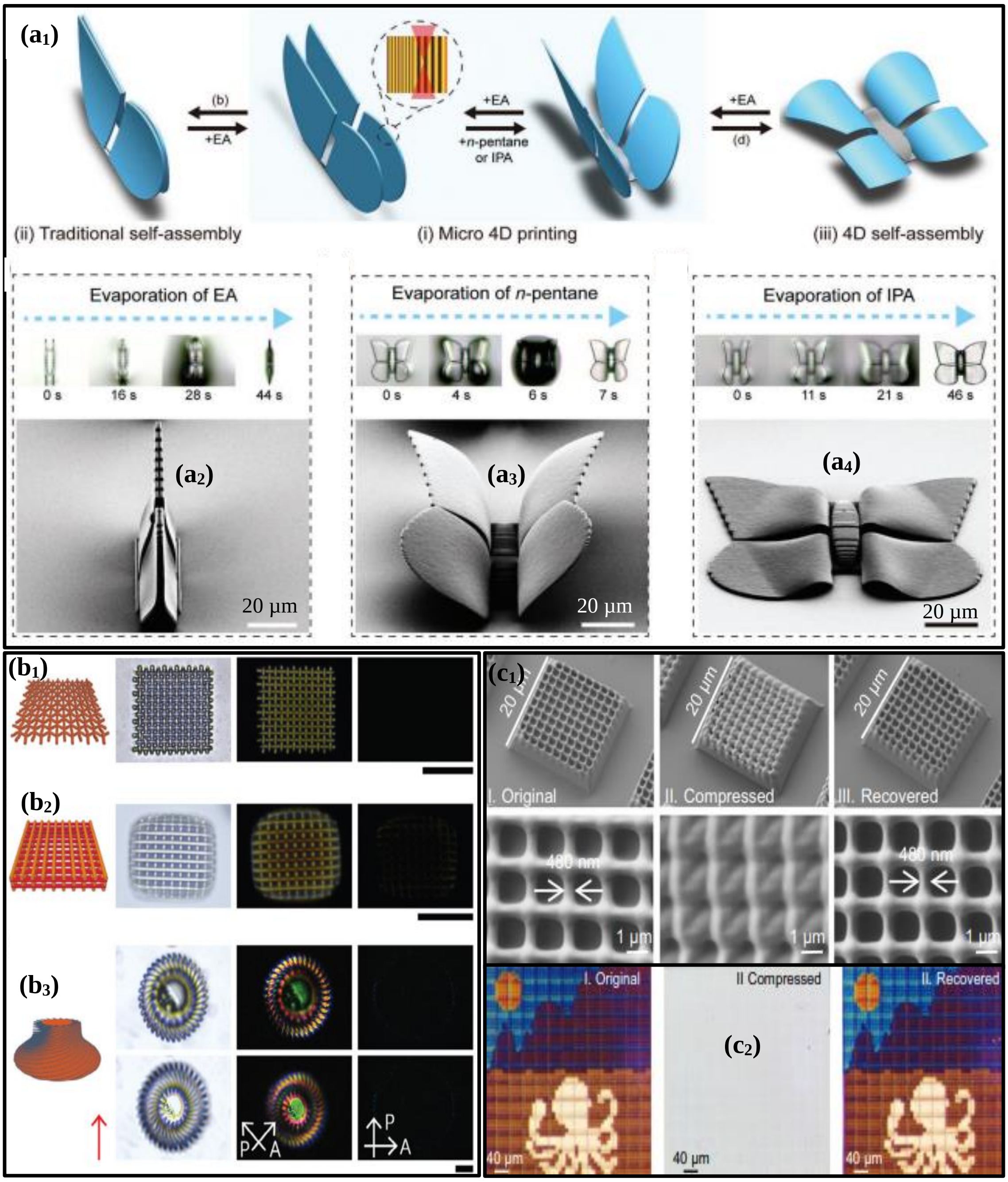

Figure 12. (a_1) A schematic illustration of 4D-printed self-assembly developed through a TPP technique triggered by liquid-responsive; (a_2- a_4) SEM and optical micrographs of the self-folded 4D-printed models, (a_2) Half open model, (a_3) Wide-open model, (a_4) Micro-butterfly model (adapted with permission from ref. [256]); 4D-printed microstructures depicting CAD on the left side and optical micrographs towards right side with (P) and without (A) cross polarizers; (b_1) An interwoven fabric architecture; (b_2) A woodpile; (b_3) A spiral disk (Scale bars: 20 µm) (adapted with permission from ref. [257]); (c_1) SEM images SMP-based 3D nano-structure manufactured through TPP depicting the behavior of SMP before and after programming and after recovery process; (c_2) 4D-printed strucutre exhibiting octopus-like shape, which can be programmed to featureless transparent image and is recovered to original state. (adapted with permission from ref. [258]).

In another study, del Pozo et al. [257] fabricated thermo-responsive LCE-based micro-actuators through the TPP technique. The developed microstructures displayed excellent fidelity to the CAD design, as illustrated in Figure 12(b). Additionally, these structures exhibited reversible anisotropic shape changes induced through thermal stimulus, which at a temperature of 200^{o}C, expanded from 10 % to 26 %. The controllable deformation and distinct polarization color can be potentially applied for real-time reporting, thus, enabling their integration in anti-counterfeiting and sensing micro-devices. Similarly, Zhang et al. [258] developed the high-resolution pattern of SMP photoresist through the TPP technique, as shown in Figure 12(c). The reported results indicated that 3D nanostructures were flattened and enabled invisibility of the printed shape and color. Furthermore, the SME recovered the original surface morphology of the structure along with its color upon temperature stimulus. Thus, the excellent reversible optical properties and microtopography can be helpful in developing 4D-printed anti-counterfeiting and tunable photonic devices.

3.4. Inkjet printing

In this liquid-based and non-contactable technique, tiny droplets of the photocurable resins are sprayed onto a printing plate through a polyjet ink head and are solidified through UV light to fabricate 3D products [259]. This technique is mainly used to print SMPC- and hydrogel-based multi-material heterogeneous structures of tunable properties [260]. The flow of ink materials during the process relies on their rheological characteristics. It is difficult to fabricate functional material-based components with embedded NPs due to stingent requirment on ink properties like low viscosity. Biocompatibility, cross-contamination prevention, and cost efficiency make this process highly appropriate for biological applications such as DNA microarray and targeted drug delivery systems [261]. Polyethylene naphthalate (PEN)- and polyethene terephthalate (PET)-based polymeric materials are mostly printed via the IJP technique to develop wearable electronic components and devices [262]. The bioprinting approach also uses IJP technology to fabricate cell-laden dynamic scaffolds by depositing smart polymers and cells through a nozzle [263]. In a review article, Wei et al. [264] reported that biomedical scaffolds developed through the IJP technique possess low residual stresses and transection efficiency of >30 %. In an experimental study, Cui et al. [265] fabricated SMP-based self-folding scaffolds/microtubes by embedding human umbilical vein endothelial cells (HUVECs), as illustrated in Figure 13(a). The results revealed that 4D-printed micro-tubes showed mimicked micro-vessels. Thus, 4DP produces cell-encapsulating 3D scaffolds with a variety of intricate shapes, through the printing of material inks into 2D-micropattern.

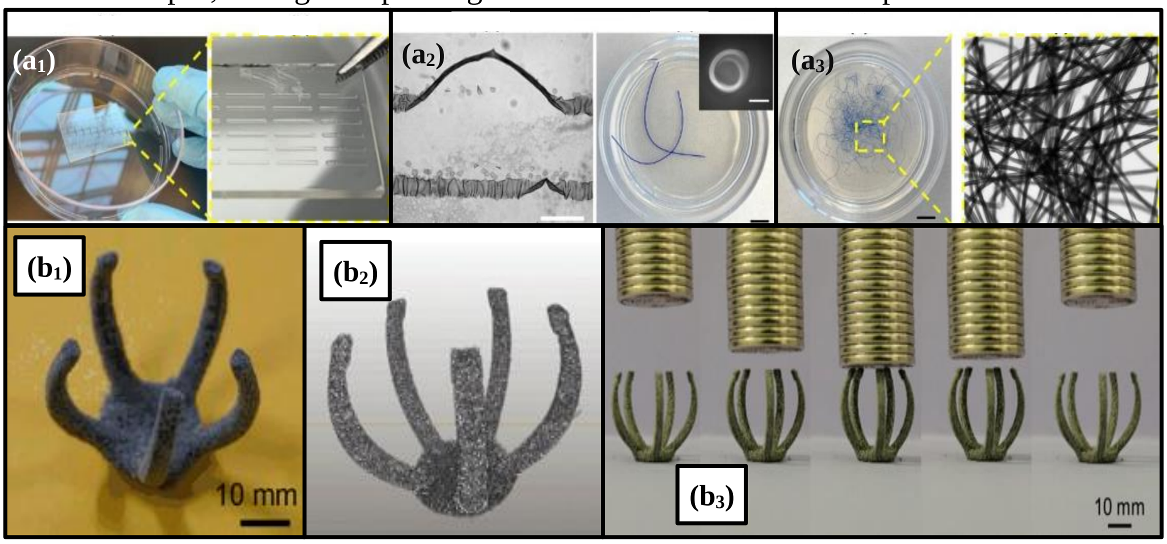

Figure 13. (a$_1$) Micro-patterns printed on a glass slide which exhibited self-folding behavior in PBS; (a$_2$) Self-folded micro-tubes of different diameters; (a$_3$) Micro-tubes placed in petri-dish for visualization (adapted with permission from ref. [265]); (b$_1$) Image of magneto-driven gripper; (b$_2$)

Micro-computed tomography image; (b_3) Deformation behavior of TPU/$Nd_2Fe_{14}B$-based gripper developed through SLS technique (adapted with permission from ref. [112]).

3.5. Selective laser melting/Selective laser sintering

4D printing of powder bed fusion is mainly applied for powder-based techniques such as SLM and SLS. These powder-based techniques use a laser beam to melt or sinter powder particles on a predefined path to develop the product through layer-by-layer deposition [266]. These techniques are extensively applied to process composites due to the ease of blending different powdered materials, which integrates a wide range of properties. Binder (polymer) undergoes melting and structural materials (metals) remain in the solid phase during partial melting or liquid phase sintering [267]. Unlike FDM technology, SLS permits the printing of hollow architectures without any support requirement. It also helps in reducing time and the recycling of the powdered material after each layer reduces cost [268]. SLS approach is vastly adopted for ceramics, metals, and polymeric powders such as PU, PCL, PEEK, and PA [236].

It is a propitious technique for 4DP of electrically conductive and magnetic materials. Most 4D-printed products are manufactured through SLS technology by integrating conductive additives into polymer matrices. However, it is essential to control the percentage of nanomaterials for achieving excellent surface quality. Magneto-responsive polymeric composites undergo deformation upon the magnetic field and magnetic force controls the shape change of the printed product. For instance, Wu et al. [112] fabricated a magnetic-driven TPU/$Nd_2Fe_{14}B$-based 4D-printed gripper, as shown in Figure 13(b). The results revealed that polymer composite-based gripper exhibited controllable deformation upon magnetic field stimulus.

SLM also known as the laser powder bed fusion is a highly flexible and robust non-contact process [269]. In this technique, metallic powder placed on the building platform is fused through a high-intensity laser beam that is melted by absorbing the thermal energy of the laser beam [270]. Once the layer is solidified, the platform moves downward and a new metallic powder layer is deposited and leveled by re-coater [271]. This process is continued until the object is completely printed. Post-processing treatments are not required for products developed via SLM technique. The technology was mainly applied by researchers to fabricate metals, alloys and ceramics-based printed parts [272]. For instance, Lu et al. [273] developed an SMA using high-performance material $Ti_{50.6}Ni_{49.4}$ using the SLM process by varying the energy input of the laser beam. Mechanical testing was done on the 4D-printed specimens and results showed the maximum tensile strength of 776 MPa was obtained at 222 J/mm^3.

Laser cladding is also known as direct energy deposition (DED) is another AM approach, in which one material is deposited over the surface of another material [274]. In this process, powdered metal or wire is deposited through feedstock over a molten pool on the surface of other material which is then hardened by a laser beam [275]. This technology is mainly applied to print metal-based products [276]–[278]. For example, Xin et al. [279] applied the LCD technique for the 4DP of auxetic metamaterials and studied the mechanical strength of the printed specimen. It was observed that the specimen displayed the maximum elastic modulus of ~1.4 GPa, tensile strength of 48 MPa, and 90 % elongation upon mechanical testing. Ceramics and polymers can also be printed using this technique.

4. SMP-based novel composite materials

SMP-based composites are extensively applied to develop novel materials including multi-materials, metamaterials as well as moldless manufacturing of composites. This section further delves into the 4DP of these materials.

4.1. Multi-material 4D printing

4DP is considered a systematic tool to develop programmed multi-material design. Multi-material 4DP alleviates the mechanical characteristics and can be done through jetting materials simultaneously or one by one [280]. Recently, multi-material 4DP has been gaining a lot of attention due to the incorporation of multiple materials into 3D products by using a single 3DP technique. Multi-material printing uses 3DP technologies to develop components by using a vareity of SRMs that can alter their characteristics upon exposure to a specific stimulus [281]. The primary feature of multi-material 4DP is the geometrical transformation after 3DP. Additionally, multi-material printing possesses excellent strength and malleability over the action of specific stimuli such as humidity, temperature, pH, solvent, or light [282]. Polyjet printing is commonly applied for successful multi-material printing in which different liquid resins are deposited onto the printing platform by using multiple inkjet printheads, followed by subsequent photo-polymerization of jetted polymers [283]. DIW and FDM are other extrusion-based printing techniques, which are suitable for multi-material 4DP via multiple nozzles [284]. The distinct features of multi-material printing have paved the way for developing micro-fluidic tubes for drug delivery as well as other biomedical applications [285]–[287]. For instance, Ge et al. [288] fabricated a multi-material SMP/hydrogel-based cardiovascular stent for drug release applications, as illustrated in Figure 14(a). The results indicated that the stent exhibited excellent SME and 4D-printed stent was squeezed into a compact shape at a programming temperature and regained its original shape after heating.

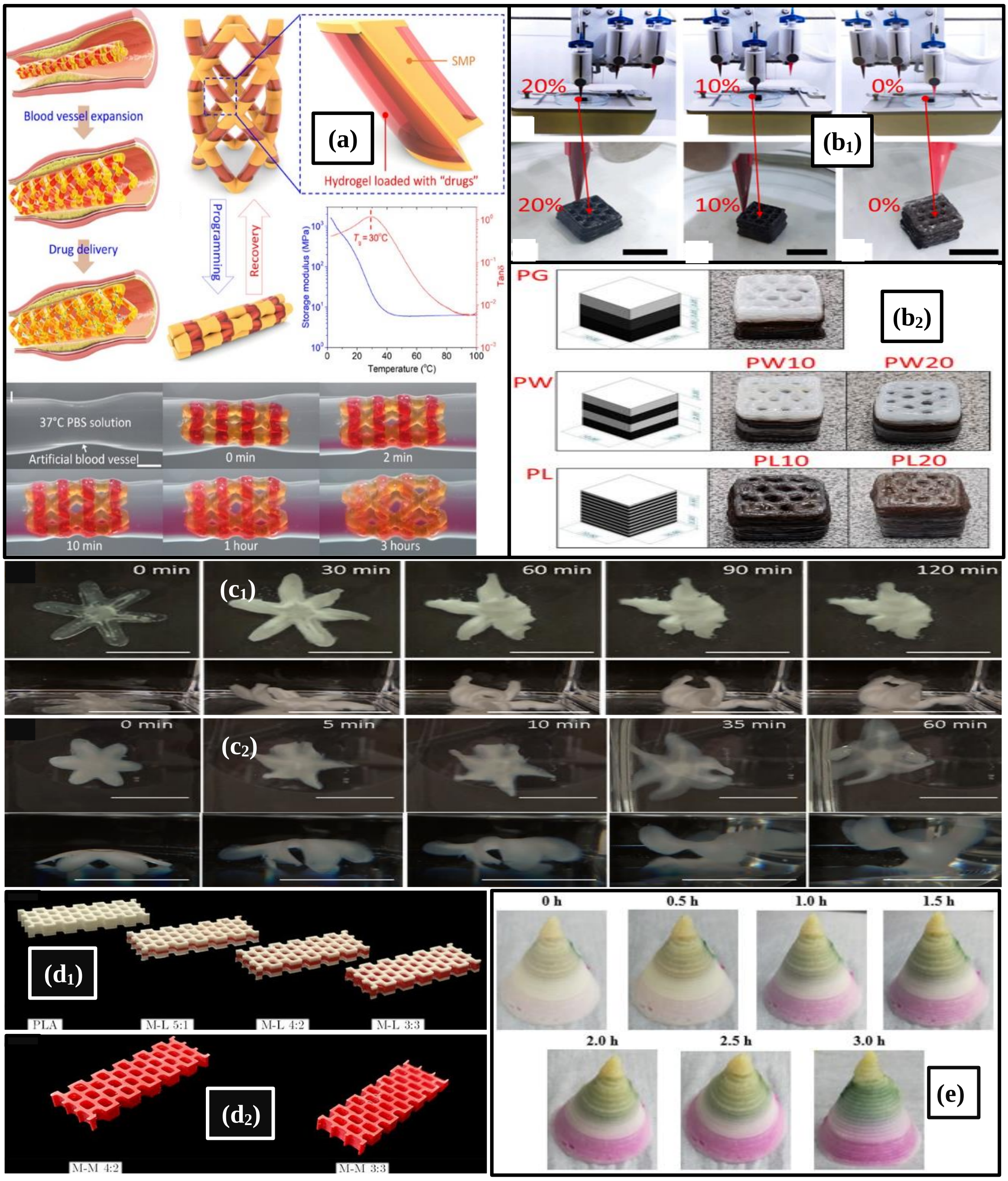

Figure 14. (a) SMPC-based multi-material 4D-printed cardiovascular stent demonstrating shape memory as well as drug releasing functions (adapted with permission from ref. [288]); (b) Multi-material 4DP of magnetic-driven hydrogel-based actuators; (b_1) 3D nanocomposite-based structures manufactured through direct printing by using varying magnetic NPs; (b_2) Different multi-material architectures; (PG: Hydrogel assembled from three type of inks; PW: Hydrogel containig two type of inks after 10 deposted layer; PL: Hydrogel containig two type of inks, which were altered after two deposited layers) (adapted with permission from ref. [156]); (c_1) HEA-based sea star showing swelling results after placing in water; (c_2) BA-based sea star showing swelling results after placing in spearmint oil (adapted with permission from ref. [289]); (d_1) TPE/PLA and PLA multi-layered sample with PLA to TPE exhibiting 5:1, 4:2, and 3:3 of volumetric ratios; (d_2) PLA/TPE-based multi-material specimen with PLA to TPE exhibiting 4:2 and 3:3 of volumetric ratios (adapted with permission from ref. [290]); (e) Multi-material 4DP of mashed potatoes with different pH/purple sweet potato puree (adapted with permission from ref. [291]).

In another study, Siminska-Stanny et al. [156] fabricated functionally graded multi-material 4D-printed architectures by using the DIW technology, as illustrated in Figure 14(b). The results revealed that hydrogel-based actuators exhibited distinct magnetic responsiveness, excellent mechanical stability, non-cytotoxicity, and tunable distribution of magnetic NPs. Thus, 4DP of magneto-responsive hydrogels and programmable patterning make these soft robots highly suitable for biomedical applications.

Schwartz et al. [289] developed 2-hydroxyethyl acrylate (HEA)/butyl acrylate (BA)-based multi-material sea water structures through the DLP technique, as shown in Figure 14(c). The results indicated that the variation in multi-material actinic spatial control formulation changed the mechanical characteristics of 4D-printed specimens. Additionally, these multi-material structures exhibited mechanical anisotropy, heterogeneous imagery, and 4DP through spatially-controlled swelling, each from resin vats simply by inputting-controlled light combination.

Shape changing characteristics can also be achieved by using a multi-material 4DP approach and through the distribution of different SMPs in the polymer matrix [292]. Recently, multi-layered active and programmable architectures have also been reported in the literature. For instance, Roudbarian et al. [290] fabricated PLA/thermoplastic elastomer (TPE)-based multi-material and multi-layered structures through the 4DP technique, as illustrated in Figure 14(d). The results indicated that SMPC-based multi-material specimens exhibited better shape recovery behavior compared to PLA specimens, due to oriented crystalline polymer structure.

Multi-material 4DP can also be applied in the food sector, which alters the shape, color, flavor, and nutrition properties of the printed product depending upon internal structural design, the difference in material properties, and spatial arrangement of food products [293], [294]. For instance, He et al. [291] fabricated multi-material 4DP of mashed potatoes/citric acid/sodium alginate (SA)/sodium bicarbonate through extrusion technique, as illustrated in Figure 14(e) and reported that the potato flake content and pH value changed the color of mashed potatoes. This multi-material printing has the potential to be applied in the food industry for producing colorful food products.

4.2.Metamaterials

Metamaterials are novel and engineered smart materials, which can attain mechanical properties not commonly observed in natural materials [295]. A variety of absorbers, sensors, antennas, and acoustic cloaks can be fabricated by using these materials [296]. Recently, 4DP is also employed to develop metamaterials-based active architectures and their mechanical properties can be regulated on the basis of changing environmental conditions [297]. The physical properties of these novel materials including mechanical, thermal, electromagnetic, and acoustic properties are tailored through the proper arrangement of microstructural elements and appropriate design [298]–[300]. Mechanical metamaterials are cellular materials that exhibit excellent mechanical characteristics due to repetitive unit cells [279]. Active mechanical metamaterials are highly sensitive to a variety of stimuli like electric current, magnetic field, temperature, pH, and light [301]. These metamaterials have shown the unbounded potential to create smarter, stronger, and more versatile materials for next-generation engineering applications [302].

Recently, SMP-based metamaterials with tunability, reconfigurability, energy absorption, mode conversion, and programmability features have been fabricated based on SME and variable stiffness [303]. For instance, Yang et al. [304] fabricated functionally deployable, geometrically reconfigurable, and mechanically tailorable lightweight bisphenol A ethoxylate dimethacrylate (BPA)/acrylic acid (AA)-based metamaterials through the PµSL technique, as illustrated in Figure 15(a). These 4D-printed metamaterials possessed extraordinary mechanical adaptation to geometrically complex environments and varying external loading. These metamaterials can be potentially applied in morphing aerospace architectures, tunable shock-absorbing interfaces, and minimally invasive medical instruments. Similarly, Li et al. [305] fabricated poly(ethylene-co-methacrylic acid) (PEMA)-based elastic/ acoustic tunable metamaterials through the FDM technique, as shown in Figure 15(b). Thermally-driven metamaterials exhibited excellent shape-memory behavior to permit rearrangement into new patterns. This behavior can be applied to manufacture intelligent devices for high-resolution medical imaging, vibration isolation, elastic-wave control, and energy harvesting.

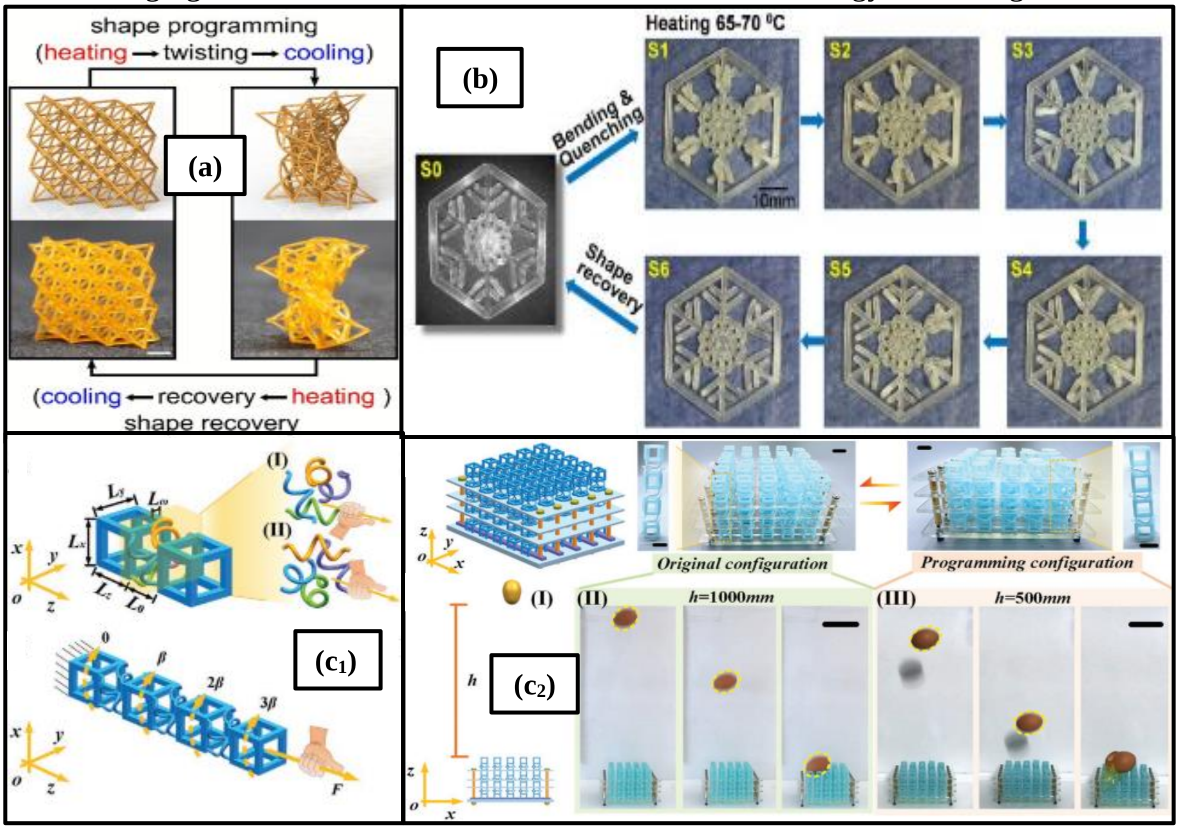

Figure 15 4D-printed AA/BPA-based metamaterial (adapted with permission from ref. [304]); (b) Shape-memory cycle of 4D-printed snowflake like unit cell from original shape to a temporary shape and back to original shape (adapted with permission from ref. [305]); (c) PLA-based pixel mechanical metamaterials with original and programmable configurations; (c_1) CAD model and deformation mechanism of metamaterials; (c_2) CAD model in (I), Egg fall freely onto unprogrammed configuration in (II); Egg fall freely onto programmed configuration in (III) (adapted with permission from ref. [306]).

Mechanical metamaterials usually suffer from a narrow deformation domain, weak tension-torsion coupling effect, and lack of adaptability. To solve these issues, Xin et al. [306] fabricated PLA-based pixel mechanical metamaterials through 4DP, which exhibited excellent programmability, reconfigurability, and tunability. The results revealed that mechanical metamaterials provided excellent protection to an egg falling from the height of 1000 mm, as shown in Figure 15(c). Additionally, these 4D-printed architectures can be potentially applied in soft robots, kinematics controllers, and buffer devices. The recent advancements in simulaltion- and machine learning-based design tools help to develop more intricate metamaterial structures.

4.3.Moldless manufacturing of composites

Conventional fabrication techniques including resin transfer molding, hand layup, vacuum bagging, filament winding, prepreg, and pultrusion are usually employed to manufacture polymer composite materials [307]–[309]. These manufacturing techniques have several limitations including the requirement of molds for the fabrication of composite products. Furthermore, it is a challenging task to regulate the processing parameters of these techniques. On the other hand, moldless composite manufacturing can be fabricated by using the concept of 4DP which was first proposed by Hoa et al. [310].

4D printing of composites (4DPCs) uses continuous fibers for developing different engineering architectures including wind turbine blades, automobiles, and aircrafts [311]. 4DPC helps in fabricating intricate geometries without the assistance of complex molds and provides design flexibility and better mechanical characteristics [312]–[314]. For instance, Hoa et al. [315] successfully developed omega (Ω)-shaped aircraft wing stiffeners by using continuous fiber-reinforced composites through the 4DP technique, as illustrated in Figure 16(a). The results indicated that printed stiffeners exhibited excellent flexural stiffness.

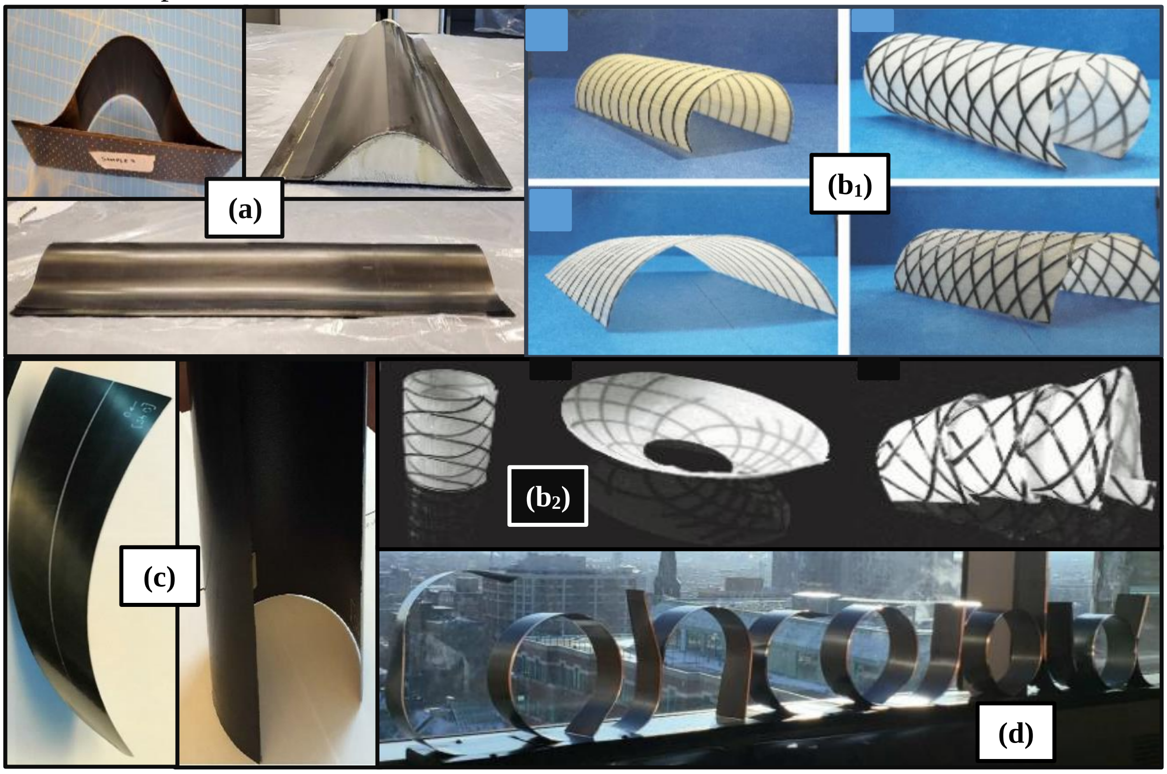

Figure 16. Ω-shape composite for aircraft wing stiffeners developed through moldless manufacturing (adapted with permission from ref. [315]); (b_1) 4D-printed continuous fiber structures at 25°C and 80°C; (b_2) Final shape and trajectory of fiber-reinforced composites (adapted with permission from ref. [316]); (c) Curved and twisted composite laminates at two layup sequences [0/30] and [0/45] developed through 4DP (adapted with permission from ref. [317]); 4DP of SMPCs to develop English alphabets showing that this technique is suitable for developing complex deformed structures (adapted with permission from ref. [318]).

Likewise, Yong et al. [316] designed a complete fiber trajectory by embedding continuous fibers into the polymer matrix, as shown in Figure 16(b_2). The results revealed that the deformation control in bilayer composite structure was achieved due to coefficients of thermal expansion between the resin substrate and embedded fibers. The adopted design model and 4DP technique can precisely control the deforming process, thus contributing further towards promoting applications of 4DP technology. In another study, Hoa et al. [317] used [0/45] and [0/30] layup sequences of carbon/epoxy-based laminates to develop 4D-printed composite architectures, as shown in Figure 16(c). The results indicated excellent twisting and curving mechanisms which are useful for the manufacturing of solar energy concentrators, hockey stick blades, actuators, and blades for vertical windmills.

Different NPs/additives/fillers such as inorganic ceramics, zeolites, and microparticles can be incorporated in the composites easily during the 4DP of fibers [319]. The incorporation of reinforcing mediums in polymers improves their thermal, mechanical, and other functional characteristics [320], [321]. However, the addition of fillers enhances the weight of manufactured parts. Additionally, inorganic fillers are not environmentally sustainable.

4.4. 4D printing of biocomposites

Hygromorphic (moisture-sensitive) materials are novel sustainable and lightweight materials for developing complex structures through 4DP [322], as illustrated in Figure 17(a), which can be potentially utilized in sensing, actuating and construction applications and do not require any additional energy for electronic or mechanical control [323], [324]. For instance, Le Duigou et al. [325] developed the HBC-based shape-changing metamaterials through the reinforcement of continuous flax fibers (CFFs) into a polybutylene succinate (PBS) and PLA matrices. The results indicated that HBC-based composites exhibited increased reactivity by 500 % and responsiveness was enhanced by 92 %. Additionally, HBC-based SMPs with controlled stiffness ratio and thickness have the potential to be employed for autonomous actuation applications, as illustrated in Figure 17(b). However, HBCs exhibited stiffness reduction in the presence of moisture contents which limits their utilization in soft actuating applications. In another study, Le Duigou et al. [326] developed multi-SRMs by introducing continuous carbon fibers (CCFs) into the polyamide (PA) matrix through 4DP, as shown in Figure 17(c). The printed specimen exhibited the microstructure same as HBCs. This actuation behavior can be utilized where actuation is triggered due to varying moisture content. Additionally, the developed HBCs upon electrical heating stimulation possessed an actuation speed ten times higher than other existing HBCs, as illustrated in Figure 17(c_2). Similarly, Correa et al. [327] combined different wood/polymer composite active layers and passive plastic layers for developing moisture-stimulated intricate reversible architectures.

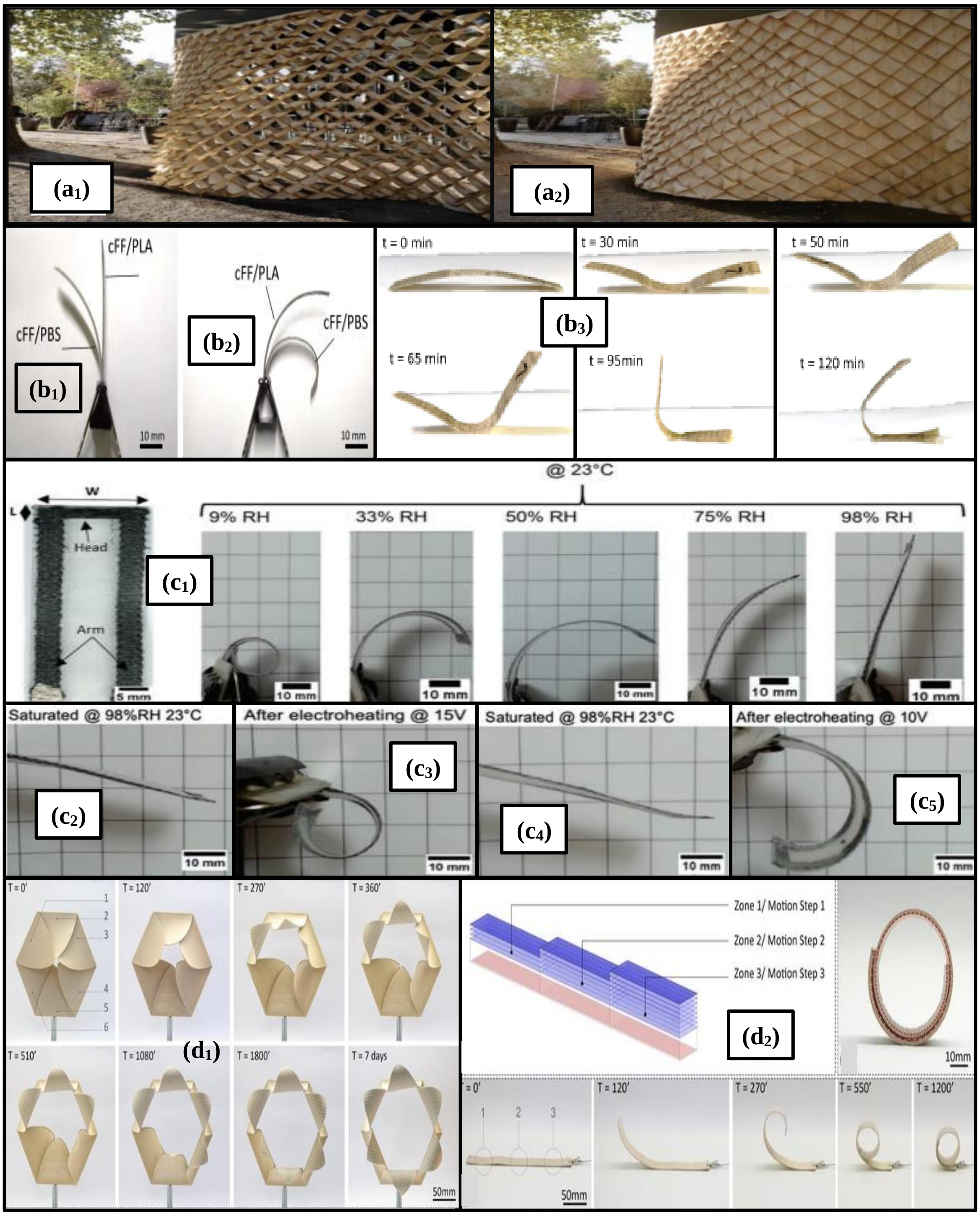

Figure 17. Different prototypes developed through the 4DP of HBCs; (a_1, a_2) Construction prototype present at the institute of computational design, University of Stuttgart showing the hygromorphic skin opened (left) and closed (right) upon external stimulus (adapted with permission from ref. [328]); (b) PLA/CFF and PBS/CFF-based 4D-printed HBCs before (b_1) and after (b_2) immersion in water; (b_3) Photograph of PBS/CFF-based HBC showing actuating behavior (adapted with permission from ref. [325]); (c_1) Photographs depicting the actuating mechanism of 4D-printed CCF/PA-based HBCs upon moisture stimulus; (c_2- c_5) CCF/PA-based HBCs showing the influence of electric stimulus on actuating behavior (adapted with permission from ref. [196]); (d_1) HBC-based 4D-printed aperture prototype with programmed motion; (d_2) HBC-based 4D-printed cantilever prototype (adapted with permission from ref. [329]).

Table 2 presents the summary of the latest research results on 4DP of SMPCs along with their specifications.

Table 2. Summary of latest research results on 4DP along with descriptions about 4DP processes

Printing Process	**Description about 3DP Processes**		**Dynamic materials**	**Stimulation method**	**Ref.**
	Build volume (mm^3)	**Nozzle details + layer resolution**			
Photopolymerization	80× 5 × 0.6	0.3 mm layer thickness	Glassy SMP composite	Temperature	[100]
FDM	80× 20 × 1	Nozzle diameter 0.4 mm, feed rate 20 mm/s, layer thickness 0.1-0.2 mm	PU/CNTs	Temperature	[330]
Extrusion-based	65× 65 × 0.6	0.8 mm tapered nozzle along with 0.6 mm layer	CMC/montmorillonite clay	Water	[331]
FDM	-	-	CMC composite	Water	[332]
IJP	-	A circular wide nozzle of 1.5 mm diameter	RGO-CNT-PEDOT:PSS composite films	Voltage	[333]
-	60 × 8 × 0.4	-	PLA/Ag-NWs composite	Voltage	[41]
Extrusion-based	-	-	CuS/PU composite	Light	[104]
SLA	150 × 150 × 100	10 µm	SCO polymer nanocomposites	Temperature	[129]
FDM	9× 9 ×13	The nozzle diameter 0.4 mm along with layer height 0.1 mm	PBS/PLA composite	NIR light	[158]
DIW	0.8× 4 ×40	Dual nozzle with S0 ink (white), and the S6 ink (green) with inner diameter of 610 µm. 0.5 mm	GF reinforced composites	Heat	[218]
Extrusion-based	-	Two-nozzle were employed	Silicone/wax microparticles composites	Heat	[216]
SLS	35× 100 with 2,4,6 and 8 mm diameters	0.4 mm layer thickness	$Nd_2Fe_{14}B$/TPU magnet composite	Magnetic field	[112]
FFF	80×20 ×40	Nozzle diameter (4 mm), 0.2 mm layer thickness	PLA wood/nanosilica composites	Temperature	[334]
FDM	-	Brass nozzles with 0.3 mm diameter	CB/PLA composite	Temperature	[335]
PolyJet	40 ×5.5 × 2	50 μm	SMPC	Temperature	[336]
FDM	90× 20 × 2	0.1 mm	Nylon and CF laminated composite	Temperature	[337]
FDM	20× 5 × 0.1	Dual-nozzle with 0.4 mm dia.	PLA/TPU composite	Temperature	[128]
FDM	10× 1 × 1	Single nozzle, layer thickness 0.05–0.3mm	Nylon 12/PLA	Current/heat	[103]
FFF	20 mm diameter and 2 mm thickness	5 mm diameter of extrusion die	Thermoplastic composite	Electric field	[338]

5. Applications of 4D-printed polymer composites

4DP is a futuristic and rapid prototyping technology, which has unbounded potential to be implemented in different engineering sectors including biomedicine, electronics, robotics, food, automotive, construction, and aerospace. However, its technological advancements in various engineering sectors require interdisciplinary research [339]. SMPCs possess the ability to substitute traditional polymers in different engineering sectors and Figure 18 summarizes the important practical and potential applications of 4D-printed SMPCs. The limited literature is available on the practical applications of this technology. This section incorporates the practical applications of 4D-printed products envisioned by researchers.

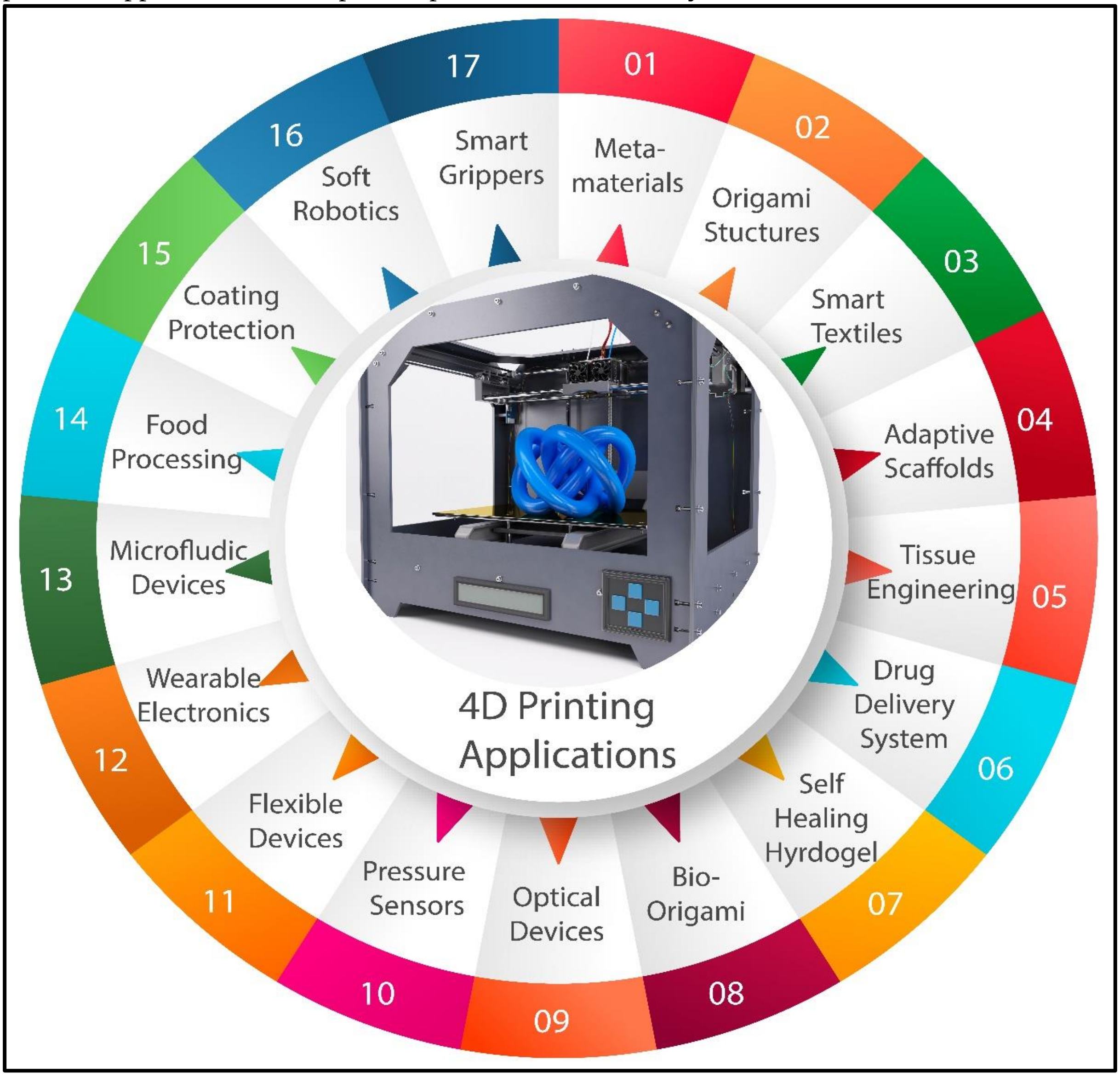

Figure 18. Potential and demonstrated applications of 4D-printed polymer composites in various high-end applications

To date, 4DP of polymer composites manufactures different materials for innovative and fascinating applications which were unachievable through conventional manufacturing processes, as illustrated in Figure 19. For instance, the selective electrical stimulation of piezoelectric active implants helps to increase the rate of bone growth and reduce the bone resorption rate. Consequently, the osseointegration of the implant can be greatly improved by using piezoelectric materials [340]–[343].

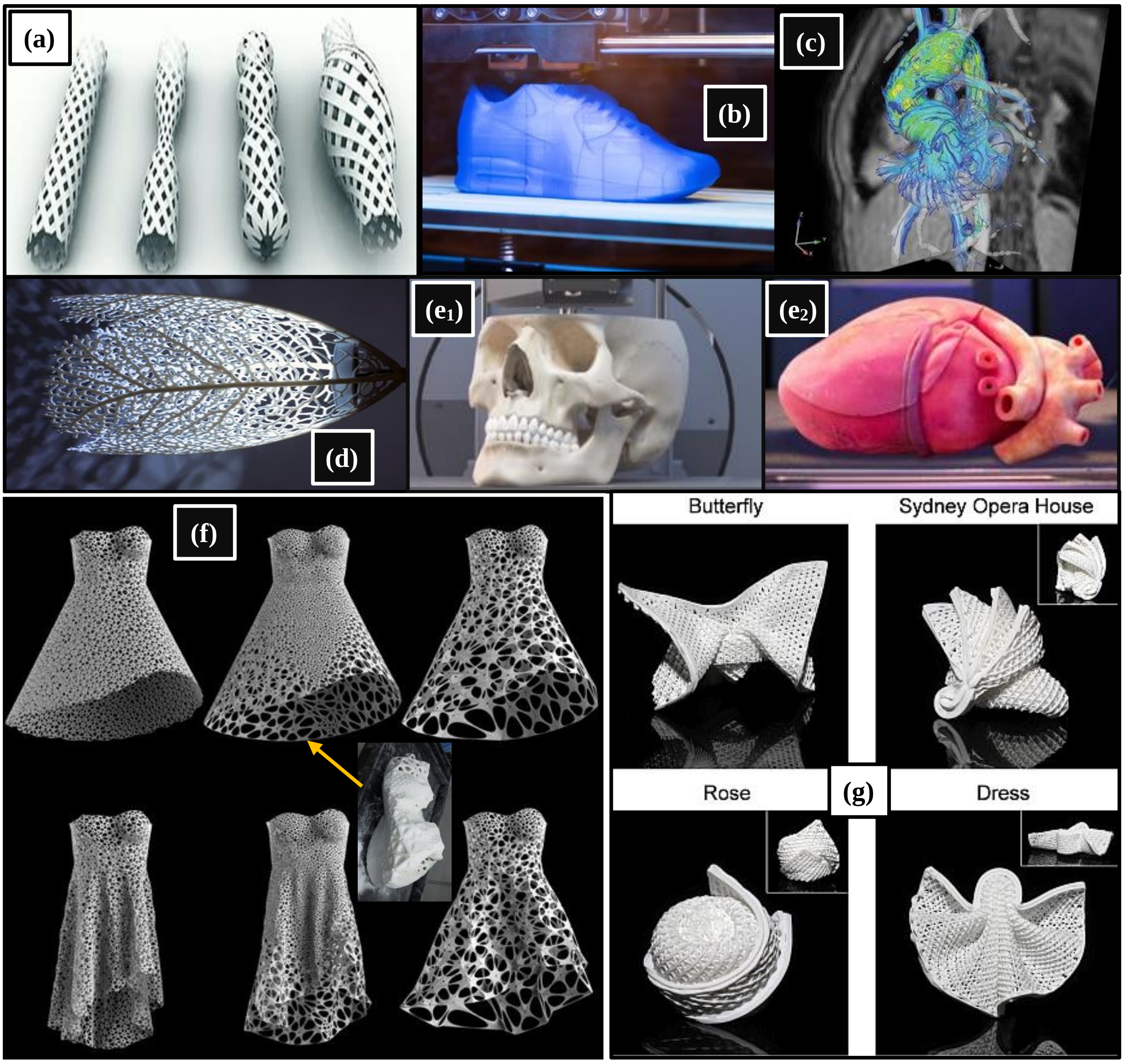

Figure 19. Applications of different 4D-printed SMP-based composites; (a) 4D-printed different pipes (adapted with permission from ref. [344]); (b) 4D-printed shoe (adapted with permission from ref. [345]); (c) 4D-printed multi-colored heart model (adapted with permission from ref. [346]); (d) 4D-printed hyphae lamp (adapted with permission from ref. [347]); (e_1) 4D-printed human skull; (e_2) Artificial heart printed through 4DP technology (adapted with permission from ref. [345]); (f) Kinematics 4DP to fabricate clothes of different designs (adapted with permission from ref. [347]); (g) 4D-printed origami structures developed by using the mixture of ceramics and SMPs (adapted with permission from ref. [348]).

5.1. Tissue engineering applications

4DP technology has the unbounded potential to be applied for organ repairing, tissue regeneration, and drug delivery applications [349]. It is due to its ability to construct complex structures and possesses high resolution [350]. Kang et al. [351] used an integrated tissue–organ printer (ITOP) to regenerate tissue for cartilage, skeletal muscle, and calvarial bone. Similarly, Miao et al. [352] 4D-printed acrylated epoxidized soybean oil (AESO)-based biocompatible porous scaffolds, which exhibited the capability to hold mesenchymal stem cells (MSCs) of bone marrow. Additionally, the scaffolds retained their original shape after reaching the body temperature. In another study, Constante et al. [353] reported the construction of tubular scroll-like scaffolds with anisotropic inner topography for the development of oriented muscle microtissues, through 4DP. A combination of methacrylic anhydride (MA), SA, and melt-electro writing of PCL fibers were employed to develop 4D-printed scaffolds. The results showed that printed photo-crosslinked SA sheet gel rolls upon swelling and produces scroll-like tubes, as presented in Figure 20(a). The proposed technique is highly adaptable in the engineering of tissues with the uniaxial orientation of cells such as cardiac, neural tissues, and skeletal muscle.

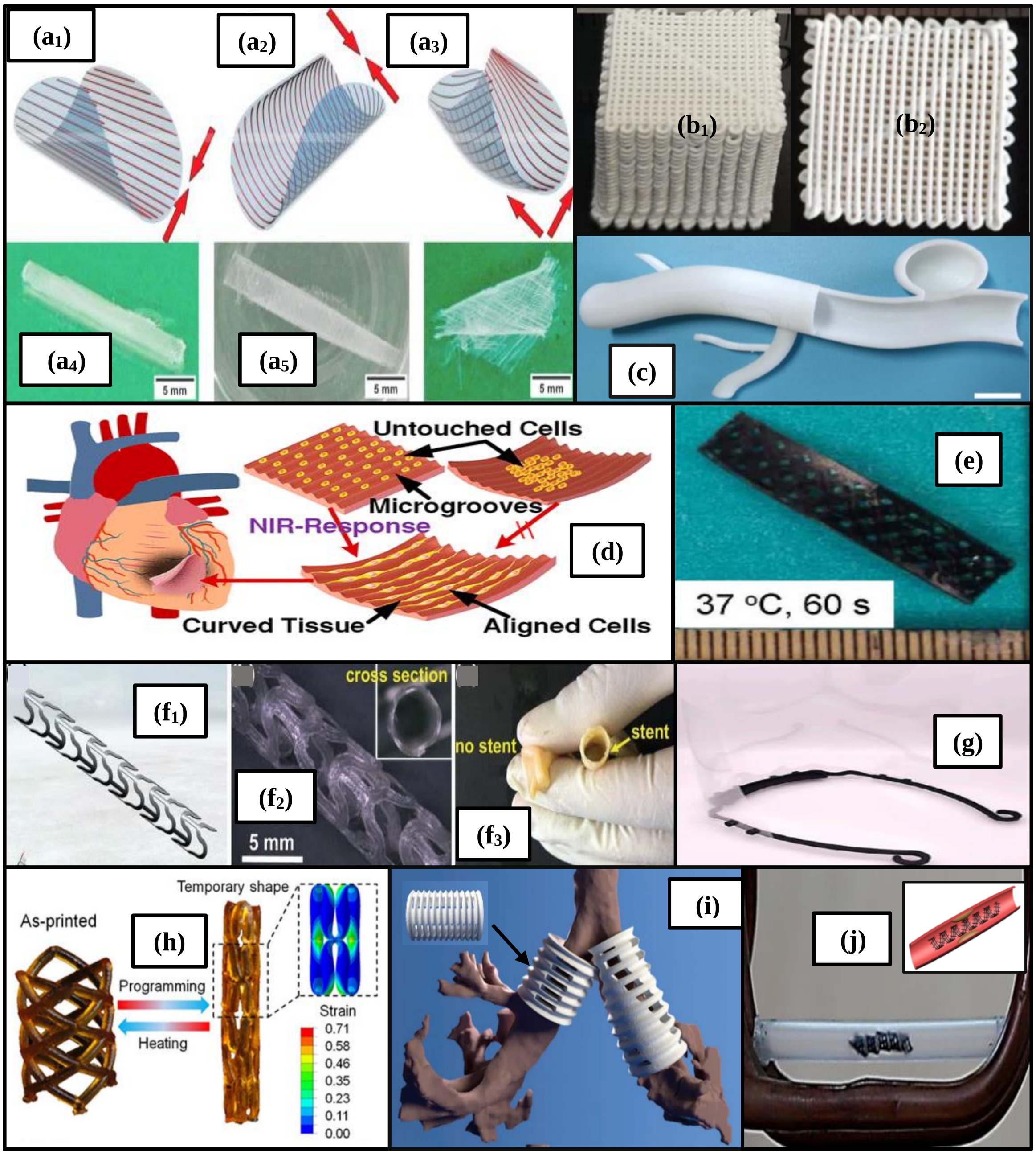

Figure 20. Various direction of folding; (a_1) Parallel-wise; (a_2) Perpendicular-wise; (a_3) Diagonal-wise of the SA-MA/PCL bilayers; (a_4, a_5) Folding of rectangular and circular-shaped scaffolds (adapted with permission from ref. [353]); (b_1-b_2) Osteogenic peptide and BP-loaded β-TCP/PLA-TMC-based nanocomposites scaffolds for bone tissue engineering applications (adapted with permission from ref. [354]); (c) Aneurysm 4D-printed PBS/PLA-based composite vascular model (adapted with permission from ref. [158]); (d) Cardiac construction through 4DP (adapted with permission from ref. [355]); (e) 4D-printed scaffold manufactured by using SMPs (adapted with permission from ref. [352]); (f_1-f_2) Illustration of 4D-fabricated stent model; (f_3) Blocked porcine blood vessel cross-section view dilatation

was due to 4D-printed stent (adapted with permission from ref. [356]); (g) 4D-printed protective visor for COVID-19 pandemic (adapted with permission from ref. [357]) (h) Stent developed through 4DP (adapted with permission from ref. [76]); (i) Surgical implantation of 4D-printed air-way splints (adapted with permission from ref. [358]); (j) 4D-printed intravascular stent (adapted with permission from ref. [359]).

In another study, Wang et al. [355] fabricated 4D-printed cardiac tissues with aligned fibers and adaptable curvature. Figure 20(d) is exhibiting the schematic representation of the aligned cells. These 4D-printed products can be potentially employed for organ and tissue regeneration applications.
4DP technology can also be employed for treating abnormalities in the orthopedics field. For instance, Wang et al. [354] developed black phosphorus nanosheets and osteogenic peptide reinforced β-tricalcium phosphate (TCP)/PLA-TMC-based bone scaffolds through the 4DP technique, as illustrated in Figure 20(b). The results indicated that the NIR stimulus helped in reconfiguring the scaffolds for implantation. The part models generated through 4DP can transform their shape upon external stimuli. Additionally, these developed replica parts can help to perform complex surgeries [360]. Similarly, 4DP can be potentially applied for the printing of kidneys, livers, and hearts using biocompatible and flexible materials like SMPs [361]. Skin grafting can be done using 4D-printed SMPs, which have the ability to generate skin of original skin color [362]. It will help to treat skin burn patients in the future.

5.2. Biomedical devices

SMP-based composites have also drawn great interest in the development of dynamic and smart biomedical devices, and electronic skins [363]. For instance, Morrison et al. [358] fabricated a PCL-based personalized medical device to treat tracheobronchomalacia, which possessed the ability to transform its form under tissue growth and resorption conditions. The results revealed that the SMP-based printed parts decomposed when airways started functioning properly. Thus, the 4D effect of degradability over time further justifies the possible use of the 4DP technology for developing biomedical devices.
Interventional embolization has huge potential in the treatment of aneurysms due to its safety and less trauma. The objective of the embolization coil is to separate the aneurysm sac from the blood circulation by providing the embolic agent to the target sac, thus, reducing the risk of rupture [364]. Lin et al. [158] developed the PBS/PLA-based aneurysm 4D models, as shown in Figure 20(c), which have found their exceptional usage in biomedicine.
4DP technology permits the fabrication of customizable products including stents [365]–[367]. SMP-based printed stents also help to minimize the surgical incision during implantation by temporarily reducing its diameter through programming. The body temperature allows the printed stent to recover its original diameter after implantation. For instance, Ge et al. [76] introduced PμSL technology to develop a 4D-printed cardiovascular stent, as shown in Figure 20(h) and the 4D-printed stent exhibited excellent shape memory behavior. In another study, Wet et al. [359] introduced viable fabrication technology to manufacture magnetically responsive PLA-based printed stents, as shown in Figure 20(j). Similarly, Wang et al. [356] evaluated the mechanical performance of PLA-based 4D-printed shape-memory stents, as depicted in Figure 20(f). These stents possessed excellent mechanical properties and a high recovery ratio. Furthermore, these 4D manufactured stents exhibited minimal medical risk and act as mild intervention devices for vascular diseases.
4DP technology also plays its part in fabricating the protective equipment during the pandemic situations and unprecedented circumstances like Coronavirus Disease 2019 (COVID-19) [368].

Various researchers also tried to fabricate high-demand products using this technology. For instance, Ji et al. [357] developed an adjustable protective visor of thermo-responsive SMP, which can help people to protect against the pandemic, as shown in Figure 20(g). Similarly, Cheng et al. [130] employed UV-assisted FDM technology to develop elbow protectors.

SMP-based composites are vastly applied to store and subsequent sustained release of drugs in the biomedical field [369]. Biorobots are proves useful in performing surgeries as well as for drug delivery systems [370]. These carry and take the drugs at the required location [371]. For instance, Azam et al. [372] developed the drug delivery polyhedral device by using SU-8 faces and thermo-responsive PCLs. Similarly, Malachowski et al. [373] developed a device for the targeted drug release in the digestive tract. In another study, Zu et al. [374] developed plant stomata-inspired, UV cross-linked PNIPAM-based hydrogel as a capsule shell through an extrusion-based technique. Due to lower critical solution temperature-induced swelling/shrinking properties, the developed PNIPAM hydrogel capsules showed microstructure changes and temperature-responsive drug release, as presented in Figure 21(a). During in vitro drug release testing, the PNIPAM-based hydrogel capsules autonomously controlled drug release behaviors due to the difference in ambient temperature. Furthermore, enhancement in the drug release rate of the hydrogel capsules was observed due to the increased molecular weights of polyethylene glycols (PEG) in the macro-porous PNIPAM hydrogel capsules. Thus, the bioinspired hydrogel capsules through 4DP have the potential to use in the smart controlled release of drugs [375].

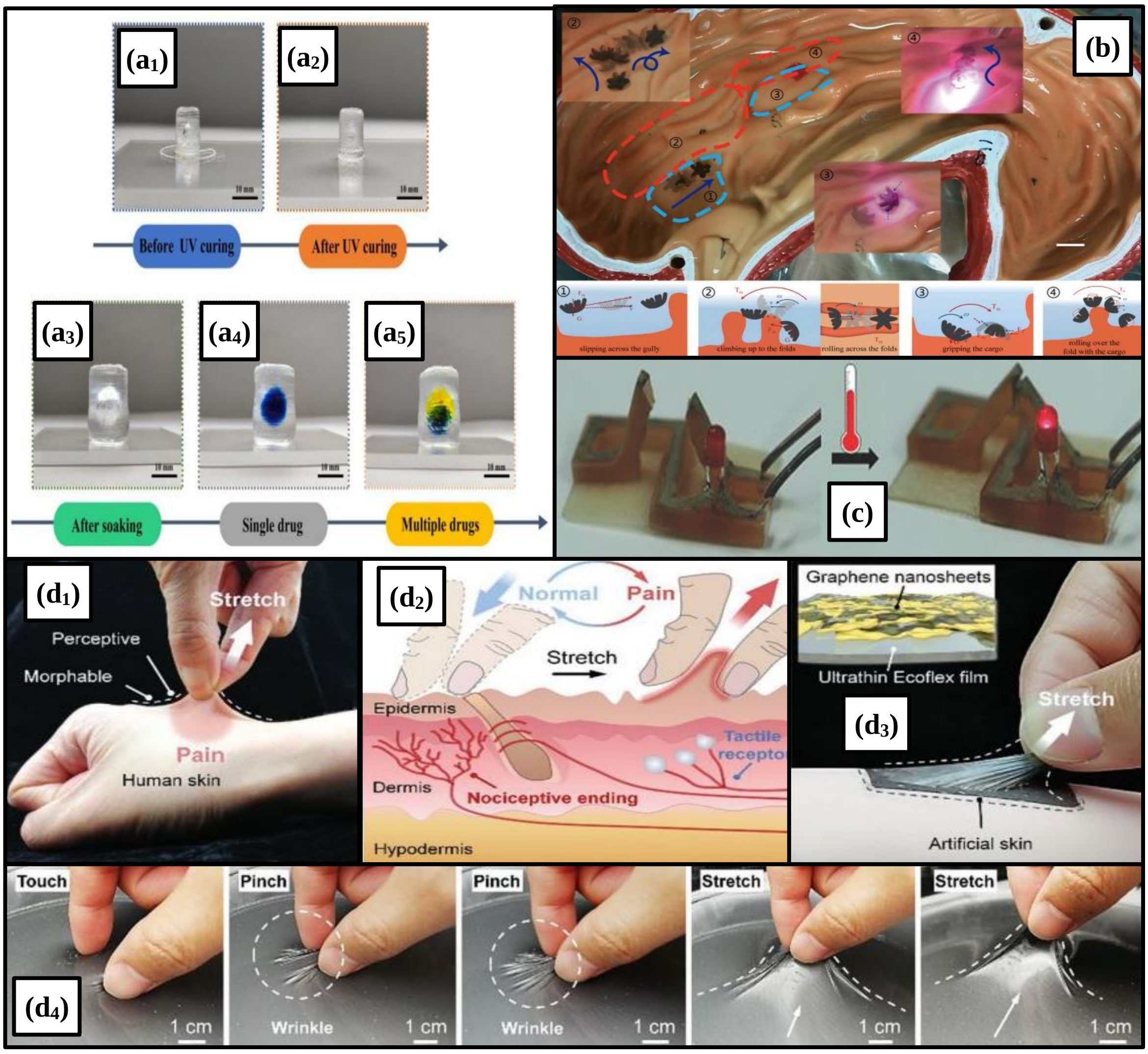

Figure 21. Sample images of hydrogel capsules; (a) Before UV curing; (b) After UV curing; (c) Sample images of hydrogel capsules after soaking in water for 96 h. Sample images of hydrogel capsules including (d) Single drugs and, (e) Multiple drugs (adapted with permission from ref. [374]); (b) Complete and active transportation of cargo in stomach model through lepta Steria-shape gripper (adapted with permission from ref. [113]); (c) PCL-based 4D-printed electrical device (adapted with permission from ref. [376]); (d_1) Real hand skin image cable of feeling pain when stretched; (d_2) Schematic depiction of skin structure demonstrating the mechanism behind tactile and pain feeling; (d_3) Human hand model with artificial skin placed on it with remarkable skin-like wrinkles; (d_4) Images of pinched and stretched behavior of artificial skin (adapted with permission from ref. [377]).

5.3. Soft robotics

In the contemporary world, soft robots and actuators have also become the major focusing area for 4DP applications [378]–[381]. The emergence of SMPC-based smart materials has also helped to attain large structural deformation compared to the robots manufactured through the traditional routes [382]. Additionally, SMPC-based 4D-printed programmable materials exhibit excellent actuating characteristics and can be applied in myriad applications ranging from drug delivery devices to programmable robots in outer space, high altitudes, and extreme weather conditions [383]. These 4D-printed robots not only help to reduce the size but also provides more functionality [384]. Additionally, SMPC-based soft robots can be applied for underwater robotic applications [385]. Likewise, many research enthusiasts developed biomimetic actuators through SMP- and hydrogel-based smart materials [386]. For instance, Hu et al. [113] developed PNIPAM-based smart hydrogel, laponite nano clay, and NdFeB-based magnetic particles for the 4DP of robots. The authors printed different soft millirobots including the lepta Steria-shape robot and shellfish-shape robot, which were capable to respond to both thermal and magnetism stimuli. The locomotion of the lepta Steria-shape robot in the human stomach model was successfully performed through completing active transportation of cargo in the form of drugs, despite many physical obstacles such as the wrinkled surface human stomach model, as depicted in Figure 21(b). Thus, these printed soft millirobots have huge prospects in the fields of medical treatment, drug delivery, and bioengineering.

5.4. Electrical devices

In the contemporary world, the rapid innovations in the electronics industry enable high output rates of electronic systems with powerful miniaturized processors [387]. However, these components need to consider the demands of particular applications while designing electrical circuits [388]. 4DP technology can also offer a lot of opportunities for the manufacturing of electric circuits and flexible devices due to its self-repairing nature, which permits devices to reconnect broken circuits [389]–[391]. For instance, Zarek et al. [376] printed a PLA-based electronic switch through the SLA technique, as shown in Figure 21(c). Furthermore, silver NPs were incorporated on the surface of the developed switch through IJP. The printed device reconfigured its shape upon heating above melting temperature and closed the electric circuit. These SMP-based electrical switches can also be applied to open electric circuits with temperature stimulus, which help in preventing the short-circuiting damage.

In another study, Xiao et al. [377] proposed the strain perception strengthening (SPS) effect for sensing the pain of soft biological skin tissues, as presented in Figure 21(d). Dynamic transformations including 2D and 3D deformation trigger warnings for overstretched strain from tactile to pain-sensing. The prosed synthetic skin derived from elastomeric thin-film and assembled graphene nanosheets having an interlocked structural interface and showed good elastic, conductive, and adaptive properties. The integrated elastic and conductive film and soft sensory systems with the SPS skin-like system effectively replicated the normal tactile and pain feeling of soft tissues.

5.5. Self-folding/origami structures

4D-printed self-folding origami structures have shown huge potential to be utilized in diverse research fields like electronics, bifurcated stents, solar panels, and self-deploying structures [392]. In response to external stimuli, these bilayer and multilayer architectures mimic the hinge-like effect required for the self-folding function [393]. 4DP integrates 3DP technology and SMPs, which endows static structures with self-adaptive, self-foldability, self-assembly, reconfiguration, and multi-functional features. Furthermore, it also helps in more freedom in designing origami structures [394].

For instance, Zou et al. [395] encoded a direct 4DP of a single-material system, which can be deployed with mixed multimodal and doubly curved structures, as illustrated in Figure 22(a). Furthermore, the inverse-design algorithm in-plane and out-of-plane deployments produced double-curved shapes such as complex 3D shapes from 2D bilayer plates. Additionally, the different abilities including stress-free and shape-locking after morphing made them highly suited for developing pop-up kirigami and origami structures. In another study, Xin et al. [396] developed PLA-based different active origami sandwich structures through the FDM technique, as illustrated in Figure 22(b). The results indicated that these thermally-activated origami structures exhibited excellent shape memory performance, large area change ratio, and good self-deployment capabilities.

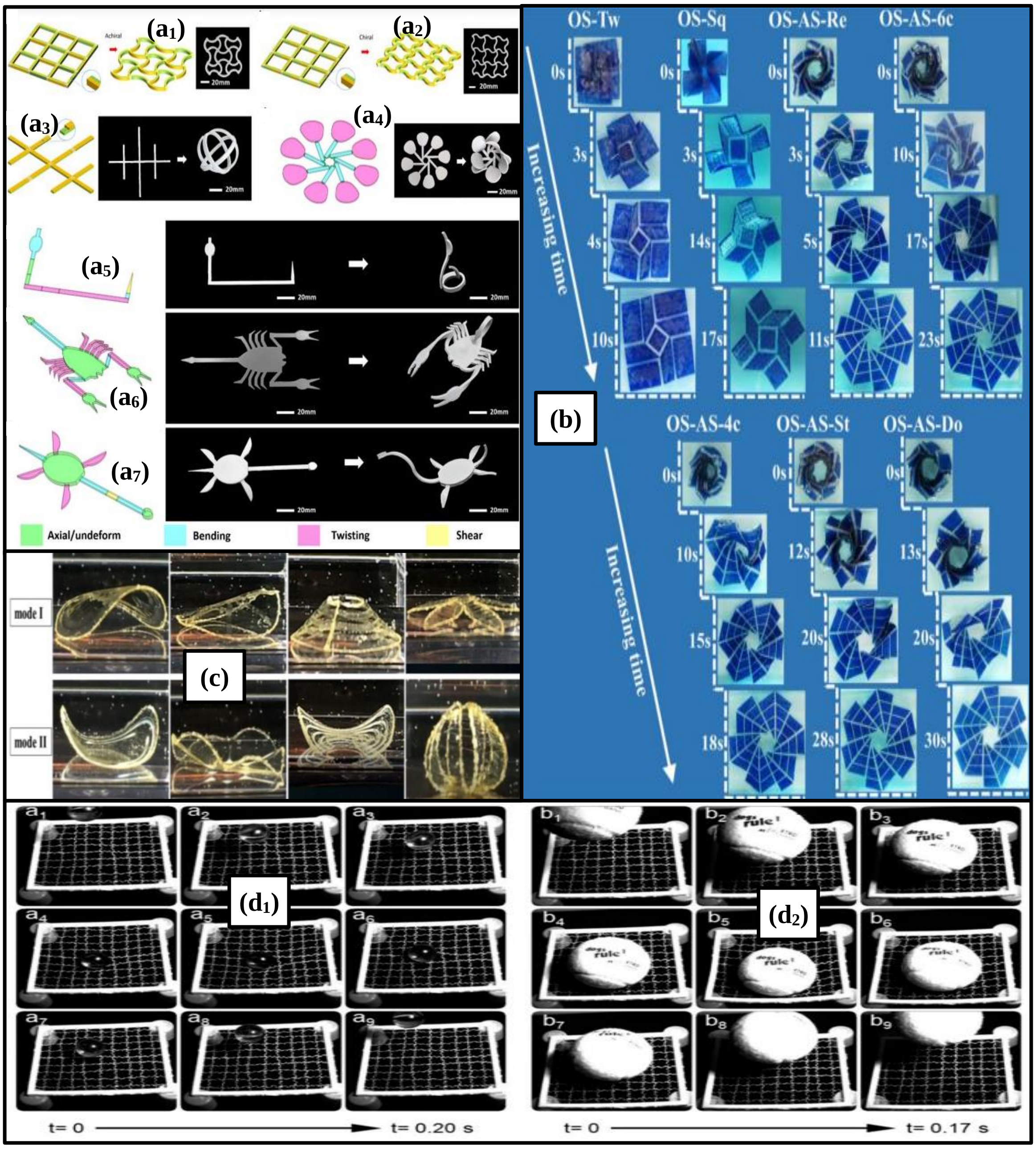

Figure 22. Various 4DP-based single and multi-modal deployments through bending, twisting and shearing; (a_1) Chiral; (a_2) Achiral square lattices; (a_3) Sphere lattice; (a_4) Flower petals; (a_5) Snake; (a_6) Scorpion; (a_7) plesiosaur (adapted with permission from ref. [395]); (b) Shape memory behavior of PLA-based active origami architectures; where ST-Re: sandwich structure with re-entrant, ST-6c: sandwich structure with hexa-chiral, ST-4c: sandwich structure with tetra-chiral, ST-St: sandwich structure with star-shaped, and ST-Do: sandwich structure with double arrowhead (adapted with permission from ref. [396]); (c) Different shape configuration of EC composite films under water stimulus (adapted with permission from ref. [397]); (d) Impact performance of 4D-printed PU (d_1) Glass ball; (d_2) Tennis ball on the bio-inspired spider silk web (adapted with permission from ref. [398]).

5.6.Food sector

4DP technology has also found its application in food sectors and permits the flexibility of food customization by integrating desired features. To date, this sector uses only a limited number of SMP-based materials, with external stimulation of water absorption, pH, temperature, and microwave [399]. 4DP of food items transform their shape, color, flavor, and nutrition, which depend upon the material properties and spatial arrangement of food items [400]. 4DP also enables the development of self-folded edible composite films. For instance, Pulatsu et al. [397] developed ethyl cellulose (EC)/gelatin-based edible composite films through the 4DP technique. Excellent shape morphing and color-transforming abilities were observed under the water-based stimulus, as presented in Figure 22(c), which also demonstrated their osmotically-driven structural changes. Furthermore, curing time affected the color of EC strips from transparent to white.

5.7. Miscellaneous applications

4DP technology also exhibits unleash its potential in space-related programs. This approach can be applied to fabricate instrument booms antennas, radar surveillance antennas, radio communication antennas, solar cells, and space vehicles [401]. It further reduces the labor cost owing to the self-assembly nature and is adaptable to different space conditions [402]. Similarly, the development of energy absorption and retention architectures through 4DP technology is another emerging application. These architectures consist of patterned shapes with a negative Poisson's ratio and absorb shock loads with negligible deformation and retain their original configuration due to actuating capability [403]. SMPCs can also help to develop micro-/nano-scaled printed devices.

4DP technology can also be employed for the efficient manufacturing of automotive components including body parts, automotive interiors, window planes, and safety systems [404]. Similarly, 4D-printed leaf springs have exhibited excellent performance comparable with the springs manufactured through traditional routes [405]. The utilization of the 4DP technology can be expanded for developing the rapid prototypes of the automobile's allied sectors including maritime and aerospace sectors [406]–[408]. 4D-printed wings of the airplane should be adaptable to the working environments that include humidity, stress, and temperature.

4D-printed shape-changing polymers can be applied in smart textile and wearable industries for transforming polymer surface texture and color design, according to environmental conditions, thus, ensuring improved insulation and ventilation [409]–[412]. The new 4D-printed smart textiles containing stimuli-responsive texture/color exhibit functionalities, control moisture, and undergo self-shape adaptation. Similarly, fashion outfits have also provoked significant attraction in recent years [413].

4D-printed SMPs have found their application in piping systems owing to their inherent self-repairing nature [414]. SMPs exhibit the ability to change their diameter upon external stimuli that include water demand and flow rate [415]. Thus, pipe leakage can be repaired instinctively. SMPC-based 4D-printed products can be employed for the construction of building materials, due to their inherent self-healing and self-organizing nature [416]. Additionally, the cleaning of tall buildings is easier through the application of 4D-printed SMPC-based products owing to the self-cleaning nature of these printed products [417].

4D-printed SMPCs have growing potential in the sports industry. HBCs possess the ability to produce curved and twisted structures. The reinforcement through the continuous fibers resulted in excellent mechanical properties of the 4D-printed parts [418]. For instance, Hoa et al. [317] found that the 4D-printed curved and twisted structures of flat sack composites can be applied for making blades for hockey sticks, solar energy concentrators, actuators, and blades for vertical windmills. Similarly, the accessories of athletes can be 4D-printed by considering the different weather conditions and types of sport [419]. These ideas can be further broadened to enhance applications, in the near future. Table 3 summarizes the different applications of 4D-printed SMPCs and smart composite materials in various fields.

Table 3. Summary of recent applications of 4D-printed SMPCs in biomedical and engineering fields

Field	**Printing**	**Actuation**	**Smart SMPs**	**Applications**	**Ref.**
Biomedical	-	Voltage	PLA/Ag-NWs composite	Biomedicine	[41]
	FDM	NIR light	PBS/PLA composite	Treatment of aneurysm	[158]
	DLW	Water	PEGDA/EPOX/Ag-NPs	The printed materials have strong antibacterial activity for Staphylococcus aureus and Pseudomonas aeruginosa bacteria.	[420]
	FFF	Electric field	Thermoplastic PA-based composite	4DP piezoelectric composite use in a knee prosthesis	[338]
	FDM	pH	ABS	pH measurement device	[421]
	FDM	Temperature	PLA	Protective visors frame	[422]
	FDM	-	PEEK-rGO	Bone scaffold design for bone implants or bone repair applications.	[423]
	FFF	Temperature	PLA	Auxetic metamaterials for biomedical applications.	[424]
	FDM	Electrical	PLA/TPU/CNT	Human-scale orthopedic devices	[425]
	DLP	Heat/Light	PCLMA/NVCL	Medical devices	[426]
	FDM	Heat	Silicone/wax micro-particles composites	Recording of ECG signal	[216]
Engineering	-	pH/Temperature	Citrus pectin/β-CD/curcumin.	Application in designing of novel food formats	[427]
	FDM	Heat	-	Smart electromagnetic wave control systems	[428]
	DLW	pH	DMAEMA/PEGDA	Design of micro actuators for micro electro-mechanical systems.	[429]
	SLA	Temperature	PEGDMA	Monitoring the air emission quality	[430]
	FDM	Heat	Ferromagnetic PLA	Deployable structures	[431]
	-	Voltage/ magnetic field	NdFeB/MPDMS/Mxene/PTFE	Intelligent crawling robots	[432]
	-	Heat	PLA	Smart textiles	[409]
	FFF	Heat	PLA	Origami structures	[93]
	FDM	Temperature	Nylon/CF laminated composite	4D-printed bowtie antenna can be employed in 5G communications.	[337]
	Extrusion-based	Temperature	CF/PLA	Metamaterials	[188]
	IJP	Heat	Mushroom scraps/ purple potato puree/ glycerol/choline chloride	Food processing application.	[433]
	SLA/DLP	Current/ temperature	-	Development of device for temperature monitoring and electrical safety.	[434]
	FDM	UV light	Shape memory copolyesters	Temperature protection devices	[92]

	-	Temperature	PNIPAM-co-DMAPMA/clay composite	Development of bionic simulator	[435]
	Extrusion-based	pH	Turmeric powder/sago flour	4D-printed foods with color transformation abilities.	[436]
	FDM	Temperature	PLA/TPU/CNT	Soft robots	[437]
	DLP	Temperature	Methacrylate and TPO	Active and passive optical sensing applications such as Fresnel lenses.	[438]
	FDM	Heat	PLA	Cellular structures for two-ways energy absorption and dissipation engineering applications.	[439]
	SLS	NIR-light	PUDA/CNT	Miura origami structures	[440]

6. Market trends of 4D-printed SMPCs

The future of 4D-printed SMPCs looks promising and quite optimistic. In near future, the 4DP materials will replace the different traditional mechanical components like gears, springs, and motors with the newly developed smart materials along with the precise control on optimization for producing efficient structures [441]. This will help in designing modern engineering systems, which allow the movement of mechanical parts, and these parts will also change their shape according to the requirement. Thus, exploring the new wide range of applications in wear electronics and actuators [442]. Furthermore, in biomedical engineering, the 4D-printed SMPCs will allow the researchers to produce the exact shape of human parts along with the same role of part movements/deformations, which will further boost our healing system.

More insightful exploration is required for investigating the behavior of HBCs which are expected to be applied in future applications. The global market share of 4DP will be ~162 million USD by the year 2022 and ~537.8 million USD by 2025, as per the estimation of reliable authority. Furthermore, the compound annual growth rate will be ~42.5 % from 2019 to 2025 in the defence, aerospace, healthcare, construction, automotive, packaging, and textile industries [443]–[445]. 4DP of biocomposites is a novel technology that employs naturally available sources to develop tuned shape morphing structures for shading systems, underwater equipment for the maritime, solar tracking systems, architectural skin systems, wireless sensing systems, and numerous other extreme applications [428], [446]–[448]. The focused exploration of these areas in 4DP of SMPCs and more collaborations among different engineering fields will bring outstanding breakthroughs within the next few years.

7. Conclusions and future perspectives

4DP is a novel rapid prototyping technology that incorporates 3DP technology and active materials for enabling printed structures to change their shapes, properties, and functions over time. This section incorporates several challenges and future perspectives related to 4DP of SMPCs.

Although, the 4DP of SMPCs has shown immense interest in a variety of engineering sectors, there are still some obstacles to effectively utilize the 4DP in these areas. For instance, shape preprogramming in SMPs is quite challenging. Moreover, complex simulation and topology transformation further add difficulty to the designing of the 4D-printed parts. Therefore, significant knowledge is required about preprogramming for the better utilization of 4DP. Furthermore, the other main challenges such as limitations in the printing processes and narrow spectrum of smart polymer composites, are demanding more researches. Figure 23 depicts some of the current challenges and these hotspots require research in the future.

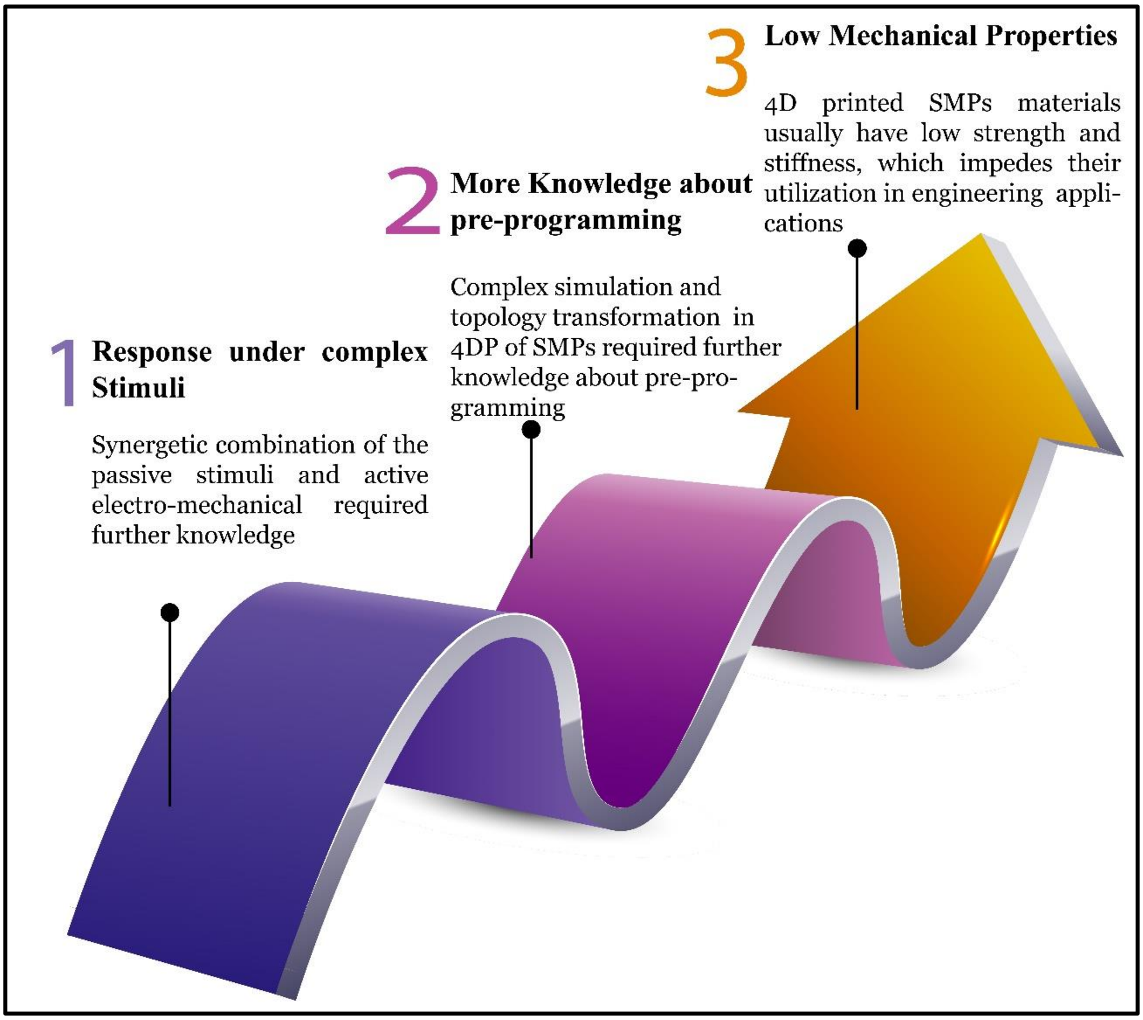

Figure 23. Current challenges and future areas of 4DP of SMPC.

Most 4D-printed SMPCs exhibit greater strain and shape-changing capability, thus compromising their different mechanical properties like low strength and stiffness, which impedes their utilization in many structural engineering applications where high strength is desired. Thus, there is a need to develop high-strength SMPCs by incorporating different fillers/additives/NFs. Furthermore, one-way SMPs have shown excellent shape memory behavior. However, focused research is required on the development of multi-way SMPs due to their increasing demand in flexible electronics and soft robotics.

The ability of 4D-printed material to retain its original shape and structure after the removal of external stimuli is still a hurdle for many researchers. The accurate multi-material 4DP and a wide range of shape functions particularly bending, folding, curling, swelling, twisting, and linear expansion require an insightful knowledge of SMPCs mechanism and their deformation behavior. There is still a need to focus on the development of multi-stimuli polymers because sometimes different stimuli on single material leads to material failure. The other significant drawback is that 4D-printed SMPCs are anisotropic, which also requires insightful exploration. Potential breakthroughs and further developments in novel programmable SMPCs will permit precise actuation, which will help to expand their applications.

The challenges in HBCs involve the actuation performance, material availability, and robustness of 4D-printed architects. Therefore, there is a need to develop high-quality filaments with a diverse range of fibers and polymer matrices. The controlled microstructure and quality are important to regulate actuation. For better comprehension of the shape-transforming ability, the future directions for HBCs are bifurcated into the geometric level and material level. By considering the geometric perspective, there is a need for the structural amplification of the actuating unit cells by developing metamaterials. In terms of material level, there is an urgent need to develop HBCs for improved hygroexpansion. Moreover, the synergetic combination of the passive stimuli responses and active electro-mechanical responses will be helpful to enhance diversity and its applications. Hence, HBCs can be employed as a building media to develop intricate architectures by carefully considering geometric and material perspectives, which will also promote environmental sustainability.

Further advancements in SMPC-based multi-material printing and the alignment of additives through magnetic and electric fields will help to realize the true potential of this novel technology. There is a need to develop 4D-printed SMP-based sustainable composites for biomedical applications. In recent years, the 4DP field is moving toward the practical applications of SMPCs. The endless potential applications of 4D-printed SMPC-based products include the development of grippers, actuators, energy absorbers, wearable electronics, aircraft wing stiffeners, solar panels, tissue constructs, medical stents, and drug delivery devices will completely revolutionize the world, in the near future. Lastly, the continuous burgeoning of this futuristic technology will help to address its current challenges and will provide astonishing results to the manufacturing world.

Conflict of interest statement

The authors declare no conflict of interest.

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References

[1] N. Singh and G. Singh, "Advances in polymers for bio-additive manufacturing: A state of art review," *J. Manuf. Process.*, vol. 72, pp. 439–457, Dec. 2021, doi: 10.1016/J.JMAPRO.2021.10.045.

[2] R. Kumar, M. Kumar, and J. S. Chohan, "The role of additive manufacturing for biomedical applications: A critical review," *J. Manuf. Process.*, vol. 64, pp. 828–850, 2021, doi: https://doi.org/10.1016/j.jmapro.2021.02.022.

[3] E. B. Joyee and Y. Pan, "Additive manufacturing of multi-material soft robot for on-demand drug delivery applications," *J. Manuf. Process.*, vol. 56, pp. 1178–1184, 2020, doi: https://doi.org/10.1016/j.jmapro.2020.03.059.

[4] W. H.-Y. Clarissa, C. H. Chia, S. Zakaria, and Y. C.-Y. Evyan, "Recent advancement in 3-D printing: nanocomposites with added functionality," *Prog. Addit. Manuf.*, 2021, doi: 10.1007/s40964-021-00232-z.

[5] C. M. González-Henríquez, M. A. Sarabia-Vallejos, and J. Rodriguez-Hernandez, "Polymers for additive manufacturing and 4D-printing: Materials, methodologies, and biomedical applications," *Prog. Polym. Sci.*, vol. 94, pp. 57–116, 2019, doi: https://doi.org/10.1016/j.progpolymsci.2019.03.001.

[6] S. Yuan, S. Li, J. Zhu, and Y. Tang, "Additive manufacturing of polymeric composites from material processing to structural design," *Compos. Part B Eng.*, vol. 219, p. 108903, 2021, doi: https://doi.org/10.1016/j.compositesb.2021.108903.

[7] X. Wang, M. Jiang, Z. Zhou, J. Gou, and D. Hui, "3D printing of polymer matrix composites: A review and prospective," *Composites Part B: Engineering*, vol. 110. Elsevier Ltd, pp. 442–458, Feb. 01, 2017, doi: 10.1016/j.compositesb.2016.11.034.

[8] M. I. Farid, W. Wu, X. Liu, and P. Wang, "Additive manufacturing landscape and materials perspective in 4D printing," *Int. J. Adv. Manuf. Technol.*, vol. 115, no. 9, pp. 2973–2988,

2021, doi: 10.1007/s00170-021-07233-w.
[9] P. Parandoush and D. Lin, “A review on additive manufacturing of polymer-fiber composites,” *Compos. Struct.*, vol. 182, pp. 36–53, 2017, doi: https://doi.org/10.1016/j.compstruct.2017.08.088.
[10] M. Bodaghi, R. Noroozi, A. Zolfagharian, M. Fotouhi, and S. Norouzi, “4D Printing Self-Morphing Structures,” *Materials* , vol. 12, no. 8. 2019, doi: 10.3390/ma12081353.
[11] Y. Wang, Y. Zhou, L. Lin, J. Corker, and M. Fan, “Overview of 3D additive manufacturing (AM) and corresponding AM composites,” *Compos. Part A Appl. Sci. Manuf.*, vol. 139, p. 106114, 2020, doi: https://doi.org/10.1016/j.compositesa.2020.106114.
[12] G. Liu *et al.*, “Additive manufacturing of structural materials,” *Mater. Sci. Eng. R Reports*, vol. 145, p. 100596, 2021, doi: https://doi.org/10.1016/j.mser.2020.100596.
[13] J. Justo, L. Távara, L. García-Guzmán, and F. París, “Characterization of 3D printed long fibre reinforced composites,” *Compos. Struct.*, vol. 185, pp. 537–548, 2018, doi: https://doi.org/10.1016/j.compstruct.2017.11.052.
[14] G. Sossou, F. Demoly, G. Montavon, and S. Gomes, “Design for 4D printing: rapidly exploring the design space around smart materials,” *Procedia CIRP*, vol. 70, pp. 120–125, 2018, doi: https://doi.org/10.1016/j.procir.2018.02.032.
[15] Y. Liu and T.-W. Chou, “Additive manufacturing of multidirectional preforms and composites: from three-dimensional to four-dimensional,” *Mater. Today Adv.*, vol. 5, p. 100045, 2020, doi: https://doi.org/10.1016/j.mtadv.2019.100045.
[16] S. M. Olhero, P. M. C. Torres, J. Mesquita-Guimarães, J. Baltazar, J. Pinho-da-Cruz, and S. Gouveia, “Conventional versus additive manufacturing in the structural performance of dense alumina-zirconia ceramics: 20 years of research, challenges and future perspectives,” *J. Manuf. Process.*, vol. 77, pp. 838–879, 2022, doi: https://doi.org/10.1016/j.jmapro.2022.02.041.
[17] A. Raina, M. I. U. Haq, M. Javaid, S. Rab, and A. Haleem, “4D Printing for Automotive Industry Applications,” *J. Inst. Eng. Ser. D*, vol. 102, no. 2, pp. 521–529, 2021, doi: 10.1007/s40033-021-00284-z.
[18] S. Tibbits, “The emergence of ‘4D printing,’” 2013.
[19] M. Y. Khalid, Z. U. Arif, and W. Ahmed, “4D printing: technological and manufacturing renaissance,” *Macromol. Mater. Eng.*, 2022, doi: 10.1002/mame.202200003.
[20] R. Noroozi *et al.*, “Additively manufactured multi-morphology bone-like porous scaffolds: experiments and micro-computed tomography-based finite element modeling approaches,” *Int. J. Bioprinting*, vol. 8, no. 3, pp. 40–53, 2022.
[21] L. G. Blok, M. L. Longana, H. Yu, and B. K. S. Woods, “An investigation into 3D printing of fibre reinforced thermoplastic composites,” *Addit. Manuf.*, vol. 22, pp. 176–186, Aug. 2018, doi: 10.1016/j.addma.2018.04.039.
[22] A. Serjouei, A. Yousefi, A. Jenaki, M. Bodaghi, and M. Mehrpouya, “4D printed shape memory sandwich structures: experimental analysis and numerical modeling,” *Smart Mater. Struct.*, vol. 31, no. 5, p. 55014, 2022, doi: 10.1088/1361-665x/ac60b5.
[23] S. Malekmohammadi *et al.*, “Smart and Biomimetic 3D and 4D Printed Composite Hydrogels: Opportunities for Different Biomedical Applications,” *Biomedicines* , vol. 9, no. 11. 2021, doi: 10.3390/biomedicines9111537.
[24] B. Subeshan, Y. Baddam, and E. Asmatulu, “Current progress of 4D-printing technology,” *Prog. Addit. Manuf.*, vol. 6, no. 3, pp. 495–516, 2021, doi: 10.1007/s40964-021-00182-6.
[25] E. Pei, G. H. Loh, and S. Nam, “Concepts and Terminologies in 4D Printing,” *Applied Sciences* , vol. 10, no. 13. 2020, doi: 10.3390/app10134443.
[26] M. Bodaghi, A. R. Damanpack, and W. H. Liao, “Self-expanding/shrinking structures by 4D printing,” *Smart Mater. Struct.*, vol. 25, no. 10, p. 105034, 2016, doi: 10.1088/0964-1726/25/10/105034.
[27] M. Nadgorny and A. Ameli, “Functional Polymers and Nanocomposites for 3D Printing of Smart Structures and Devices,” *ACS Appl. Mater. Interfaces*, vol. 10, no. 21, pp. 17489–17507, May 2018, doi: 10.1021/acsami.8b01786.
[28] Y. Mao *et al.*, “3D printed reversible shape changing components with stimuli responsive materials,” *Sci. Rep.*, vol. 6, no. 1, pp. 1–13, 2016.

[29] Y. Mao, K. Yu, M. S. Isakov, J. Wu, M. L. Dunn, and H. J. Qi, "Sequential self-folding structures by 3D printed digital shape memory polymers," *Sci. Rep.*, vol. 5, no. 1, pp. 1–12, 2015.

[30] J. Choi, O.-C. Kwon, W. Jo, H. J. Lee, and M.-W. Moon, "4D Printing Technology: A Review," *3D Print. Addit. Manuf.*, vol. 2, no. 4, pp. 159–167, Dec. 2015, doi: 10.1089/3dp.2015.0039.

[31] J. Patdiya and B. Kandasubramanian, "Progress in 4D printing of stimuli responsive materials," *Polym. Technol. Mater.*, vol. 60, no. 17, pp. 1845–1883, Nov. 2021, doi: 10.1080/25740881.2021.1934016.

[32] S. Mallakpour, F. Tabesh, and C. M. Hussain, "3D and 4D printing: From innovation to evolution," *Adv. Colloid Interface Sci.*, vol. 294, p. 102482, 2021, doi: https://doi.org/10.1016/j.cis.2021.102482.

[33] A. Sharma and A. Rai, "Fused deposition modelling (FDM) based 3D & 4D Printing: A state of art review," *Mater. Today Proc.*, 2022, doi: https://doi.org/10.1016/j.matpr.2022.03.679.

[34] H. Ramezani Dana, F. Barbe, L. Delbreilh, M. Ben Azzouna, A. Guillet, and T. Breteau, "Polymer additive manufacturing of ABS structure: Influence of printing direction on mechanical properties," *J. Manuf. Process.*, vol. 44, pp. 288–298, 2019, doi: https://doi.org/10.1016/j.jmapro.2019.06.015.

[35] X. Huang, M. Panahi-Sarmad, K. Dong, R. Li, T. Chen, and X. Xiao, "Tracing evolutions in electro-activated shape memory polymer composites with 4D printing strategies: A systematic review," *Compos. Part A Appl. Sci. Manuf.*, vol. 147, p. 106444, 2021, doi: https://doi.org/10.1016/j.compositesa.2021.106444.

[36] A. Mitchell, U. Lafont, M. Hołyńska, and C. Semprimoschnig, "Additive manufacturing — A review of 4D printing and future applications," *Addit. Manuf.*, vol. 24, pp. 606–626, Dec. 2018.

[37] A. P. Piedade, "4D Printing: The Shape-Morphing in Additive Manufacturing," *Journal of Functional Biomaterials* , vol. 10, no. 1. 2019, doi: 10.3390/jfb10010009.

[38] X. Kuang *et al.*, "Advances in 4D Printing: Materials and Applications," *Adv. Funct. Mater.*, vol. 29, no. 2, p. 1805290, Jan. 2019, doi: https://doi.org/10.1002/adfm.201805290.

[39] I. T. Garces and C. Ayranci, "Advances in additive manufacturing of shape memory polymer composites," *Rapid Prototyp. J.*, vol. 27, no. 2, pp. 379–398, Jan. 2021, doi: 10.1108/RPJ-07-2020-0174.

[40] S. Joshi *et al.*, "4D printing of materials for the future: Opportunities and challenges," *Appl. Mater. Today*, vol. 18, p. 100490, Mar. 2020, doi: 10.1016/J.APMT.2019.100490.

[41] L. H. Shao, B. Zhao, Q. Zhang, Y. Xing, and K. Zhang, "4D printing composite with electrically controlled local deformation," *Extrem. Mech. Lett.*, vol. 39, p. 100793, Sep. 2020, doi: 10.1016/J.EML.2020.100793.

[42] Y. Wang, H. Cui, T. Esworthy, D. Mei, Y. Wang, and L. G. Zhang, "Emerging 4D printing strategies for next-generation tissue regeneration and medical devices," *Adv. Mater.*, vol. n/a, no. n/a, p. 2109198, Dec. 2021, doi: https://doi.org/10.1002/adma.202109198.

[43] H. Meng and G. Li, "Feature article A review of stimuli-responsive shape memory polymer composites," *Polymer (Guildf).*, vol. 54, no. 9, pp. 2199–2221, 2013, doi: 10.1016/j.polymer.2013.02.023.

[44] A. Kotikian, R. L. Truby, J. W. Boley, T. J. White, and J. A. Lewis, "3D Printing of Liquid Crystal Elastomeric Actuators with Spatially Programed Nematic Order," *Adv. Mater.*, vol. 30, no. 10, p. 1706164, Mar. 2018, doi: https://doi.org/10.1002/adma.201706164.

[45] Y. Liu, H. Lv, X. Lan, J. Leng, and S. Du, "Review of electro-active shape-memory polymer composite," *Compos. Sci. Technol.*, vol. 69, no. 13, pp. 2064–2068, 2009, doi: 10.1016/j.compscitech.2008.08.016.

[46] J. del Barrio and C. Sánchez-Somolinos, "Light to Shape the Future: From Photolithography to 4D Printing," *Adv. Opt. Mater.*, vol. 7, no. 16, p. 1900598, Aug. 2019, doi: https://doi.org/10.1002/adom.201900598.

[47] A. M. Schmidt, "Electromagnetic Activation of Shape Memory Polymer Networks Containing Magnetic Nanoparticles a," pp. 1168–1172, 2006, doi: 10.1002/marc.200600225.

[48] A. Haleem, M. Javaid, R. P. Singh, and R. Suman, "Significant roles of 4D printing using

smart materials in the field of manufacturing," *Adv. Ind. Eng. Polym. Res.*, vol. 4, no. 4, pp. 301–311, Oct. 2021, doi: 10.1016/J.AIEPR.2021.05.001.
[49] A. Subash and B. Kandasubramanian, "4D printing of shape memory polymers," *Eur. Polym. J.*, vol. 134, p. 109771, 2020, doi: https://doi.org/10.1016/j.eurpolymj.2020.109771.
[50] M. Nadgorny, Z. Xiao, C. Chen, and L. A. Connal, "Three-Dimensional Printing of pH-Responsive and Functional Polymers on an Affordable Desktop Printer," *ACS Appl. Mater. Interfaces*, vol. 8, no. 42, pp. 28946–28954, Oct. 2016, doi: 10.1021/acsami.6b07388.
[51] A. Zolfagharian, H. R. Jarrah, and M. Bodaghi, "4D Printing Classroom in Modern Interactive Learning Environments," *Bioprinting*, vol. 24, p. e00169, 2021, doi: https://doi.org/10.1016/j.bprint.2021.e00169.
[52] A. Zolfagharian, L. Durran, S. Gharaie, B. Rolfe, A. Kaynak, and M. Bodaghi, "4D printing soft robots guided by machine learning and finite element models," *Sensors Actuators A Phys.*, vol. 328, p. 112774, 2021, doi: https://doi.org/10.1016/j.sna.2021.112774.
[53] A. Zolfagharian, M. A. P. Mahmud, S. Gharaie, M. Bodaghi, A. Z. Kouzani, and A. Kaynak, "3D/4D-printed bending-type soft pneumatic actuators: fabrication, modelling, and control," *Virtual Phys. Prototyp.*, vol. 15, no. 4, pp. 373–402, Oct. 2020, doi: 10.1080/17452759.2020.1795209.
[54] M. Bodaghi and W. H. Liao, "4D printed tunable mechanical metamaterials with shape memory operations," *Smart Mater. Struct.*, vol. 28, no. 4, p. 45019, 2019, doi: 10.1088/1361-665x/ab0b6b.
[55] A. J. Boydston *et al.*, "Additive manufacturing with stimuli-responsive materials," *J. Mater. Chem. A*, vol. 6, no. 42, pp. 20621–20645, 2018, doi: 10.1039/C8TA07716A.
[56] P. Prathumrat, M. Nikzad, E. Hajizadeh, R. Arablouei, and I. Sbarski, "Shape memory elastomers: A review of synthesis, design, advanced manufacturing, and emerging applications," *Polym. Adv. Technol.*, vol. 33, no. 6, pp. 1782–1808, Jun. 2022, doi: https://doi.org/10.1002/pat.5652.
[57] D. S. Cheah, Y. S. Alshebly, M. S. Mohamed Ali, and M. Nafea, "Development of 4D-printed shape memory polymer large-stroke XY micropositioning stages," *J. Micromechanics Microengineering*, vol. 32, no. 6, p. 65006, 2022, doi: 10.1088/1361-6439/ac68ca.
[58] M. Stanisz, Ł. Klapiszewski, and T. Jesionowski, "Recent advances in the fabrication and application of biopolymer-based micro- and nanostructures: A comprehensive review," *Chem. Eng. J.*, vol. 397, p. 125409, 2020, doi: https://doi.org/10.1016/j.cej.2020.125409.
[59] G. Liu *et al.*, "Development of Bioimplants with 2D, 3D, and 4D Additive Manufacturing Materials," *Engineering*, vol. 6, no. 11, pp. 1232–1243, 2020, doi: https://doi.org/10.1016/j.eng.2020.04.015.
[60] S. Valvez, P. N. B. Reis, L. Susmel, and F. Berto, "Fused Filament Fabrication-4D-Printed Shape Memory Polymers: A Review," *Polymers* , vol. 13, no. 5. 2021, doi: 10.3390/polym13050701.
[61] X. Xin, L. Liu, Y. Liu, and J. Leng, "Mechanical Models, Structures, and Applications of Shape-Memory Polymers and Their Composites," *Acta Mech. Solida Sin.*, vol. 32, no. 5, pp. 535–565, 2019, doi: 10.1007/s10338-019-00103-9.
[62] E. Yarali *et al.*, "Magneto-/ electro-responsive polymers toward manufacturing, characterization, and biomedical/ soft robotic applications," *Appl. Mater. Today*, vol. 26, p. 101306, Mar. 2022, doi: 10.1016/J.APMT.2021.101306.
[63] H. M. El-Husseiny *et al.*, "Smart/stimuli-responsive hydrogels: Cutting-edge platforms for tissue engineering and other biomedical applications," *Mater. Today Bio*, vol. 13, p. 100186, Jan. 2022, doi: 10.1016/J.MTBIO.2021.100186.
[64] S. Kumar, R. Singh, A. Batish, and T. P. Singh, "Additive manufacturing of smart materials exhibiting 4-D properties: A state of art review," *J. Thermoplast. Compos. Mater.*, p. 0892705719895052, Dec. 2019, doi: 10.1177/0892705719895052.
[65] R. A. Ilyas *et al.*, "Polylactic Acid (PLA) Biocomposite: Processing, Additive Manufacturing and Advanced Applications," *Polymers* , vol. 13, no. 8. 2021, doi: 10.3390/polym13081326.
[66] N. Ranjan, R. Kumar, R. Singh, and V. Kumar, "On PVC-PP composite matrix for 4D applications: Flowability, mechanical, thermal, and morphological characterizations," *J. Thermoplast. Compos. Mater.*, p. 08927057211059754, Nov. 2021, doi:

10.1177/08927057211059754.
[67] L. Wang, F. Zhang, Y. Liu, and J. Leng, “Shape Memory Polymer Fibers: Materials, Structures, and Applications,” *Adv. Fiber Mater.*, vol. 4, no. 1, pp. 5–23, 2022, doi: 10.1007/s42765-021-00073-z.
[68] A. Melocchi *et al.*, “Shape memory materials and 4D printing in pharmaceutics,” *Adv. Drug Deliv. Rev.*, vol. 173, pp. 216–237, Jun. 2021, doi: 10.1016/J.ADDR.2021.03.013.
[69] Z. X. Khoo *et al.*, “3D printing of smart materials: A review on recent progresses in 4D printing,” *Virtual Phys. Prototyp.*, vol. 10, no. 3, pp. 103–122, Jul. 2015, doi: 10.1080/17452759.2015.1097054.
[70] P. Heidarian, A. Kaynak, M. Paulino, A. Zolfagharian, R. J. Varley, and A. Z. Kouzani, “Dynamic nanocellulose hydrogels: Recent advancements and future outlook,” *Carbohydr. Polym.*, vol. 270, p. 118357, 2021, doi: https://doi.org/10.1016/j.carbpol.2021.118357.
[71] P. Heidarian *et al.*, “Dynamic plant-derived polysaccharide-based hydrogels,” *Carbohydr. Polym.*, vol. 231, p. 115743, 2020, doi: https://doi.org/10.1016/j.carbpol.2019.115743.
[72] M. Baniasadi, E. Yarali, M. Bodaghi, A. Zolfagharian, and M. Baghani, “Constitutive Modeling of multi-stimuli-responsive shape memory polymers with multi-functional capabilities,” *Int. J. Mech. Sci.*, vol. 192, p. 106082, 2021, doi: https://doi.org/10.1016/j.ijmecsci.2020.106082.
[73] A. Y. Chen, E. Pegg, A. Chen, Z. Jin, and G. X. Gu, “4D Printing of Electroactive Materials,” *Adv. Intell. Syst.*, vol. n/a, no. n/a, p. 2100019, Jul. 2021, doi: https://doi.org/10.1002/aisy.202100019.
[74] S. Y. Hann, H. Cui, M. Nowicki, and L. G. Zhang, “4D printing soft robotics for biomedical applications,” *Addit. Manuf.*, vol. 36, p. 101567, 2020, doi: https://doi.org/10.1016/j.addma.2020.101567.
[75] D. Khorsandi *et al.*, “3D and 4D printing in dentistry and maxillofacial surgery: Printing techniques, materials, and applications,” *Acta Biomater.*, vol. 122, pp. 26–49, Mar. 2021, doi: 10.1016/J.ACTBIO.2020.12.044.
[76] Q. Ge, A. H. Sakhaei, H. Lee, C. K. Dunn, N. X. Fang, and M. L. Dunn, “Multimaterial 4D Printing with Tailorable Shape Memory Polymers,” *Sci. Rep.*, vol. 6, no. 1, p. 31110, 2016, doi: 10.1038/srep31110.
[77] F. Demoly, M. L. Dunn, K. L. Wood, H. J. Qi, and J.-C. André, “The status, barriers, challenges, and future in design for 4D printing,” *Mater. Des.*, vol. 212, p. 110193, 2021, doi: https://doi.org/10.1016/j.matdes.2021.110193.
[78] A. Y. Lee, J. An, and C. K. Chua, “Two-Way 4D Printing: A Review on the Reversibility of 3D-Printed Shape Memory Materials,” *Engineering*, vol. 3, no. 5, pp. 663–674, 2017, doi: https://doi.org/10.1016/J.ENG.2017.05.014.
[79] E. Pei and G. H. Loh, “Technological considerations for 4D printing: an overview,” *Prog. Addit. Manuf.*, vol. 3, no. 1, pp. 95–107, 2018, doi: 10.1007/s40964-018-0047-1.
[80] A. Kaynak and A. Zolfagharian, “Functional Polymers in Sensors and Actuators: Fabrication and Analysis,” *Polymers* , vol. 12, no. 7. 2020, doi: 10.3390/polym12071569.
[81] J. Zhang *et al.*, “Advances in 4D Printed Shape Memory Polymers: From 3D Printing, Smart Excitation, and Response to Applications,” *Adv. Mater. Technol.*, vol. n/a, no. n/a, p. 2101568, Mar. 2022, doi: https://doi.org/10.1002/admt.202101568.
[82] A. Kaynak and A. Zolfagharian, “Stimuli-Responsive Polymer Systems—Recent Manufacturing Techniques and Applications,” *Materials* , vol. 12, no. 15. 2019, doi: 10.3390/ma12152380.
[83] de M. Carmela, P. Salvador, and N. B. J., “4D printing and robotics,” *Sci. Robot.*, vol. 3, no. 18, p. eaau0449, May 2018, doi: 10.1126/scirobotics.aau0449.
[84] J. Patadiya, A. Gawande, G. Joshi, and B. Kandasubramanian, “Additive Manufacturing of Shape Memory Polymer Composites for Futuristic Technology,” *Ind. Eng. Chem. Res.*, vol. 60, no. 44, pp. 15885–15912, Nov. 2021, doi: 10.1021/acs.iecr.1c03083.
[85] H. Wu *et al.*, “A Material Combination Concept to Realize 4D Printed Products with Newly Emerging Property/Functionality,” *Adv. Sci.*, vol. 7, no. 9, p. 1903208, May 2020, doi: https://doi.org/10.1002/advs.201903208.
[86] K. McLellan, Y.-C. Sun, and H. Naguib, “A review of 4D printing: Materials, structures, and

designs towards the printing of biomedical wearable devices," *Bioprinting*, p. e00217, 2022, doi: https://doi.org/10.1016/j.bprint.2022.e00217.
[87] D. Ke *et al.*, "Recent advances of two-way shape memory polymers and four-dimensional printing under stress-free conditions," *Smart Mater. Struct.*, vol. 29, no. 2, p. 23001, 2020, doi: 10.1088/1361-665x/ab5e6d.
[88] K. R. Ryan, M. P. Down, and C. E. Banks, "Future of additive manufacturing: Overview of 4D and 3D printed smart and advanced materials and their applications," *Chem. Eng. J.*, vol. 403, p. 126162, 2021, doi: https://doi.org/10.1016/j.cej.2020.126162.
[89] C. Yuan, T. Lu, and T. J. Wang, "Mechanics-based design strategies for 4D printing: A review," *Forces Mech.*, vol. 7, p. 100081, 2022, doi: https://doi.org/10.1016/j.finmec.2022.100081.
[90] S. Dimassi *et al.*, "An ontology-based framework to formalize and represent 4D printing knowledge in design," *Comput. Ind.*, vol. 126, p. 103374, Apr. 2021, doi: 10.1016/J.COMPIND.2020.103374.
[91] P. Cataldi, M. Liu, M. Bissett, and I. A. Kinloch, "A Review on Printing of Responsive Smart and 4D Structures Using 2D Materials," *Adv. Mater. Technol.*, vol. n/a, no. n/a, p. 2200025, Apr. 2022, doi: https://doi.org/10.1002/admt.202200025.
[92] D. Wu *et al.*, "4D Printing of a Fully Biobased Shape Memory Copolyester via a UV-Assisted FDM Strategy," *ACS Sustain. Chem. Eng.*, vol. 10, no. 19, pp. 6304–6312, May 2022, doi: 10.1021/acssuschemeng.2c00721.
[93] B. Jian, F. Demoly, Y. Zhang, H. J. Qi, J.-C. André, and S. Gomes, "Origami-based design for 4D printing of 3D support-free hollow structures," *Engineering*, 2022, doi: https://doi.org/10.1016/j.eng.2021.06.028.
[94] D. M. Solis and A. Czekanski, "The effect of the printing temperature on 4D DLP printed pNIPAM hydrogels," *Soft Matter*, vol. 18, no. 17, pp. 3422–3429, 2022, doi: 10.1039/D2SM00201A.
[95] K. N. Bardakova *et al.*, "4D Printing of Shape-Memory Semi-Interpenetrating Polymer Networks Based On Aromatic Heterochain Polymers," *Adv. Mater. Technol.*, vol. 7, no. 1, p. 2100790, Jan. 2022, doi: https://doi.org/10.1002/admt.202100790.
[96] J. W. Seo, S. R. Shin, Y. J. Park, and H. Bae, "Hydrogel Production Platform with Dynamic Movement Using Photo-Crosslinkable/Temperature Reversible Chitosan Polymer and Stereolithography 4D Printing Technology," *Tissue Eng. Regen. Med.*, vol. 17, no. 4, pp. 423–431, 2020, doi: 10.1007/s13770-020-00264-6.
[97] H. Li *et al.*, "Single-Layer 4D Printing System Using Focused Light: A Tool for Untethered Microrobot Applications," *Chem. Mater.*, vol. 33, no. 19, pp. 7703–7712, Oct. 2021, doi: 10.1021/acs.chemmater.1c01854.
[98] M. A. P. Mahmud, T. Tat, X. Xiao, P. Adhikary, and J. Chen, "Advances in 4D-printed physiological monitoring sensors," *Exploration*, vol. 1, no. 3, p. 20210033, Dec. 2021, doi: https://doi.org/10.1002/EXP.20210033.
[99] L. K. Rivera-Tarazona, T. Shukla, K. A. Singh, A. K. Gaharwar, Z. T. Campbell, and T. H. Ware, "4D Printing of Engineered Living Materials," *Adv. Funct. Mater.*, vol. 32, no. 4, p. 2106843, Jan. 2022, doi: https://doi.org/10.1002/adfm.202106843.
[100] D. Zhen, Y. Chao, P. Xirui, W. Tiejun, Q. H. Jerry, and D. M. L., "Direct 4D printing via active composite materials," *Sci. Adv.*, vol. 3, no. 4, p. e1602890, Oct. 2021, doi: 10.1126/sciadv.1602890.
[101] H. Bhanushali, S. Amrutkar, S. Mestry, and S. T. Mhaske, "Shape memory polymer nanocomposite: a review on structure–property relationship," *Polym. Bull.*, vol. 79, no. 6, pp. 3437–3493, 2022, doi: 10.1007/s00289-021-03686-x.
[102] H. Zhang *et al.*, "4D Printing of Ag Nanowire-Embedded Shape Memory Composites with Stable and Controllable Electrical Responsivity: Implications for Flexible Actuators," *ACS Appl. Nano Mater.*, vol. 5, no. 5, pp. 6221–6231, May 2022, doi: 10.1021/acsanm.2c00264.
[103] Y. Pyo *et al.*, "Design of a shape memory composite(SMC) using 4D printing technology," *Sensors Actuators A Phys.*, vol. 283, pp. 187–195, Nov. 2018, doi: 10.1016/J.SNA.2018.08.049.
[104] V. Vitola, I. Bite, I. Apsite, A. Zolotarjovs, and A. Biswas, "CuS/polyurethane composite

appropriate for 4D printing," *J. Polym. Res.*, vol. 28, no. 1, p. 13, 2021, doi: 10.1007/s10965-020-02375-z.
[105] H. Cui *et al.*, "A novel near-infrared light responsive 4D printed nanoarchitecture with dynamically and remotely controllable transformation," *Nano Res.*, vol. 12, pp. 1381–1388, 2019, doi: 10.1007/s12274-019-2340-9.
[106] T. Yao, Y. Wang, B. Zhu, D. Wei, Y. Yang, and X. Han, "4D printing and collaborative design of highly flexible shape memory alloy structures: a case study for a metallic robot prototype," *Smart Mater. Struct.*, vol. 30, no. 1, p. 15018, 2020, doi: 10.1088/1361-665x/abcc0a.
[107] A. Milleret, "4D printing of Ni–Mn–Ga magnetic shape memory alloys: a review," *Mater. Sci. Technol.*, vol. 38, no. 10, pp. 593–606, Jul. 2022, doi: 10.1080/02670836.2022.2062655.
[108] V. Khare, S. Sonkaria, G.-Y. Lee, S.-H. Ahn, and W.-S. Chu, "From 3D to 4D printing – design, material and fabrication for multi-functional multi-materials," *Int. J. of Precis. Eng. and Manuf.-Green Tech.*, vol. 4, no. 3, pp. 291–299, 2017, doi: 10.1007/s40684-017-0035-9.
[109] M. Q. Zafar and H. Zhao, "4D Printing: Future Insight in Additive Manufacturing," *Met. Mater. Int.*, vol. 26, no. 5, pp. 564–585, May 2020, doi: 10.1007/S12540-019-00441-W.
[110] P. Rastogi and B. Kandasubramanian, "Breakthrough in the printing tactics for stimuli-responsive materials: 4D printing," *Chem. Eng. J.*, vol. 366, pp. 264–304, 2019, doi: https://doi.org/10.1016/j.cej.2019.02.085.
[111] S. Namathoti, R. kumar V.M., and R. S. P.S., "A review on progress in magnetic, microwave, ultrasonic responsive Shape-memory polymer composites," *Mater. Today Proc.*, vol. 56, pp. 1182–1191, 2022, doi: https://doi.org/10.1016/j.matpr.2021.11.151.
[112] H. Wu *et al.*, "Selective Laser Sintering-Based 4D Printing of Magnetism-Responsive Grippers," *ACS Appl. Mater. Interfaces*, vol. 13, no. 11, pp. 12679–12688, Mar. 2021, doi: 10.1021/acsami.0c17429.
[113] X. Hu, Z. Ge, X. Wang, N. Jiao, S. Tung, and L. Liu, "Multifunctional thermo-magnetically actuated hybrid soft millirobot based on 4D printing," *Compos. Part B Eng.*, vol. 228, p. 109451, 2022, doi: https://doi.org/10.1016/j.compositesb.2021.109451.
[114] H. Zhu, Y. He, Y. Wang, Y. Zhao, and C. Jiang, "Mechanically-Guided 4D Printing of Magnetoresponsive Soft Materials across Different Length Scale," *Adv. Intell. Syst.*, vol. 4, no. 3, p. 2100137, Mar. 2022, doi: https://doi.org/10.1002/aisy.202100137.
[115] S. Huang *et al.*, "4D printing of soybean oil based shape memory polymer and its magnetic-sensitive composite via digital light processing," *Polym. Technol. Mater.*, pp. 1–14, Feb. 2022, doi: 10.1080/25740881.2022.2029891.
[116] M. Y. Khalid, Z. U. Arif, W. Ahmed, R. Umer, A. Zolfagharian, and M. Bodaghi, "4D printing: Technological developments in robotics applications," *Sensors Actuators A Phys.*, p. 113670, 2022, doi: https://doi.org/10.1016/j.sna.2022.113670.
[117] C. Lin *et al.*, "4D-Printed Biodegradable and Remotely Controllable Shape Memory Occlusion Devices," *Adv. Funct. Mater.*, vol. 29, no. 51, p. 1906569, Dec. 2019, doi: https://doi.org/10.1002/adfm.201906569.
[118] Y. Zhang *et al.*, "4D Printing of Magnetoactive Soft Materials for On-Demand Magnetic Actuation Transformation," *ACS Appl. Mater. Interfaces*, vol. 13, no. 3, pp. 4174–4184, Jan. 2021, doi: 10.1021/acsami.0c19280.
[119] X. Wan, Y. He, Y. Liu, and J. Leng, "4D printing of multiple shape memory polymer and nanocomposites with biocompatible, programmable and selectively actuated properties," *Addit. Manuf.*, vol. 53, p. 102689, 2022, doi: https://doi.org/10.1016/j.addma.2022.102689.
[120] L. Ren *et al.*, "4D Printing Dual Stimuli-Responsive Bilayer Structure Toward Multiple Shape-Shifting ," *Frontiers in Materials* , vol. 8. p. 134, 2021.
[121] E. Yarali, R. Noroozi, A. Yousefi, M. Bodaghi, and M. Baghani, "Multi-Trigger Thermo-Electro-Mechanical Soft Actuators under Large Deformations," *Polymers* , vol. 12, no. 2. 2020, doi: 10.3390/polym12020489.
[122] T. Liu *et al.*, "Stimulus methods of multi-functional shape memory polymer nanocomposites: A review," *Compos. Part A Appl. Sci. Manuf.*, vol. 100, pp. 20–30, 2017, doi: https://doi.org/10.1016/j.compositesa.2017.04.022.
[123] D. M. Solis and A. Czekanski, "3D and 4D additive manufacturing techniques for vascular-

like structures – A review,” *Bioprinting*, vol. 25, p. e00182, 2022, doi: https://doi.org/10.1016/j.bprint.2021.e00182.
[124] J.-W. Su *et al.*, “4D printing of polyurethane paint-based composites,” *Int. J. Smart Nano Mater.*, 2019.
[125] A. C. Pinho, C. S. Buga, and A. P. Piedade, “The chemistry behind 4D printing,” *Appl. Mater. Today*, vol. 19, p. 100611, 2020, doi: https://doi.org/10.1016/j.apmt.2020.100611.
[126] M. Mehrpouya, H. Vahabi, S. Janbaz, A. Darafsheh, T. R. Mazur, and S. Ramakrishna, “4D printing of shape memory polylactic acid (PLA),” *Polymer (Guildf).*, vol. 230, p. 124080, Sep. 2021, doi: 10.1016/J.POLYMER.2021.124080.
[127] S. K. Leist and J. Zhou, “Current status of 4D printing technology and the potential of light-reactive smart materials as 4D printable materials,” *Virtual Phys. Prototyp.*, vol. 11, no. 4, pp. 249–262, Oct. 2016, doi: 10.1080/17452759.2016.1198630.
[128] Y. Wang and X. Li, “4D-printed bi-material composite laminate for manufacturing reversible shape-change structures,” *Compos. Part B Eng.*, vol. 219, p. 108918, Aug. 2021, doi: 10.1016/J.COMPOSITESB.2021.108918.
[129] M. Piedrahita-Bello *et al.*, “4D printing with spin-crossover polymer composites,” *J. Mater. Chem. C*, vol. 8, no. 18, pp. 6001–6005, 2020, doi: 10.1039/D0TC01532F.
[130] C. Cheng *et al.*, “4D printing of shape memory aliphatic copolyester via UV-assisted FDM strategy for medical protective devices,” vol. 396, no. April, 2020, doi: 10.1016/j.cej.2020.125242.
[131] S. Ma *et al.*, “4D printing of PLA/PCL shape memory composites with controllable sequential deformation,” *Bio-Design Manuf.*, vol. 4, no. 4, pp. 867–878, 2021.
[132] Z. U. Arif, M. Y. Khalid, M. F. Sheikh, A. Zolfagharian, and M. Bodaghi, “Biopolymeric sustainable materials and their emerging applications,” *J. Environ. Chem. Eng.*, vol. 10, no. 4, p. 108159, 2022, doi: https://doi.org/10.1016/j.jece.2022.108159.
[133] M. Bhuvanesh Kumar and P. Sathiya, “Methods and materials for additive manufacturing: A critical review on advancements and challenges,” *Thin-Walled Struct.*, vol. 159, p. 107228, 2021, doi: https://doi.org/10.1016/j.tws.2020.107228.
[134] Y. Zhang *et al.*, “Photopolymerization of Pollen Based Biosourced Composites and Applications in 3D and 4D Printing,” *Macromol. Mater. Eng.*, vol. 306, no. 6, p. 2000774, 2021.
[135] Z. Lin, K. Song, and X. Yu, “A review on wire and arc additive manufacturing of titanium alloy,” *J. Manuf. Process.*, vol. 70, pp. 24–45, 2021, doi: https://doi.org/10.1016/j.jmapro.2021.08.018.
[136] A. Ji, S. Zhang, S. Bhagia, C. G. Yoo, and A. J. Ragauskas, “3D printing of biomass-derived composites: application and characterization approaches,” *RSC Adv.*, vol. 10, no. 37, pp. 21698–21723, 2020, doi: 10.1039/D0RA03620J.
[137] A. J. M. Van Wijk and I. van Wijk, *3D printing with biomaterials: Towards a sustainable and circular economy*. IOS press, 2015.
[138] Z. U. Arif, M. Y. Khalid, and E. ur Rehman, “Laser-aided additive manufacturing of high entropy alloys: Processes, properties, and emerging applications,” *J. Manuf. Process.*, vol. 78, pp. 131–171, 2022, doi: https://doi.org/10.1016/j.jmapro.2022.04.014.
[139] S. C. Altıparmak and B. Xiao, “A market assessment of additive manufacturing potential for the aerospace industry,” *J. Manuf. Process.*, vol. 68, pp. 728–738, 2021, doi: https://doi.org/10.1016/j.jmapro.2021.05.072.
[140] B. I. Oladapo, A. V Adebiyi, and E. Ifeoluwa Elemure, “Microstructural 4D printing investigation of ultra-sonication biocomposite polymer,” *J. King Saud Univ. - Eng. Sci.*, vol. 33, no. 1, pp. 54–60, 2021, doi: https://doi.org/10.1016/j.jksues.2019.12.002.
[141] S. Cooke, K. Ahmadi, S. Willerth, and R. Herring, “Metal additive manufacturing: Technology, metallurgy and modelling,” *J. Manuf. Process.*, vol. 57, pp. 978–1003, 2020, doi: https://doi.org/10.1016/j.jmapro.2020.07.025.
[142] M. Moradi, M. Karami Moghadam, M. Shamsborhan, and M. Bodaghi, “The Synergic Effects of FDM 3D Printing Parameters on Mechanical Behaviors of Bronze Poly Lactic Acid Composites,” *Journal of Composites Science* , vol. 4, no. 1. 2020, doi: 10.3390/jcs4010017.
[143] S. Van Hoa, “Development of composite springs using 4D printing method,” *Compos. Struct.*,

vol. 210, pp. 869–876, 2019, doi: https://doi.org/10.1016/j.compstruct.2018.12.003.
[144] M. Bodaghi, A. R. Damanpack, and W. H. Liao, "Adaptive metamaterials by functionally graded 4D printing," *Mater. Des.*, vol. 135, pp. 26–36, Dec. 2017, doi: 10.1016/J.MATDES.2017.08.069.
[145] J. Sonatkar, B. Kandasubramanian, and S. Oluwarotimi Ismail, "4D printing: Pragmatic progression in biofabrication," *Eur. Polym. J.*, p. 111128, 2022, doi: https://doi.org/10.1016/j.eurpolymj.2022.111128.
[146] L. Ren *et al.*, "Programmable 4D Printing of Bioinspired Solvent-Driven Morphing Composites," *Adv. Mater. Technol.*, vol. 6, no. 8, p. 2001289, Aug. 2021, doi: https://doi.org/10.1002/admt.202001289.
[147] A. Zolfagharian, A. Kaynak, M. Bodaghi, A. Z. Kouzani, S. Gharaie, and S. Nahavandi, "Control-Based 4D Printing: Adaptive 4D-Printed Systems," *Applied Sciences* , vol. 10, no. 9. 2020, doi: 10.3390/app10093020.
[148] A. Sydney Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan, and J. A. Lewis, "Biomimetic 4D printing," *Nat. Mater.*, vol. 15, no. 4, pp. 413–418, 2016, doi: 10.1038/nmat4544.
[149] Ayushi, U. Kumar Vates, S. Mishra, and N. Jee Kanu, "Biomimetic 4D printed materials: A state-of-the-art review on concepts, opportunities, and challenges," *Mater. Today Proc.*, vol. 47, pp. 3313–3319, 2021, doi: https://doi.org/10.1016/j.matpr.2021.07.148.
[150] N. J. Kanu, E. Gupta, U. K. Vates, and G. K. Singh, "An insight into biomimetic 4D printing," *RSC Adv.*, vol. 9, no. 65, pp. 38209–38226, 2019, doi: 10.1039/C9RA07342F.
[151] P. Imrie and J. Jin, "Polymer 4D printing: Advanced shape-change and beyond," *J. Polym. Sci.*, vol. 60, no. 2, pp. 149–174, Jan. 2022, doi: https://doi.org/10.1002/pol.20210718.
[152] S. Basak, "Redesigning the modern applied medical sciences and engineering with shape memory polymers," *Adv. Compos. Hybrid Mater.*, vol. 4, no. 2, pp. 223–234, 2021, doi: 10.1007/s42114-021-00216-1.
[153] Y. Xia, Y. He, F. Zhang, Y. Liu, and J. Leng, "A Review of Shape Memory Polymers and Composites: Mechanisms, Materials, and Applications," *Adv. Mater.*, vol. 33, no. 6, p. 2000713, Feb. 2021, doi: https://doi.org/10.1002/adma.202000713.
[154] M. Danish *et al.*, "4D printed stereolithography printed plant-based sustainable polymers: Preliminary investigation and optimization," *J. Appl. Polym. Sci.*, vol. 138, no. 36, p. 50903, Sep. 2021, doi: https://doi.org/10.1002/app.50903.
[155] M. Cianchetti, C. Laschi, A. Menciassi, and P. Dario, "Biomedical applications of soft robotics," *Nat. Rev. Mater.*, vol. 3, no. 6, pp. 143–153, 2018, doi: 10.1038/s41578-018-0022-y.
[156] J. Simińska-Stanny *et al.*, "4D printing of patterned multimaterial magnetic hydrogel actuators," *Addit. Manuf.*, vol. 49, p. 102506, 2022, doi: https://doi.org/10.1016/j.addma.2021.102506.
[157] X. Dong, F. Zhang, L. Wang, Y. Liu, and J. Leng, "4D printing of electroactive shape-changing composite structures and their programmable behaviors," *Compos. Part A Appl. Sci. Manuf.*, vol. 157, p. 106925, 2022, doi: https://doi.org/10.1016/j.compositesa.2022.106925.
[158] C. Lin, L. Liu, Y. Liu, and J. Leng, "4D printing of shape memory polybutylene succinate/polylactic acid (PBS/PLA) and its potential applications," *Compos. Struct.*, vol. 279, p. 114729, Jan. 2022, doi: 10.1016/J.COMPSTRUCT.2021.114729.
[159] C. A. Spiegel *et al.*, "4D Printing at the Microscale," *Adv. Funct. Mater.*, vol. 30, no. 26, p. 1907615, Jun. 2020, doi: https://doi.org/10.1002/adfm.201907615.
[160] C. A. Spiegel, M. Hackner, V. P. Bothe, J. P. Spatz, and E. Blasco, "4D Printing of Shape Memory Polymers: From Macro to Micro," *Adv. Funct. Mater.*, vol. n/a, no. n/a, p. 2110580, Feb. 2022, doi: https://doi.org/10.1002/adfm.202110580.
[161] L. Li and J. T. Fourkas, "Multiphoton polymerization," *Mater. Today*, vol. 10, no. 6, pp. 30–37, 2007, doi: https://doi.org/10.1016/S1369-7021(07)70130-X.
[162] C. Maibohm, O. F. Silvestre, J. Borme, M. Sinou, K. Heggarty, and J. B. Nieder, "Multi-beam two-photon polymerization for fast large area 3D periodic structure fabrication for bioapplications," *Sci. Rep.*, vol. 10, no. 1, p. 8740, 2020, doi: 10.1038/s41598-020-64955-9.
[163] Z. Guan, L. Wang, and J. Bae, "Advances in 4D Printing of Liquid Crystalline Elastomers: Materials, Techniques, and Applications," *Mater. Horizons*, 2022, doi:

10.1039/D2MH00232A.
[164] S. Yamamura and E. Iwase, “Hybrid hinge structure with elastic hinge on self-folding of 4D printing using a fused deposition modeling 3D printer,” *Mater. Des.*, vol. 203, p. 109605, 2021.
[165] T. Agarwal *et al.*, “4D printing in biomedical applications: emerging trends and technologies,” *J. Mater. Chem. B*, vol. 9, no. 37, pp. 7608–7632, 2021, doi: 10.1039/D1TB01335A.
[166] U. Chadha, A. Abrol, N. P. Vora, A. Tiwari, S. K. Shanker, and S. K. Selvaraj, “Performance evaluation of 3D printing technologies: a review, recent advances, current challenges, and future directions,” *Prog. Addit. Manuf.*, 2022, doi: 10.1007/s40964-021-00257-4.
[167] Y. S. Lui, W. T. Sow, L. P. Tan, Y. Wu, Y. Lai, and H. Li, “4D printing and stimuli-responsive materials in biomedical aspects,” *Acta Biomater.*, vol. 92, pp. 19–36, Jul. 2019, doi: 10.1016/J.ACTBIO.2019.05.005.
[168] E. Vahabli *et al.*, “The Technological Advancement to Engineer Next-Generation Stent-Grafts: Design, Material, and Fabrication Techniques,” *Adv. Healthc. Mater.*, vol. n/a, no. n/a, p. 2200271, Apr. 2022, doi: https://doi.org/10.1002/adhm.202200271.
[169] M. Layani, X. Wang, and S. Magdassi, “Novel Materials for 3D Printing by Photopolymerization,” *Adv. Mater.*, vol. 30, no. 41, p. 1706344, Oct. 2018, doi: https://doi.org/10.1002/adma.201706344.
[170] N. Ashammakhi *et al.*, “Advances and Future Perspectives in 4D Bioprinting,” *Biotechnol. J.*, vol. 13, no. 12, p. 1800148, Dec. 2018, doi: https://doi.org/10.1002/biot.201800148.
[171] S. Bharani Kumar, S. D. Sekar, G. Sivakumar, J. Srinivas, R. Lavanya, and G. Suresh, “Modern concepts and application of soft robotics in 4D printing,” *J. Phys. Conf. Ser.*, vol. 2054, no. 1, p. 12056, 2021, doi: 10.1088/1742-6596/2054/1/012056.
[172] A. Cano-Vicent *et al.*, “Fused deposition modelling: Current status, methodology, applications and future prospects,” *Addit. Manuf.*, vol. 47, p. 102378, Nov. 2021, doi: 10.1016/J.ADDMA.2021.102378.
[173] M. Barletta, A. Gisario, and M. Mehrpouya, “4D printing of shape memory polylactic acid (PLA) components: Investigating the role of the operational parameters in fused deposition modelling (FDM),” *J. Manuf. Process.*, vol. 61, pp. 473–480, Jan. 2021, doi: 10.1016/J.JMAPRO.2020.11.036.
[174] S. Singh, G. Singh, C. Prakash, and S. Ramakrishna, “Current status and future directions of fused filament fabrication,” *J. Manuf. Process.*, vol. 55, pp. 288–306, 2020, doi: https://doi.org/10.1016/j.jmapro.2020.04.049.
[175] J. Carrell, G. Gruss, and E. Gomez, “Four-dimensional printing using fused-deposition modeling: a review,” *Rapid Prototyp. J.*, vol. 26, no. 5, pp. 855–869, May 2020, doi: 10.1108/RPJ-12-2018-0305/FULL/PDF.
[176] Z. Zhang, K. G. Demir, and G. X. Gu, “Developments in 4D-printing: a review on current smart materials, technologies, and applications,” *https://doi.org/10.1080/19475411.2019.1591541*, vol. 10, no. 3, pp. 205–224, Jul. 2019, doi: 10.1080/19475411.2019.1591541.
[177] B. Peng, Y. Yang, T. Ju, and K. A. Cavicchi, “Fused Filament Fabrication 4D Printing of a Highly Extensible, Self-Healing, Shape Memory Elastomer Based on Thermoplastic Polymer Blends,” *ACS Appl. Mater. Interfaces*, vol. 13, no. 11, pp. 12777–12788, Mar. 2021, doi: 10.1021/ACSAMI.0C18618/SUPPL_FILE/AM0C18618_SI_001.PDF.
[178] Y. Saad, M. Nafea, M. Sultan, M. Ali, A. Haider, and F. Almurib, “Review on recent advances in 4D printing of shape memory polymers,” *Eur. Polym. J.*, vol. 159, no. June, p. 110708, 2021, doi: 10.1016/j.eurpolymj.2021.110708.
[179] T. van Manen, S. Janbaz, K. M. B. Jansen, and A. A. Zadpoor, “4D printing of reconfigurable metamaterials and devices,” *Commun. Mater. 2021 21*, vol. 2, no. 1, pp. 1–8, Jun. 2021, doi: 10.1038/s43246-021-00165-8.
[180] S. C. Daminabo, S. Goel, S. A. Grammatikos, H. Y. Nezhad, and V. K. Thakur, “Fused deposition modeling-based additive manufacturing (3D printing): techniques for polymer material systems,” *Mater. Today Chem.*, vol. 16, p. 100248, Jun. 2020, doi: 10.1016/J.MTCHEM.2020.100248.
[181] A. A. Rashid and M. Koç, “Fused Filament Fabrication Process: A Review of Numerical

Simulation Techniques," *Polymers* , vol. 13, no. 20. 2021, doi: 10.3390/polym13203534.
[182] A. R. Damanpack, A. Sousa, and M. Bodaghi, "Porous PLAs with Controllable Density by FDM 3D Printing and Chemical Foaming Agent," *Micromachines* , vol. 12, no. 8. 2021, doi: 10.3390/mi12080866.
[183] R. and S. Noroozi Mohammad Amin and mahmoudi, Reza and Zolfagharian, Ali and Asgari, Fatemeh and Mousavizadeh, Ali and Bodaghi, Mahdi and Hadi, amin and Haghighipour, Nooshin, "In vitro static and dynamic cell culture study of novel bone scaffolds based on 3D-printed PLA and cell-laden alginate hydrogel," *Biomed. Mater.*, 2022.
[184] A. Melocchi *et al.*, "3D printing by fused deposition modeling of single- and multi-compartment hollow systems for oral delivery – A review," *Int. J. Pharm.*, vol. 579, p. 119155, Apr. 2020, doi: 10.1016/J.IJPHARM.2020.119155.
[185] G. Sodeifian, S. Ghaseminejad, and A. A. Yousefi, "Preparation of polypropylene/short glass fiber composite as Fused Deposition Modeling (FDM) filament," *Results Phys.*, vol. 12, pp. 205–222, Mar. 2019, doi: 10.1016/J.RINP.2018.11.065.
[186] M. Falahati *et al.*, "Smart polymers and nanocomposites for 3D and 4D printing," *Mater. Today*, vol. 40, pp. 215–245, Nov. 2020, doi: 10.1016/J.MATTOD.2020.06.001.
[187] M. Bodaghi, A. Serjouei, A. Zolfagharian, M. Fotouhi, H. Rahman, and D. Durand, "Reversible energy absorbing meta-sandwiches by FDM 4D printing," *Int. J. Mech. Sci.*, vol. 173, p. 105451, 2020, doi: https://doi.org/10.1016/j.ijmecsci.2020.105451.
[188] C. Zeng, L. Liu, W. Bian, J. Leng, and Y. Liu, "Temperature-dependent mechanical response of 4D printed composite lattice structures reinforced by continuous fiber," *Compos. Struct.*, vol. 280, p. 114952, 2022, doi: https://doi.org/10.1016/j.compstruct.2021.114952.
[189] H. Yang *et al.*, "3D Printed Photoresponsive Devices Based on Shape Memory Composites," *Adv. Mater.*, vol. 29, no. 33, p. 1701627, Sep. 2017, doi: https://doi.org/10.1002/adma.201701627.
[190] W. W. Yu, J. Zhang, J. R. Wu, X. Z. Wang, and Y. H. Deng, "Incorporation of graphitic nano-filler and poly(lactic acid) in fused deposition modeling," *J. Appl. Polym. Sci.*, vol. 134, no. 15, Apr. 2017, doi: https://doi.org/10.1002/app.44703.
[191] C. Yang, B. Wang, D. Li, and X. Tian, "Modelling and characterisation for the responsive performance of CF/PLA and CF/PEEK smart materials fabricated by 4D printing," *Virtual Phys. Prototyp.*, vol. 12, no. 1, pp. 69–76, Jan. 2017, doi: 10.1080/17452759.2016.1265992.
[192] I. Akbar, M. El Hadrouz, M. El Mansori, and D. Lagoudas, "Continuum and subcontinuum simulation of FDM process for 4D printed shape memory polymers," *J. Manuf. Process.*, vol. 76, pp. 335–348, 2022, doi: https://doi.org/10.1016/j.jmapro.2022.02.028.
[193] H. A. Alshahrani, "Review of 4D printing materials and reinforced composites: Behaviors, applications and challenges," *J. Sci. Adv. Mater. Devices*, vol. 6, no. 2, pp. 167–185, 2021, doi: https://doi.org/10.1016/j.jsamd.2021.03.006.
[194] M. H. Ali, A. Abilgaziyev, and D. Adair, "4D printing: a critical review of current developments, and future prospects," *Int. J. Adv. Manuf. Technol.*, vol. 105, no. 1, pp. 701–717, 2019, doi: 10.1007/s00170-019-04258-0.
[195] J. Castro, E. A. Rojas-Nastrucci, A. Ross, T. M. Weller, and J. Wang, "Fabrication, Modeling, and Application of Ceramic-Thermoplastic Composites for Fused Deposition Modeling of Microwave Components," *IEEE Trans. Microw. Theory Tech.*, vol. 65, no. 6, pp. 2073–2084, 2017, doi: 10.1109/TMTT.2017.2655057.
[196] Q. Chen, L. Han, J. Ren, L. Rong, P. Cao, and R. C. Advincula, "4D Printing via an Unconventional Fused Deposition Modeling Route to High-Performance Thermosets," 2020, doi: 10.1021/acsami.0c13976.
[197] F. Zhang, L. Wang, Z. Zheng, Y. Liu, and J. Leng, "Magnetic programming of 4D printed shape memory composite structures," *Compos. Part A Appl. Sci. Manuf.*, vol. 125, p. 105571, 2019, doi: https://doi.org/10.1016/j.compositesa.2019.105571.
[198] J. Wang, Z. Wang, Z. Song, L. Ren, Q. Liu, and L. Ren, "Biomimetic Shape–Color Double-Responsive 4D Printing," *Adv. Mater. Technol.*, vol. 4, no. 9, p. 1900293, 2019.
[199] W. Liu, N. Wu, and K. Pochiraju, "Shape recovery characteristics of SiC/C/PLA composite filaments and 3D printed parts," *Compos. Part A Appl. Sci. Manuf.*, vol. 108, pp. 1–11, 2018, doi: https://doi.org/10.1016/j.compositesa.2018.02.017.

[200] A. I. Nurhudan, S. Supriadi, Y. Whulanza, and A. S. Saragih, “Additive manufacturing of metallic based on extrusion process: A review,” *J. Manuf. Process.*, vol. 66, pp. 228–237, 2021, doi: https://doi.org/10.1016/j.jmapro.2021.04.018.

[201] A. Le Duigou, M. Castro, R. Bevan, and N. Martin, “3D printing of wood fibre biocomposites: From mechanical to actuation functionality,” *Mater. Des.*, vol. 96, pp. 106–114, 2016, doi: https://doi.org/10.1016/j.matdes.2016.02.018.

[202] W. T. Nugroho, Y. Dong, A. Pramanik, J. Leng, and S. Ramakrishna, “Smart polyurethane composites for 3D or 4D printing: General-purpose use, sustainability and shape memory effect,” *Compos. Part B Eng.*, vol. 223, p. 109104, Oct. 2021, doi: 10.1016/J.COMPOSITESB.2021.109104.

[203] M. D. Monzón *et al.*, “4D printing: processability and measurement of recovery force in shape memory polymers,” *Int. J. Adv. Manuf. Technol.*, vol. 89, no. 5–8, pp. 1827–1836, 2017.

[204] M. Bodaghi, A. R. Damanpack, and W. H. Liao, “Triple shape memory polymers by 4D printing,” *Smart Mater. Struct.*, vol. 27, no. 6, p. 65010, 2018, doi: 10.1088/1361-665x/aabc2a.

[205] S. T. Ly and J. Y. Kim, “4D printing–fused deposition modeling printing with thermal-responsive shape memory polymers,” *Int. J. of Precis. Eng. and Manuf.-Green Tech.*, vol. 4, no. 3, pp. 267–272, 2017.

[206] J. A. Lewis and G. M. Gratson, “Direct writing in three dimensions,” *Mater. Today*, vol. 7, no. 7, pp. 32–39, 2004, doi: 10.1016/S1369-7021(04)00344-X.

[207] Y. Guo, Y. Liu, J. Liu, J. Zhao, H. Zhang, and Z. Zhang, “Shape memory epoxy composites with high mechanical performance manufactured by multi-material direct ink writing,” *Compos. Part A Appl. Sci. Manuf.*, vol. 135, p. 105903, 2020.

[208] X. Wan, L. Luo, Y. Liu, and J. Leng, “Direct ink writing based 4D printing of materials and their applications,” *Adv. Sci.*, vol. 7, no. 16, p. 2001000, 2020.

[209] V. G. Rocha, E. Saiz, I. S. Tirichenko, and E. García-Tuñón, “Direct ink writing advances in multi-material structures for a sustainable future,” *J. Mater. Chem. A*, vol. 8, no. 31, pp. 15646–15657, 2020.

[210] G. Franchin, L. Wahl, and P. Colombo, “Direct ink writing of ceramic matrix composite structures,” *J. Am. Ceram. Soc.*, vol. 100, no. 10, pp. 4397–4401, 2017.

[211] S. Brooks, Z. Cartwright, D. Merckle, and A. C. Weems, “4D Aliphatic photopolymer polycarbonates as direct ink writing of biodegradable, conductive graphite-composite materials,” *Polym. Compos.*, vol. 42, no. 10, pp. 5134–5143, 2021.

[212] G. Franchin *et al.*, “Direct ink writing of geopolymeric inks,” *J. Eur. Ceram. Soc.*, vol. 37, no. 6, pp. 2481–2489, 2017, doi: https://doi.org/10.1016/j.jeurceramsoc.2017.01.030.

[213] D. Ravichandran, W. Xu, M. Kakarla, S. Jambhulkar, Y. Zhu, and K. Song, “Multiphase direct ink writing (MDIW) for multilayered polymer/nanoparticle composites,” *Addit. Manuf.*, vol. 47, p. 102322, 2021, doi: https://doi.org/10.1016/j.addma.2021.102322.

[214] Y. Dong *et al.*, “4D printed hydrogels: fabrication, materials, and applications,” *Adv. Mater. Technol.*, vol. 5, no. 6, p. 2000034, 2020.

[215] Q. Zhang *et al.*, “Direct Ink Writing of Moldable Electrochemical Energy Storage Devices: Ongoing Progress, Challenges, and Prospects,” *Adv. Eng. Mater.*, p. 2100068, 2021.

[216] H. Deng *et al.*, “4D Printing Elastic Composites for Strain-Tailored Multistable Shape Morphing,” *ACS Appl. Mater. Interfaces*, vol. 13, no. 11, pp. 12719–12725, Mar. 2021, doi: 10.1021/acsami.0c17618.

[217] Y. Sui *et al.*, “Patterning, morphing, and coding of gel composites by direct ink writing,” *J. Mater. Chem. A*, vol. 9, no. 13, pp. 8586–8597, 2021.

[218] S. Weng *et al.*, “4D Printing of Glass Fiber-Regulated Shape Shifting Structures with High Stiffness,” *ACS Appl. Mater. Interfaces*, vol. 13, no. 11, pp. 12797–12804, Mar. 2021, doi: 10.1021/acsami.0c18988.

[219] D. Mohan, T. Zee, M. Shaiful, and H. Kaco, “Well-dispersed cellulose-graphene in 4D printing biopolymer,” *Mater. Lett.*, vol. 303, no. March, p. 130522, 2021, doi: 10.1016/j.matlet.2021.130522.

[220] J. N. Rodriguez, C. Zhu, E. B. Duoss, T. S. Wilson, C. M. Spadaccini, and J. P. Lewicki, “Shape-morphing composites with designed micro-architectures,” *Sci. Rep.*, vol. 6, no. 1, pp. 1–10, 2016.

[221] K. Chen, X. Kuang, V. Li, G. Kang, and H. J. Qi, “Fabrication of tough epoxy with shape memory effects by UV-assisted direct-ink write printing,” *Soft Matter*, vol. 14, no. 10, pp. 1879–1886, 2018.
[222] A. Li, A. Challapalli, and G. Li, “4D Printing of Recyclable Lightweight Architectures Using High Recovery Stress Shape Memory Polymer,” *Sci. Rep.*, no. November 2018, pp. 1–13, 2019, doi: 10.1038/s41598-019-44110-9.
[223] A. Hansen, M. Renner, A. G. Griesbeck, and T. Büsgen, “From 3D to 4D printing: a reactor for photochemical experiments using hybrid polyurethane acrylates for vat-based polymerization and surface functionalization,” *Chem. Commun.*, vol. 56, no. 96, pp. 15161–15164, 2020.
[224] H. Chu *et al.*, “4D printing: a review on recent progresses,” *Micromachines*, vol. 11, no. 9, p. 796, 2020.
[225] Y. Tang, B. Dai, B. Su, and Y. Shi, “Recent Advances of 4D Printing Technologies Toward Soft Tactile Sensors,” *Front. Mater.*, vol. 8, p. 110, 2021.
[226] A. Al Rashid, W. Ahmed, M. Y. Khalid, and M. Koç, “Vat photopolymerization of polymers and polymer composites: Processes and applications,” *Addit. Manuf.*, vol. 47, p. 102279, Nov. 2021, doi: 10.1016/J.ADDMA.2021.102279.
[227] M. Han, Y. Yang, and L. Li, “Energy consumption modeling of 4D printing thermal-responsive polymers with integrated compositional design for material,” *Addit. Manuf.*, vol. 34, p. 101223, 2020.
[228] S. Monneret, V. Loubère, S. Corbel, D. De Chimie, and B. P. N. Cedex, “Microstereolithography using a dynamic mask generator and a non-coherent visible light source,” vol. 3680, no. April, pp. 553–561, 1999.
[229] A. Andreu *et al.*, “4D printing materials for vat photopolymerization,” *Addit. Manuf.*, vol. 44, p. 102024, Aug. 2021, doi: 10.1016/J.ADDMA.2021.102024.
[230] Z. U. Arif, M. Y. Khalid, W. Ahmed, and H. Arshad, “A review on four-dimensional bioprinting in pursuit of advanced tissue engineering applications,” *Bioprinting*, p. e00203, Mar. 2022, doi: 10.1016/J.BPRINT.2022.E00203.
[231] Y. Y. C. Choong, S. Maleksaeedi, H. Eng, J. Wei, and P.-C. Su, “4D printing of high performance shape memory polymer using stereolithography,” *Mater. Des.*, vol. 126, pp. 219–225, 2017, doi: https://doi.org/10.1016/j.matdes.2017.04.049.
[232] M. Rafiee, R. D. Farahani, and D. Therriault, “Multi-Material 3D and 4D Printing: A Survey,” *Adv. Sci.*, vol. 7, no. 12, Jun. 2020, doi: 10.1002/ADVS.201902307.
[233] J. Liu *et al.*, “Dual-Gel 4D Printing of Bioinspired Tubes,” *ACS Appl. Mater. Interfaces*, vol. 11, no. 8, pp. 8492–8498, Feb. 2019, doi: 10.1021/acsami.8b17218.
[234] T. Zhao *et al.*, “4D printing of shape memory polyurethane via stereolithography,” *Eur. Polym. J.*, vol. 101, no. January, pp. 120–126, 2018, doi: 10.1016/j.eurpolymj.2018.02.021.
[235] A. Al Rashid, S. A. Khan, S. G. Al-Ghamdi, and M. Koç, “Additive manufacturing of polymer nanocomposites: Needs and challenges in materials, processes, and applications,” *Journal of Materials Research and Technology*, vol. 14. Elsevier Editora Ltda, pp. 910–941, Sep. 01, 2021, doi: 10.1016/j.jmrt.2021.07.016.
[236] P. Makvandi *et al.*, “Bioinspired microneedle patches: Biomimetic designs, fabrication, and biomedical applications,” *Matter*, vol. 5, no. 2, pp. 390–429, 2022, doi: https://doi.org/10.1016/j.matt.2021.11.021.
[237] L. Chen *et al.*, “Color-Changeable Four-Dimensional Printing Enabled with Ultraviolet-Curable and Thermochromic Shape Memory Polymers,” *ACS Appl. Mater. Interfaces*, vol. 13, no. 15, pp. 18120–18127, Apr. 2021, doi: 10.1021/acsami.1c02656.
[238] Y. Y. C. Choong, S. Maleksaeedi, H. Eng, S. Yu, J. Wei, and P. C. Su, “High speed 4D printing of shape memory polymers with nanosilica,” *Appl. Mater. Today*, vol. 18, Mar. 2020.
[239] Q. Zhang *et al.*, “Shape-Memory Balloon Structures by Pneumatic Multi-material 4D Printing,” vol. 2010872, pp. 1–8, 2021, doi: 10.1002/adfm.202010872.
[240] D. Merckle, E. Constant, Z. Cartwright, and A. C. Weems, “Ring Opening Copolymerization of Four-Dimensional Printed Shape Memory Polyester Photopolymers Using Digital Light Processing,” *Macromolecules*, vol. 54, no. 6, pp. 2681–2690, 2021.
[241] C. Yuan, F. Wang, and Q. Ge, “Multimaterial direct 4D printing of high stiffness structures

with large bending curvature," *Extrem. Mech. Lett.*, vol. 42, p. 101122, 2021, doi: https://doi.org/10.1016/j.eml.2020.101122.
[242] J.-J. Wu, L.-M. Huang, Q. Zhao, and T. Xie, "4D printing: history and recent progress," *Chinese J. Polym. Sci.*, vol. 36, no. 5, pp. 563–575, 2018.
[243] S. Lantean, I. Roppolo, M. Sangermano, M. Hayoun, H. Dammak, and G. Rizza, "Programming the microstructure of magnetic nanocomposites in DLP 3D printing," *Addit. Manuf.*, vol. 47, p. 102343, 2021, doi: https://doi.org/10.1016/j.addma.2021.102343.
[244] B. Zhang *et al.*, "Mechanically Robust and UV-Curable Shape-Memory Polymers for Digital Light Processing Based 4D Printing," *Adv. Mater.*, vol. 33, no. 27, p. 2101298, Jul. 2021, doi: https://doi.org/10.1002/adma.202101298.
[245] A. Cortés *et al.*, "DLP 4D-Printing of Remotely, Modularly, and Selectively Controllable Shape Memory Polymer Nanocomposites Embedding Carbon Nanotubes," *Adv. Funct. Mater.*, vol. 31, no. 50, p. 2106774, Dec. 2021, doi: https://doi.org/10.1002/adfm.202106774.
[246] J. M. McCracken *et al.*, "3D-Printed Hydrogel Composites for Predictive Temporal (4D) Cellular Organizations and Patterned Biogenic Mineralization," *Adv. Healthc. Mater.*, vol. 8, no. 1, p. 1800788, Jan. 2019, doi: https://doi.org/10.1002/adhm.201800788.
[247] Y. Shi *et al.*, "Digital light fabrication of reversible shape memory polymers," *Chem. Eng. J.*, vol. 426, p. 131306, 2021, doi: https://doi.org/10.1016/j.cej.2021.131306.
[248] L. Wang, F. Zhang, Y. Liu, S. Du, and J. Leng, "Photosensitive Composite Inks for Digital Light Processing Four-Dimensional Printing of Shape Memory Capture Devices," *ACS Appl. Mater. Interfaces*, vol. 13, no. 15, pp. 18110–18119, 2021.
[249] Q. Mu *et al.*, "Digital light processing 3D printing of conductive complex structures," *Addit. Manuf.*, vol. 18, pp. 74–83, 2017, doi: 10.1016/j.addma.2017.08.011.
[250] A. Cortés, X. F. Sánchez Romate, J. L. Aguilar, A. Jiménez-Suárez, M. Campo, and S. G. Prolongo, "Electrothermally triggered selective shape memory capabilities of CNT doped nanocomposites by Digital Light Processing," *Compos. Sci. Technol.*, vol. 218, p. 109185, 2022, doi: https://doi.org/10.1016/j.compscitech.2021.109185.
[251] A. Nishiguchi, H. Zhang, S. Schweizerhof, M. F. Schulte, A. Mourran, and M. Möller, "4D Printing of a Light-Driven Soft Actuator with Programmed Printing Density," *ACS Appl. Mater. Interfaces*, vol. 12, no. 10, pp. 12176–12185, Mar. 2020, doi: 10.1021/acsami.0c02781.
[252] J. Li, C. Wu, P. K. Chu, and M. Gelinsky, "3D printing of hydrogels: Rational design strategies and emerging biomedical applications," *Mater. Sci. Eng. R Reports*, vol. 140, p. 100543, Apr. 2020, doi: 10.1016/J.MSER.2020.100543.
[253] Y. Liu, R. Liu, J. Qiu, and S. Wang, "4D printing of thermal responsive structure for environmentally adaptive radiative cooling and heating," *J. Adv. Manuf. Process.*, vol. 4, no. 2, p. e10107, Apr. 2022, doi: https://doi.org/10.1002/amp2.10107.
[254] T. Ritacco *et al.*, "Tuning Cholesteric Selective Reflection In Situ Upon Two-Photon Polymerization Enables Structural Multicolor 4D Microfabrication," *Adv. Opt. Mater.*, vol. 10, no. 2, p. 2101526, Jan. 2022, doi: https://doi.org/10.1002/adom.202101526.
[255] A. K. Nguyen and R. J. Narayan, "Two-photon polymerization for biological applications," *Mater. Today*, vol. 20, no. 6, pp. 314–322, 2017, doi: https://doi.org/10.1016/j.mattod.2017.06.004.
[256] X. Liu *et al.*, "Capillary-Force-Driven Self-Assembly of 4D-Printed Microstructures," *Adv. Mater.*, vol. 33, no. 22, p. 2100332, Jun. 2021, doi: https://doi.org/10.1002/adma.202100332.
[257] M. del Pozo, C. Delaney, M. Pilz da Cunha, M. G. Debije, L. Florea, and A. P. H. J. Schenning, "Temperature-Responsive 4D Liquid Crystal Microactuators Fabricated by Direct Laser Writing by Two-Photon Polymerization," *Small Struct.*, vol. 3, no. 2, p. 2100158, Feb. 2022, doi: https://doi.org/10.1002/sstr.202100158.
[258] W. Zhang *et al.*, "Structural multi-colour invisible inks with submicron 4D printing of shape memory polymers," *Nat. Commun.*, vol. 12, no. 1, pp. 1–8, 2021.
[259] R. Suriano, R. Bernasconi, L. Magagnin, and M. Levi, "4D Printing of Smart Stimuli-Responsive Polymers," *J. Electrochem. Soc.*, vol. 166, no. 9, pp. B3274–B3281, 2019, doi: 10.1149/2.0411909jes.
[260] S. Mallakpour, F. Tabesh, and C. M. Hussain, "A new trend of using poly(vinyl alcohol) in 3D and 4D printing technologies: Process and applications," *Adv. Colloid Interface Sci.*, vol. 301,

p. 102605, 2022, doi: https://doi.org/10.1016/j.cis.2022.102605.
[261] N. G. A. Willemen *et al.*, "From oral formulations to drug-eluting implants: using 3D and 4D printing to develop drug delivery systems and personalized medicine," *Bio-Design Manuf.*, 2021, doi: 10.1007/s42242-021-00157-0.
[262] M. M. Tentzeris *et al.*, "Inkjet-/3D-/4D-Printed Nanotechnology-Enabled Radar, Sensing, and RFID Modules for Internet of Things, 'Smart Skin,' and 'Zero Power' Medical Applications," *Antenna and Sensor Technologies in Modern Medical Applications*. pp. 399–434, Apr. 2021, doi: https://doi.org/10.1002/9781119683285.ch11.
[263] B. Yilmaz, A. Al Rashid, Y. A. Mou, Z. Evis, and M. Koç, "Bioprinting: A review of processes, materials and applications," *Bioprinting*, vol. 23, p. e00148, 2021, doi: https://doi.org/10.1016/j.bprint.2021.e00148.
[264] M. Wei, Y. Gao, X. Li, and M. J. Serpe, "Stimuli-responsive polymers and their applications," *Polym. Chem.*, vol. 8, no. 1, pp. 127–143, 2017, doi: 10.1039/C6PY01585A.
[265] C. Cui *et al.*, "4D printing of self-folding and cell-encapsulating 3D microstructures as scaffolds for tissue-engineering applications," *Biofabrication*, vol. 12, no. 4, p. 45018, 2020, doi: 10.1088/1758-5090/aba502.
[266] Z. U. Arif, M. Y. Khalid, E. ur Rehman, S. Ullah, M. Atif, and A. Tariq, "A review on laser cladding of high-entropy alloys, their recent trends and potential applications," *J. Manuf. Process.*, vol. 68, pp. 225–273, Aug. 2021, doi: 10.1016/J.JMAPRO.2021.06.041.
[267] I. Akbar, M. El Hadrouz, M. El Mansori, and D. Lagoudas, "Toward enabling manufacturing paradigm of 4D printing of shape memory materials: Open literature review," *Eur. Polym. J.*, vol. 168, p. 111106, 2022, doi: https://doi.org/10.1016/j.eurpolymj.2022.111106.
[268] D. Yang *et al.*, "3D/4D printed tunable electrical metamaterials with more sophisticated structures," *J. Mater. Chem. C*, vol. 9, no. 36, pp. 12010–12036, 2021, doi: 10.1039/D1TC02588K.
[269] S. R. Narasimharaju *et al.*, "A comprehensive review on laser powder bed fusion of steels: Processing, microstructure, defects and control methods, mechanical properties, current challenges and future trends," *J. Manuf. Process.*, vol. 75, pp. 375–414, 2022, doi: https://doi.org/10.1016/j.jmapro.2021.12.033.
[270] Z. U. Arif, M. Y. Khalid, A. Al Rashid, E. ur Rehman, and M. Atif, "Laser deposition of high-entropy alloys: A comprehensive review," *Opt. Laser Technol.*, vol. 145, p. 107447, Jan. 2022, doi: 10.1016/J.OPTLASTEC.2021.107447.
[271] C. Y. Yap, C. K. Chua, Z. L. Dong, Z. H. Liu, D. Q. Zhang, and L. E. Loh, "APPLIED PHYSICS REVIEWS — FOCUSED REVIEW Review of selective laser melting : Materials and applications," vol. 041101, 2015, doi: 10.1063/1.4935926.
[272] M. Speirs, B. Van Hooreweder, J. Van Humbeeck, and J.-P. Kruth, "Fatigue behaviour of NiTi shape memory alloy scaffolds produced by SLM, a unit cell design comparison," *J. Mech. Behav. Biomed. Mater.*, vol. 70, pp. 53–59, 2017, doi: https://doi.org/10.1016/j.jmbbm.2017.01.016.
[273] H. Z. Lu *et al.*, "Materials Science & Engineering A Ultrahigh-performance TiNi shape memory alloy by 4D printing," vol. 763, no. July, 2019, doi: 10.1016/j.msea.2019.138166.
[274] M. Lalegani Dezaki *et al.*, "A Review on Additive/Subtractive Hybrid Manufacturing of Directed Energy Deposition (DED) Process," *Adv. Powder Mater.*, p. 100054, 2022, doi: https://doi.org/10.1016/j.apmate.2022.100054.
[275] B. Wu *et al.*, "A review of the wire arc additive manufacturing of metals: properties, defects and quality improvement," *J. Manuf. Process.*, vol. 35, pp. 127–139, 2018, doi: https://doi.org/10.1016/j.jmapro.2018.08.001.
[276] J. Mazumder, *1 - Laser-aided direct metal deposition of metals and alloys*. Elsevier Ltd, 2017.
[277] J. J. Marattukalam *et al.*, "Microstructure and corrosion behavior of laser processed NiTi alloy," *Mater. Sci. Eng. C*, vol. 57, pp. 309–313, 2015, doi: https://doi.org/10.1016/j.msec.2015.07.067.
[278] S. Bernard, V. Krishna Balla, S. Bose, and A. Bandyopadhyay, "Compression fatigue behavior of laser processed porous NiTi alloy," *J. Mech. Behav. Biomed. Mater.*, vol. 13, pp. 62–68, 2012, doi: https://doi.org/10.1016/j.jmbbm.2012.04.010.
[279] X. Xin, L. Liu, Y. Liu, and J. Leng, "4D Printing Auxetic Metamaterials with Tunable ,

Programmable , and Reconfigurable Mechanical Properties," vol. 2004226, pp. 1–10, 2020, doi: 10.1002/adfm.202004226.

[280] X. Zheng, C. Williams, C. M. Spadaccini, and K. Shea, "Perspectives on multi-material additive manufacturing," *J. Mater. Res.*, vol. 36, no. 18, pp. 3549–3557, 2021, doi: 10.1557/s43578-021-00388-y.

[281] A. Bandyopadhyay and B. Heer, "Additive manufacturing of multi-material structures," *Mater. Sci. Eng. R Reports*, vol. 129, pp. 1–16, 2018, doi: https://doi.org/10.1016/j.mser.2018.04.001.

[282] A. Nyabadza, J. Kane, M. Vázquez, S. Sreenilayam, and D. Brabazon, "Multi-Material Production of 4D Shape Memory Polymer Composites," D. B. T.-E. of M. C. Brabazon, Ed. Oxford: Elsevier, 2021, pp. 879–894.

[283] S. M. Montgomery, X. Kuang, C. D. Armstrong, and H. J. Qi, "Recent advances in additive manufacturing of active mechanical metamaterials," *Curr. Opin. Solid State Mater. Sci.*, vol. 24, no. 5, p. 100869, 2020, doi: https://doi.org/10.1016/j.cossms.2020.100869.

[284] B. Narupai, P. T. Smith, and A. Nelson, "4D Printing of Multi-Stimuli Responsive Protein-Based Hydrogels for Autonomous Shape Transformations," *Adv. Funct. Mater.*, vol. 31, no. 23, p. 2011012, Jun. 2021, doi: https://doi.org/10.1002/adfm.202011012.

[285] S. Zu *et al.*, "4D printing of core–shell hydrogel capsules for smart controlled drug release," *Bio-Design Manuf.*, 2022, doi: 10.1007/s42242-021-00175-y.

[286] Q. Ge, B. Jian, and H. Li, "Shaping soft materials via digital light processing-based 3D printing: A review," *Forces Mech.*, vol. 6, p. 100074, 2022, doi: https://doi.org/10.1016/j.finmec.2022.100074.

[287] D. J. Roach, X. Kuang, C. M. Hamel, M. L. Dunn, and H. J. Qi, "4D Printing Based on Multi-Material Design," in *Manufacturing in the Era of 4th Industrial Revolution*, World Scientific, 2020, pp. 163–194.

[288] G. Qi *et al.*, "3D printing of highly stretchable hydrogel with diverse UV curable polymers," *Sci. Adv.*, vol. 7, no. 2, p. eaba4261, Jun. 2022, doi: 10.1126/sciadv.aba4261.

[289] J. J. Schwartz and A. J. Boydston, "Multimaterial actinic spatial control 3D and 4D printing," *Nat. Commun.*, vol. 10, no. 1, p. 791, 2019, doi: 10.1038/s41467-019-08639-7.

[290] N. Roudbarian, M. Baniasadi, P. Nayyeri, M. Ansari, R. Hedayati, and M. Baghani, "Enhancing shape memory properties of multi-layered and multi-material polymer composites in 4D printing," *Smart Mater. Struct.*, vol. 30, no. 10, p. 105006, 2021, doi: 10.1088/1361-665x/ac1b3b.

[291] C. He, M. Zhang, and C. Guo, "4D printing of mashed potato/purple sweet potato puree with spontaneous color change," *Innov. Food Sci. Emerg. Technol.*, vol. 59, p. 102250, 2020, doi: https://doi.org/10.1016/j.ifset.2019.102250.

[292] P. Fu *et al.*, "4D printing of polymers: Techniques, materials, and prospects," *Prog. Polym. Sci.*, vol. 126, p. 101506, Mar. 2022, doi: 10.1016/J.PROGPOLYMSCI.2022.101506.

[293] A. F. Ghazal, M. Zhang, and 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.*, vol. 12, no. 10, pp. 1627–1645, 2019, doi: 10.1007/s11947-019-02327-6.

[294] M. Y. Khalid and Z. U. Arif, "Novel biopolymer-based sustainable composites for food packaging applications: A narrative review," *Food Packag. Shelf Life*, vol. 33, p. 100892, 2022, doi: https://doi.org/10.1016/j.fpsl.2022.100892.

[295] R. Hamzehei, A. Zolfagharian, S. Dariushi, and M. Bodaghi, "3D-printed bio-inspired zero Poisson's ratio graded metamaterials with high energy absorption performance," *Smart Mater. Struct.*, vol. 31, no. 3, p. 35001, 2022, doi: 10.1088/1361-665x/ac47d6.

[296] N. Ghavidelnia, M. Bodaghi, and R. Hedayati, "Idealized 3D Auxetic Mechanical Metamaterial: An Analytical, Numerical, and Experimental Study," *Materials* , vol. 14, no. 4. 2021, doi: 10.3390/ma14040993.

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

[298] R. Hedayati and M. Bodaghi, "Acoustic Metamaterials and Acoustic Foams: Recent Advances," *Applied Sciences* , vol. 12, no. 6. 2022, doi: 10.3390/app12063096.

[299] Q. Ji *et al.*, “4D Thermomechanical metamaterials for soft microrobotics,” *Commun. Mater.*, vol. 2, no. 1, p. 93, 2021, doi: 10.1038/s43246-021-00189-0.
[300] R. Noroozi, M. Bodaghi, H. Jafari, A. Zolfagharian, and M. Fotouhi, “Shape-Adaptive Metastructures with Variable Bandgap Regions by 4D Printing,” *Polymers* , vol. 12, no. 3. 2020, doi: 10.3390/polym12030519.
[301] R. Hedayati, N. Ghavidelnia, M. Sadighi, and M. Bodaghi, “Improving the Accuracy of Analytical Relationships for Mechanical Properties of Permeable Metamaterials,” *Applied Sciences* , vol. 11, no. 3. 2021, doi: 10.3390/app11031332.
[302] M. Wallbanks, M. F. Khan, M. Bodaghi, A. Triantaphyllou, and A. Serjouei, “On the design workflow of auxetic metamaterials for structural applications,” *Smart Mater. Struct.*, vol. 31, no. 2, p. 23002, 2021, doi: 10.1088/1361-665x/ac3f78.
[303] X. Yuan *et al.*, “Recent progress in the design and fabrication of multifunctional structures based on metamaterials,” *Curr. Opin. Solid State Mater. Sci.*, vol. 25, no. 1, p. 100883, 2021, doi: https://doi.org/10.1016/j.cossms.2020.100883.
[304] C. Yang *et al.*, “4D printing reconfigurable, deployable and mechanically tunable metamaterials,” *Mater. Horizons*, vol. 6, no. 6, pp. 1244–1250, 2019, doi: 10.1039/C9MH00302A.
[305] B. Li, C. Zhang, F. Peng, W. Wang, B. D. Vogt, and K. T. Tan, “4D printed shape memory metamaterial for vibration bandgap switching and active elastic-wave guiding,” *J. Mater. Chem. C*, vol. 9, no. 4, pp. 1164–1173, 2021, doi: 10.1039/D0TC04999A.
[306] X. Xin, L. Liu, Y. Liu, and J. Leng, “4D Pixel Mechanical Metamaterials with Programmable and Reconfigurable Properties,” *Adv. Funct. Mater.*, vol. 32, no. 6, p. 2107795, Feb. 2022, doi: https://doi.org/10.1002/adfm.202107795.
[307] M. Y. Khalid, Z. U. Arif, M. F. Sheikh, and M. A. Nasir, “Mechanical characterization of glass and jute fiber-based hybrid composites fabricated through compression molding technique,” *Int. J. Mater. Form.*, 2021, doi: 10.1007/s12289-021-01624-w.
[308] M. Y. Khalid, A. Al Rashid, Z. U. Arif, M. F. Sheikh, H. Arshad, and M. A. Nasir, “Tensile strength evaluation of glass/jute fibers reinforced composites: An experimental and numerical approach,” *Results Eng.*, vol. 10, p. 100232, 2021, doi: https://doi.org/10.1016/j.rineng.2021.100232.
[309] M. Y. Khalid *et al.*, “Interlaminar Shear Strength (ILSS) Characterization of Fiber Metal Laminates (FMLs) manufactured through VARTM Process,” *Forces Mech.*, p. 100038, Jul. 2021, doi: 10.1016/J.FINMEC.2021.100038.
[310] S. Hoa *et al.*, “Development of a new flexible wing concept for Unmanned Aerial Vehicle using corrugated core made by 4D printing of composites,” *Compos. Struct.*, vol. 290, p. 115444, 2022, doi: https://doi.org/10.1016/j.compstruct.2022.115444.
[311] F. Momeni and J. Ni, “Laws of 4D Printing,” *Engineering*, vol. 6, no. 9, pp. 1035–1055, 2020, doi: https://doi.org/10.1016/j.eng.2020.01.015.
[312] F. Momeni, S. M.Mehdi Hassani.N, X. Liu, and J. Ni, “A review of 4D printing,” *Mater. Des.*, vol. 122, pp. 42–79, 2017, doi: https://doi.org/10.1016/j.matdes.2017.02.068.
[313] A. N. Patil and S. H. Sarje, “Additive manufacturing with shape changing/memory materials: A review on 4D printing technology,” *Mater. Today Proc.*, vol. 44, pp. 1744–1749, 2021, doi: https://doi.org/10.1016/j.matpr.2020.11.907.
[314] S. Van Hoa, “Factors affecting the properties of composites made by 4D printing (moldless composites manufacturing),” *Adv. Manuf. Polym. Compos. Sci.*, vol. 3, no. 3, pp. 101–109, Jul. 2017, doi: 10.1080/20550340.2017.1355519.
[315] S. Hoa, B. Reddy, and D. Rosca, “Development of omega stiffeners using 4D printing of composites,” *Compos. Struct.*, vol. 272, p. 114264, Sep. 2021, doi: 10.1016/J.COMPSTRUCT.2021.114264.
[316] X. Tian, Q. Wang, and D. Li, “Design of a continuous fiber trajectory for 4D printing of thermally stimulated composite structures,” *Sci. China Technol. Sci.*, vol. 63, no. 4, pp. 571–577, 2020, doi: 10.1007/s11431-019-1485-5.
[317] S. V. Hoa and X. Cai, “Twisted composite structures made by 4D printing method,” *Compos. Struct.*, vol. 238, p. 111883, Apr. 2020, doi: 10.1016/J.COMPSTRUCT.2020.111883.
[318] S. V Hoa and D. I. Rosca, “Formation of letters in the alphabet using 4D printing of

composites," *Mater. Today Commun.*, vol. 25, p. 101115, 2020, doi: https://doi.org/10.1016/j.mtcomm.2020.101115.

[319] H. Chen *et al.*, "Electrothermal shape memory behavior and recovery force of four-dimensional printed continuous carbon fiber/polylactic acid composite," *Smart Mater. Struct.*, vol. 30, no. 2, p. 25040, 2021, doi: 10.1088/1361-665x/abd912.

[320] F. Momeni, S. Sabzpoushan, R. Valizadeh, M. R. Morad, X. Liu, and J. Ni, "Plant leaf-mimetic smart wind turbine blades by 4D printing," *Renew. Energy*, vol. 130, pp. 329–351, 2019, doi: https://doi.org/10.1016/j.renene.2018.05.095.

[321] Y. L. Tee and P. Tran, "On bioinspired 4d printing: materials, design and potential applications," *Aust. J. Mech. Eng.*, pp. 1–11, Oct. 2021, doi: 10.1080/14484846.2021.1988434.

[322] A. Le Duigou, V. Keryvin, J. Beaugrand, M. Pernes, F. Scarpa, and M. Castro, "Humidity responsive actuation of bioinspired hygromorph biocomposites (HBC) for adaptive structures," *Compos. Part A Appl. Sci. Manuf.*, vol. 116, pp. 36–45, 2019, doi: https://doi.org/10.1016/j.compositesa.2018.10.018.

[323] C. Gauss, K. L. Pickering, and L. P. Muthe, "The use of cellulose in bio-derived formulations for 3D/4D printing: A review," *Compos. Part C Open Access*, vol. 4, p. 100113, Mar. 2021, doi: 10.1016/J.JCOMC.2021.100113.

[324] M. Li *et al.*, "Recent advancements of plant-based natural fiber–reinforced composites and their applications," *Compos. Part B Eng.*, vol. 200, p. 108254, 2020, doi: https://doi.org/10.1016/j.compositesb.2020.108254.

[325] A. Le Duigou, T. Fruleux, R. Matsuzaki, G. Chabaud, M. Ueda, and M. Castro, "4D printing of continuous flax-fibre based shape-changing hygromorph biocomposites: Towards sustainable metamaterials," *Mater. Des.*, vol. 211, p. 110158, 2021.

[326] A. Le Duigou, G. Chabaud, F. Scarpa, and M. Castro, "Bioinspired electro-thermo-hygro reversible shape-changing materials by 4D printing," *Adv. Funct. Mater.*, vol. 29, no. 40, p. 1903280, 2019.

[327] D. Correa *et al.*, "4D pine scale: biomimetic 4D printed autonomous scale and flap structures capable of multi-phase movement," *Philos. Trans. R. Soc. A*, vol. 378, no. 2167, p. 20190445, 2020.

[328] A. Menges and S. Reichert, "Material Capacity: Embedded Responsiveness," *Archit. Des.*, vol. 82, no. 2, pp. 52–59, Mar. 2012, doi: https://doi.org/10.1002/ad.1379.

[329] Y. Tahouni *et al.*, "Programming sequential motion steps in 4D-printed hygromorphs by architected mesostructure and differential hygro-responsiveness," *Bioinspiration & Biomimetics*, vol. 16, no. 5, p. 55002, 2021, doi: 10.1088/1748-3190/ac0c8e.

[330] T. T. Nguyen and J. Kim, "4D-Printing — Fused Deposition Modeling Printing and PolyJet Printing with Shape Memory Polymers Composite," *Fibers Polym.*, vol. 21, no. 10, pp. 2364–2372, 2020, doi: 10.1007/s12221-020-9882-z.

[331] M. C. Mulakkal, R. S. Trask, V. P. Ting, and A. M. Seddon, "Responsive cellulose-hydrogel composite ink for 4D printing," *Mater. Des.*, vol. 160, pp. 108–118, Dec. 2018, doi: 10.1016/J.MATDES.2018.09.009.

[332] B. I. Oladapo, E. A. Oshin, and A. M. Olawumi, "Nanostructural computation of 4D printing carboxymethylcellulose (CMC) composite," *Nano-Structures & Nano-Objects*, vol. 21, p. 100423, Feb. 2020, doi: 10.1016/J.NANOSO.2020.100423.

[333] Y. Zhou, C. B. Parker, P. Joshi, A. K. Naskar, J. T. Glass, and C. Cao, "4D Printing of Stretchable Supercapacitors via Hybrid Composite Materials," *Adv. Mater. Technol.*, vol. 6, no. 1, p. 2001055, 2021.

[334] A. Sharma and A. K. S. Singholi, "Shape memory and mechanical characterization of polylactic acid wood composite fabricated by fused filament fabrication 4D printing technology," *Materwiss. Werksttech.*, vol. 52, no. 6, pp. 635–643, Jun. 2021, doi: https://doi.org/10.1002/mawe.202000284.

[335] D. Chen *et al.*, "4D Printing Strain Self-Sensing and Temperature Self-Sensing Integrated Sensor–Actuator with Bioinspired Gradient Gaps," *Adv. Sci.*, vol. 7, no. 13, p. 2000584, Jul. 2020, doi: https://doi.org/10.1002/advs.202000584.

[336] H. Y. Jeong, B. H. Woo, N. Kim, and Y. C. Jun, "Multicolor 4D printing of shape-memory polymers for light-induced selective heating and remote actuation," *Sci. Rep.*, vol. 10, no. 1, p.

6258, 2020, doi: 10.1038/s41598-020-63020-9.
[337] L. Wu *et al.*, "Deformable Bowtie Antenna Realized by 4D Printing," *Electronics* , vol. 10, no. 15. 2021, doi: 10.3390/electronics10151792.
[338] D. Grinberg, S. Siddique, M.-Q. Le, R. Liang, J.-F. Capsal, and P.-J. Cottinet, "4D Printing based piezoelectric composite for medical applications," *J. Polym. Sci. Part B Polym. Phys.*, vol. 57, no. 2, pp. 109–115, Jan. 2019, doi: https://doi.org/10.1002/polb.24763.
[339] W. Wang, Y. Liu, and J. Leng, "Recent developments in shape memory polymer nanocomposites: Actuation methods and mechanisms," *Coord. Chem. Rev.*, vol. 320–321, pp. 38–52, 2016, doi: https://doi.org/10.1016/j.ccr.2016.03.007.
[340] A. Ahmed, S. Arya, V. Gupta, H. Furukawa, and A. Khosla, "4D printing: Fundamentals, materials, applications and challenges," *Polymer (Guildf).*, vol. 228, p. 123926, 2021, doi: https://doi.org/10.1016/j.polymer.2021.123926.
[341] S. Amukarimi and M. Mozafari, "4D bioprinting of tissues and organs," *Bioprinting*, vol. 23, p. e00161, 2021, doi: https://doi.org/10.1016/j.bprint.2021.e00161.
[342] S. Miao *et al.*, "4D printing of polymeric materials for tissue and organ regeneration," *Mater. Today*, vol. 20, no. 10, pp. 577–591, 2017, doi: https://doi.org/10.1016/j.mattod.2017.06.005.
[343] M. Askari, M. Afzali Naniz, M. Kouhi, A. Saberi, A. Zolfagharian, and M. Bodaghi, "Recent progress in extrusion 3D bioprinting of hydrogel biomaterials for tissue regeneration: a comprehensive review with focus on advanced fabrication techniques," *Biomater. Sci.*, vol. 9, no. 3, pp. 535–573, 2021, doi: 10.1039/D0BM00973C.
[344] "The Fourth Dimension: 4D Printing | Prospector." https://knowledge.ulprospector.com/3164/pe-the-fourth-dimension/ (accessed Dec. 15, 2021).
[345] "4D printing: When having a job does not guarantee a dignified life - Iberdrola." https://www.iberdrola.com/innovation/what-is-print-4d (accessed Dec. 15, 2021).
[346] "4D printing promises biomedical applications - ASME." https://www.asme.org/topics-resources/content/biotechnology-anticipates-4d-printing (accessed Dec. 15, 2021).
[347] "Kinematics 4D Printed Dress – Nervous System – Rhine Capital Partners." http://www.rhinecapital.com/kinematics-4d-printed-dress-nervous-system/ (accessed Dec. 15, 2021).
[348] "Special 'ink' developed at CityU enables world's first 4D printing for ceramics | Office of the Vice-President (Research & Technology) - City University of Hong Kong." https://www.cityu.edu.hk/vprt/news/2018/special-ink-developed-at-cityu-enables-worlds-first-4D-printing-for-ceramics/ (accessed Dec. 15, 2021).
[349] H. Ding, X. Zhang, Y. Liu, and S. Ramakrishna, "Review of mechanisms and deformation behaviors in 4D printing," *Int. J. Adv. Manuf. Technol.*, vol. 105, no. 11, pp. 4633–4649, 2019, doi: 10.1007/s00170-019-03871-3.
[350] C. Zhang *et al.*, "4D Printing of shape-memory polymeric scaffolds for adaptive biomedical implantation," *Acta Biomater.*, vol. 122, pp. 101–110, 2021, doi: https://doi.org/10.1016/j.actbio.2020.12.042.
[351] H.-W. Kang, S. J. Lee, I. K. Ko, C. Kengla, J. J. Yoo, and A. Atala, "A 3D bioprinting system to produce human-scale tissue constructs with structural integrity," *Nat. Biotechnol.*, vol. 34, no. 3, pp. 312–319, 2016, doi: 10.1038/nbt.3413.
[352] S. Miao *et al.*, "4D printing smart biomedical scaffolds with novel soybean oil epoxidized acrylate," *Sci. Rep.*, vol. 6, no. 1, p. 27226, 2016, doi: 10.1038/srep27226.
[353] G. Constante *et al.*, "4D Biofabrication Using a Combination of 3D Printing and Melt-Electrowriting of Shape-Morphing Polymers," *ACS Appl. Mater. Interfaces*, vol. 13, no. 11, pp. 12767–12776, Mar. 2021, doi: 10.1021/acsami.0c18608.
[354] C. Wang *et al.*, "Advanced reconfigurable scaffolds fabricated by 4D printing for treating critical-size bone defects of irregular shapes," *Biofabrication*, vol. 12, no. 4, p. 45025, 2020, doi: 10.1088/1758-5090/abab5b.
[355] Y. Wang *et al.*, "4D Printed Cardiac Construct with Aligned Myofibers and Adjustable Curvature for Myocardial Regeneration," *ACS Appl. Mater. Interfaces*, vol. 13, no. 11, pp. 12746–12758, Mar. 2021, doi: 10.1021/acsami.0c17610.
[356] X. Wang *et al.*, "Preparation of 4D printed peripheral vascular stent and its degradation behavior under fluid shear stress after deployment," *Biomater. Sci.*, 2022, doi:

10.1039/D2BM00088A.
[357] Q. Ji, M. Chen, X. V. Wang, L. Wang, and L. Feng, “Optimal shape morphing control of 4D printed shape memory polymer based on reinforcement learning,” *Robot. Comput. Integr. Manuf.*, vol. 73, p. 102209, 2022, doi: https://doi.org/10.1016/j.rcim.2021.102209.
[358] R. J. Morrison *et al.*, “Mitigation of tracheobronchomalacia with 3D-printed personalized medical devices in pediatric patients,” *Sci. Transl. Med.*, vol. 7, no. 285, pp. 285ra64-285ra64, 2015.
[359] H. Wei, Q. Zhang, Y. Yao, L. Liu, Y. Liu, and J. Leng, “Direct-Write Fabrication of 4D Active Shape-Changing Structures Based on a Shape Memory Polymer and Its Nanocomposite,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 1, pp. 876–883, Jan. 2017, doi: 10.1021/acsami.6b12824.
[360] A. Haleem, M. Javaid, and R. Vaishya, “4D printing and its applications in orthopaedics,” *J. Clin. Orthop. trauma*, vol. 9, no. 3, p. 275, 2018.
[361] M. Javaid and A. Haleem, “4D printing applications in medical field: A brief review,” *Clin. Epidemiol. Glob. Heal.*, vol. 7, no. 3, pp. 317–321, 2019, doi: https://doi.org/10.1016/j.cegh.2018.09.007.
[362] P. He *et al.*, “Bioprinting of skin constructs for wound healing,” *Burn. Trauma*, vol. 6, Dec. 2018, doi: 10.1186/s41038-017-0104-x.
[363] S. Shakibania, L. Ghazanfari, M. Raeeszadeh-Sarmazdeh, and M. Khakbiz, “Medical application of biomimetic 4D printing,” *Drug Dev. Ind. Pharm.*, vol. 47, no. 4, pp. 521–534, Apr. 2021, doi: 10.1080/03639045.2020.1862179.
[364] H. R. Jarrah, A. Zolfagharian, and M. Bodaghi, “Finite element modeling of shape memory polyurethane foams for treatment of cerebral aneurysms,” *Biomech. Model. Mechanobiol.*, vol. 21, no. 1, pp. 383–399, 2022, doi: 10.1007/s10237-021-01540-7.
[365] Y. Zhou *et al.*, “4D Printing of Shape Memory Vascular Stent Based on βCD-g-Polycaprolactone,” *Macromol. Rapid Commun.*, vol. 42, no. 14, p. 2100176, Jul. 2021, doi: https://doi.org/10.1002/marc.202100176.
[366] C. Lin, L. Zhang, Y. Liu, L. Liu, and J. Leng, “4D printing of personalized shape memory polymer vascular stents with negative Poisson’s ratio structure: A preliminary study,” *Sci. China Technol. Sci.*, vol. 63, no. 4, pp. 578–588, 2020, doi: 10.1007/s11431-019-1468-2.
[367] S. B. Kumar, J. Jeevamalar, P. Ramu, G. Suresh, and K. Senthilnathan, “Evaluation in 4D printing – A review,” *Mater. Today Proc.*, vol. 45, pp. 1433–1437, 2021, doi: https://doi.org/10.1016/j.matpr.2020.07.335.
[368] H. W. Tan and Y. Y. C. Choong, “Additive manufacturing in COVID-19: recognising the challenges and driving for assurance,” *Virtual Phys. Prototyp.*, vol. 16, no. 4, pp. 498–503, Jul. 2021, doi: 10.1080/17452759.2021.1975882.
[369] A. Melocchi *et al.*, “Retentive device for intravesical drug delivery based on water-induced shape memory response of poly(vinyl alcohol): design concept and 4D printing feasibility,” *Int. J. Pharm.*, vol. 559, pp. 299–311, Mar. 2019, doi: 10.1016/J.IJPHARM.2019.01.045.
[370] D. Han *et al.*, “4D Printing of a Bioinspired Microneedle Array with Backward-Facing Barbs for Enhanced Tissue Adhesion,” *Adv. Funct. Mater.*, vol. 30, no. 11, p. 1909197, Mar. 2020, doi: https://doi.org/10.1002/adfm.201909197.
[371] J. C. Breger *et al.*, “Self-Folding Thermo-Magnetically Responsive Soft Microgrippers,” *ACS Appl. Mater. Interfaces*, vol. 7, no. 5, pp. 3398–3405, Feb. 2015, doi: 10.1021/am508621s.
[372] A. Azam, K. E. Laflin, M. Jamal, R. Fernandes, and D. H. Gracias, “Self-folding micropatterned polymeric containers,” *Biomed. Microdevices*, vol. 13, no. 1, pp. 51–58, 2011, doi: 10.1007/s10544-010-9470-x.
[373] K. Malachowski *et al.*, “Stimuli-Responsive Theragrippers for Chemomechanical Controlled Release,” *Angew. Chemie Int. Ed.*, vol. 53, no. 31, pp. 8045–8049, Jul. 2014, doi: https://doi.org/10.1002/anie.201311047.
[374] S. Zu *et al.*, “A bioinspired 4D printed hydrogel capsule for smart controlled drug release,” *Mater. Today Chem.*, vol. 24, p. 100789, 2022, doi: https://doi.org/10.1016/j.mtchem.2022.100789.
[375] B. Shen, O. Erol, L. Fang, and S. H. Kang, “Programming the time into 3D printing: current advances and future directions in 4D printing,” *Multifunct. Mater.*, vol. 3, no. 1, p. 12001,

2020, doi: 10.1088/2399-7532/ab54ea.
[376] M. Zarek, M. Layani, I. Cooperstein, E. Sachyani, D. Cohn, and S. Magdassi, "3D Printing of Shape Memory Polymers for Flexible Electronic Devices," *Adv. Mater.*, vol. 28, no. 22, pp. 4449–4454, Jun. 2016, doi: https://doi.org/10.1002/adma.201503132.
[377] P. Xiao, W. Zhou, Y. Liang, S.-W. Kuo, Q. Yang, and T. Chen, "Biomimetic Skins Enable Strain-Perception-Strengthening Soft Morphing," *Adv. Funct. Mater.*, vol. n/a, no. n/a, p. 2201812, Apr. 2022, doi: https://doi.org/10.1002/adfm.202201812.
[378] A. Zolfagharian, A. Kaynak, S. Y. Khoo, and A. Kouzani, "Pattern-driven 4D printing," *Sensors Actuators A Phys.*, vol. 274, pp. 231–243, 2018, doi: https://doi.org/10.1016/j.sna.2018.03.034.
[379] X. Lu *et al.*, "4D-Printing of Photoswitchable Actuators," *Angew. Chemie Int. Ed.*, vol. 60, no. 10, pp. 5536–5543, Mar. 2021, doi: https://doi.org/10.1002/anie.202012618.
[380] J. Lee, H.-C. Kim, J.-W. Choi, and I. H. Lee, "A review on 3D printed smart devices for 4D printing," *Int. J. of Precis. Eng. and Manuf.-Green Tech.*, vol. 4, no. 3, pp. 373–383, 2017, doi: 10.1007/s40684-017-0042-x.
[381] H. Y. Jeong, E. Lee, S. Ha, N. Kim, and Y. C. Jun, "Multistable Thermal Actuators Via Multimaterial 4D Printing," *Adv. Mater. Technol.*, vol. 4, no. 3, p. 1800495, Mar. 2019, doi: https://doi.org/10.1002/admt.201800495.
[382] G. Adam, A. Benouhiba, K. Rabenorosoa, C. Clévy, and D. J. Cappelleri, "4D Printing: Enabling Technology for Microrobotics Applications," *Adv. Intell. Syst.*, vol. 3, no. 5, p. 2000216, May 2021, doi: https://doi.org/10.1002/aisy.202000216.
[383] M. S. Xavier *et al.*, "Soft Pneumatic Actuators: A Review of Design, Fabrication, Modeling, Sensing, Control and Applications," *IEEE Access*, p. 1, 2022, doi: 10.1109/ACCESS.2022.3179589.
[384] F. Rajabasadi, L. Schwarz, M. Medina-Sánchez, and O. G. Schmidt, "3D and 4D lithography of untethered microrobots," *Prog. Mater. Sci.*, vol. 120, p. 100808, 2021, doi: https://doi.org/10.1016/j.pmatsci.2021.100808.
[385] Y. Feng, J. Xu, S. Zeng, Y. Gao, and J. Tan, "Controlled helical deformation of programmable bilayer structures: design and fabrication," *Smart Mater. Struct.*, vol. 29, no. 8, p. 85042, 2020, doi: 10.1088/1361-665x/ab905d.
[386] J. Kim, J. W. Kim, H. C. Kim, L. Zhai, H.-U. Ko, and R. M. Muthoka, "Review of Soft Actuator Materials," *Int. J. Precis. Eng. Manuf.*, vol. 20, no. 12, pp. 2221–2241, 2019, doi: 10.1007/s12541-019-00255-1.
[387] Q. Ge, C. K. Dunn, H. J. Qi, and M. L. Dunn, "Active origami by 4D printing," *Smart Mater. Struct.*, vol. 23, no. 9, p. 94007, 2014, doi: 10.1088/0964-1726/23/9/094007.
[388] L. R. Hart *et al.*, "Chapter 15 - 3D and 4D printing of biomaterials and biocomposites, bioinspired composites, and related transformers," K. K. Sadasivuni, K. Deshmukh, and M. A. B. T.-3D and 4D P. of P. N. M. Almaadeed, Eds. Elsevier, 2020, pp. 467–504.
[389] J. Huang, S. Xia, Z. Li, X. Wu, and J. Ren, "Applications of four-dimensional printing in emerging directions: Review and prospects," *J. Mater. Sci. Technol.*, vol. 91, pp. 105–120, 2021, doi: https://doi.org/10.1016/j.jmst.2021.02.040.
[390] K. Mondal and P. K. Tripathy, "Preparation of Smart Materials by Additive Manufacturing Technologies: A Review," *Materials* , vol. 14, no. 21. 2021, doi: 10.3390/ma14216442.
[391] A. Bajpai, A. Baigent, S. Raghav, C. Ó. Brádaigh, V. Koutsos, and N. Radacsi, "4D Printing: Materials, Technologies, and Future Applications in the Biomedical Field," *Sustainability* , vol. 12, no. 24. 2020, doi: 10.3390/su122410628.
[392] Y. Liu *et al.*, "Shape memory behavior and recovery force of 4D printed laminated Miura-origami structures subjected to compressive loading," *Compos. Part B*, vol. 153, no. July, pp. 233–242, 2018, doi: 10.1016/j.compositesb.2018.07.053.
[393] A. Zolfagharian, A. Kaynak, and A. Kouzani, "Closed-loop 4D-printed soft robots," *Mater. Des.*, vol. 188, p. 108411, 2020, doi: https://doi.org/10.1016/j.matdes.2019.108411.
[394] G. Duan, H. Liu, Z. Liu, and J. Tan, "A 4D-Printed Structure With Reversible Deformation for the Soft Crawling Robot ," *Frontiers in Materials* , vol. 9. 2022.
[395] B. Zou, C. Song, Z. He, and J. Ju, "Encoding of direct 4D printing of isotropic single-material system for double-curvature and multimodal morphing," *Extrem. Mech. Lett.*, vol. 54, p.

101779, 2022, doi: https://doi.org/10.1016/j.eml.2022.101779.
[396] X. Xin, L. Liu, Y. Liu, and J. Leng, “Origami-inspired self-deployment 4D printed honeycomb sandwich structure with large shape transformation,” *Smart Mater. Struct.*, vol. 29, no. 6, p. 65015, 2020, doi: 10.1088/1361-665x/ab85a4.
[397] E. Pulatsu, J.-W. Su, J. Lin, and M. Lin, “Utilization of Ethyl Cellulose in the Osmotically-Driven and Anisotropically-Actuated 4D Printing Concept of Edible Food Composites,” *Carbohydr. Polym. Technol. Appl.*, vol. 3, p. 100183, 2022, doi: https://doi.org/10.1016/j.carpta.2022.100183.
[398] G. Li *et al.*, “Bio-Inspired 4D Printing of Dynamic Spider Silks,” *Polymers* , vol. 14, no. 10. 2022, doi: 10.3390/polym14102069.
[399] T. Liu, L. Liu, C. Zeng, Y. Liu, and J. Leng, “4D printed anisotropic structures with tailored mechanical behaviors and shape memory effects,” *Compos. Sci. Technol.*, vol. 186, p. 107935, 2020, doi: https://doi.org/10.1016/j.compscitech.2019.107935.
[400] X. Teng, M. Zhang, and A. S. Mujumdar, “4D printing: Recent advances and proposals in the food sector,” *Trends Food Sci. Technol.*, vol. 110, pp. 349–363, 2021, doi: https://doi.org/10.1016/j.tifs.2021.01.076.
[401] O. Testoni *et al.*, “A 4D printed active compliant hinge for potential space applications using shape memory alloys and polymers,” *Smart Mater. Struct.*, vol. 30, no. 8, p. 85004, 2021, doi: 10.1088/1361-665x/ac01fa.
[402] D. Singla *et al.*, “Resilience and Performance of Deployable Space Structures Based on a Shape Memory Polymer Bus,” *ASME 2021 Conference on Smart Materials, Adaptive Structures and Intelligent Systems*. Sep. 2021, doi: 10.1115/SMASIS2021-68392.
[403] A. R. Damanpack, M. Bodaghi, and W. H. Liao, “Contact/impact modeling and analysis of 4D printed shape memory polymer beams,” *Smart Mater. Struct.*, vol. 29, no. 8, p. 85016, 2020, doi: 10.1088/1361-665x/ab883a.
[404] S. Ramesh, S. Kiran reddy, C. Usha, N. K. Naulakha, C. R. Adithyakumar, and M. Lohith Kumar Reddy, “Advancements in the Research of 4D Printing-A Review,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 376, p. 12123, 2018, doi: 10.1088/1757-899x/376/1/012123.
[405] S. Nam and E. Pei, “A taxonomy of shape-changing behavior for 4D printed parts using shape-memory polymers,” *Prog. Addit. Manuf.*, vol. 4, no. 2, pp. 167–184, 2019, doi: 10.1007/s40964-019-00079-5.
[406] K. Ntouanoglou, P. Stavropoulos, and D. Mourtzis, “4D Printing Prospects for the Aerospace Industry: a critical review,” *Procedia Manuf.*, vol. 18, pp. 120–129, 2018, doi: https://doi.org/10.1016/j.promfg.2018.11.016.
[407] J. E. M. Teoh, J. An, C. K. Chua, M. Lv, V. Krishnasamy, and Y. Liu, “Hierarchically self-morphing structure through 4D printing,” *Virtual Phys. Prototyp.*, vol. 12, no. 1, pp. 61–68, Jan. 2017, doi: 10.1080/17452759.2016.1272174.
[408] A. Y. Lee, A. Zhou, J. An, C. K. Chua, and Y. Zhang, “Contactless reversible 4D-printing for 3D-to-3D shape morphing,” *Virtual Phys. Prototyp.*, vol. 15, no. 4, pp. 481–495, Oct. 2020, doi: 10.1080/17452759.2020.1822189.
[409] D. Schmelzeisen, H. Koch, C. Pastore, and T. Gries, “4D Textiles: Hybrid Textile Structures that Can Change Structural Form with Time by 3D Printing BT - Narrow and Smart Textiles,” Y. Kyosev, B. Mahltig, and A. Schwarz-Pfeiffer, Eds. Cham: Springer International Publishing, 2018, pp. 189–201.
[410] C. Maraveas, I. S. Bayer, and T. Bartzanas, “4D printing: Perspectives for the production of sustainable plastics for agriculture,” *Biotechnol. Adv.*, p. 107785, 2021, doi: https://doi.org/10.1016/j.biotechadv.2021.107785.
[411] G. A. Pacillo, G. Ranocchiai, F. Loccarini, and M. Fagone, “Additive manufacturing in construction: A review on technologies, processes, materials, and their applications of 3D and 4D printing,” *Mater. Des. Process. Commun.*, vol. 3, no. 5, p. e253, Oct. 2021, doi: https://doi.org/10.1002/mdp2.253.
[412] H. C. Koch, D. Schmelzeisen, and T. Gries, “4D Textiles Made by Additive Manufacturing on Pre-Stressed Textiles—An Overview,” *Actuators* , vol. 10, no. 2. 2021, doi: 10.3390/act10020031.
[413] E. Pei, J. Shen, and J. Watling, “Direct 3D printing of polymers onto textiles: experimental

studies and applications," *Rapid Prototyp. J.*, vol. 21, no. 5, pp. 556–571, Jan. 2015, doi: 10.1108/RPJ-09-2014-0126.
[414] M. Baniasadi, E. Yarali, A. Foyouzat, and M. Baghani, "Crack self-healing of thermo-responsive shape memory polymers with application to control valves, filtration, and drug delivery capsule," *Eur. J. Mech. - A/Solids*, vol. 85, p. 104093, 2021, doi: https://doi.org/10.1016/j.euromechsol.2020.104093.
[415] G. J. M. Antony, S. Raja, and S. T. Aruna, "Stimuli-Responsive Self-Healable Materials," *Self-Healing Smart Materials and Allied Applications*. pp. 361–377, May 2021, doi: https://doi.org/10.1002/9781119710219.ch14.
[416] J. E. M. Teoh, C. K. Chua, Y. Liu, and J. An, "4D printing of customised smart sunshade: A conceptual study," in *Challenges for technology innovation: an agenda for the future*, CRC Press, 2017, pp. 105–108.
[417] X. Li, J. Shang, and Z. Wang, "Intelligent materials: a review of applications in 4D printing," *Assem. Autom.*, vol. 37, no. 2, pp. 170–185, Jan. 2017, doi: 10.1108/AA-11-2015-093.
[418] D. Beiderbeck, H. Krüger, and T. Minshall, "The Future of Additive Manufacturing in Sports BT - 21st Century Sports: How Technologies Will Change Sports in the Digital Age," S. L. Schmidt, Ed. Cham: Springer International Publishing, 2020, pp. 111–132.
[419] G. Wang, Y. Tao, O. B. Capunaman, H. Yang, and L. Yao, "A-Line: 4D Printing Morphing Linear Composite Structures," in *Proceedings of the 2019 CHI Conference on Human Factors in Computing Systems*, 2019, pp. 1–12, doi: 10.1145/3290605.3300656.
[420] H. Chen *et al.*, "Interpenetrating polymer network hydrogels using natural based dyes initiating systems: Antibacterial activity and 3D/4D performance," *Eur. Polym. J.*, vol. 166, p. 111042, 2022, doi: https://doi.org/10.1016/j.eurpolymj.2022.111042.
[421] C.-Y. Wu, J.-R. Chen, and C.-K. Su, "4D-printed pH sensing claw," *Anal. Chim. Acta*, vol. 1204, p. 339733, 2022, doi: https://doi.org/10.1016/j.aca.2022.339733.
[422] Q. Ji, X. V. Wang, L. Wang, and L. Feng, "Customized protective visors enabled by closed loop controlled 4D printing," *Sci. Rep.*, vol. 12, no. 1, p. 7566, 2022, doi: 10.1038/s41598-022-11629-3.
[423] B. I. Oladapo, S. O. Ismail, O. M. Ikumapayi, and J. F. Kayode, "Impact of rGO-coated PEEK and lattice on bone implant," *Colloids Surfaces B Biointerfaces*, p. 112583, 2022, doi: https://doi.org/10.1016/j.colsurfb.2022.112583.
[424] M. Wan, K. Yu, and H. Sun, "4D printed programmable auxetic metamaterials with shape memory effects," *Compos. Struct.*, vol. 279, p. 114791, 2022, doi: https://doi.org/10.1016/j.compstruct.2021.114791.
[425] K. Dong, M. Panahi-Sarmad, Z. Cui, X. Huang, and X. Xiao, "Electro-induced shape memory effect of 4D printed auxetic composite using PLA/TPU/CNT filament embedded synergistically with continuous carbon fiber: A theoretical & experimental analysis," *Compos. Part B Eng.*, vol. 220, p. 108994, Sep. 2021, doi: 10.1016/J.COMPOSITESB.2021.108994.
[426] E. Sachyani Keneth, R. Lieberman, M. Rednor, G. Scalet, F. Auricchio, and S. Magdassi, "Multi-Material 3D Printed Shape Memory Polymer with Tunable Melting and Glass Transition Temperature Activated by Heat or Light," *Polymers* , vol. 12, no. 3. 2020, doi: 10.3390/polym12030710.
[427] S. Cen *et al.*, "4D printing of a citrus pectin/β-CD Pickering emulsion: A study on temperature induced color transformation," *Addit. Manuf.*, vol. 56, p. 102925, 2022, doi: https://doi.org/10.1016/j.addma.2022.102925.
[428] H. Jeong, E. Park, and S. Lim, "Four-Dimensional Printed Shape Memory Metasurface to Memorize Absorption and Reflection Functions," *ACS Appl. Mater. Interfaces*, Dec. 2021, doi: 10.1021/acsami.1c17968.
[429] J.-Y. Wang, F. Jin, X.-Z. Dong, J. Liu, and M.-L. Zheng, "Flytrap Inspired pH-Driven 3D Hydrogel Actuator by Femtosecond Laser Microfabrication," *Adv. Mater. Technol.*, vol. n/a, no. n/a, p. 2200276, Apr. 2022, doi: https://doi.org/10.1002/admt.202200276.
[430] M. Han, L. Li, and J. Zhao, "Volatile Organic Compound Emissions from 4D printing: Effects of Material Composition and External Stimulus," *Addit. Manuf.*, p. 102894, 2022, doi: https://doi.org/10.1016/j.addma.2022.102894.
[431] T. Y. Koh and A. Sutradhar, "Untethered selectively actuated microwave 4D printing through

ferromagnetic PLA," *Addit. Manuf.*, p. 102866, 2022, doi: https://doi.org/10.1016/j.addma.2022.102866.

[432] W. Li *et al.*, "Dual-mode biomimetic soft actuator with electrothermal and magneto-responsive performance," *Compos. Part B Eng.*, vol. 238, p. 109880, 2022, doi: https://doi.org/10.1016/j.compositesb.2022.109880.

[433] J. Chen, M. Zhang, A. S. Mujumdar, and P. Phuhongsunge, "4D printing induced by microwave and ultrasound for mushroom mixtures: Efficient conversion of ergosterol into vitamin D2," *Food Chem.*, vol. 387, p. 132840, 2022, doi: https://doi.org/10.1016/j.foodchem.2022.132840.

[434] B. Q. Y. Chan *et al.*, "Synergistic combination of 4D printing and electroless metallic plating for the fabrication of a highly conductive electrical device," *Chem. Eng. J.*, vol. 430, p. 132513, 2022, doi: https://doi.org/10.1016/j.cej.2021.132513.

[435] Y. Li, W. Zheng, B. Li, J. Dong, G.-L. Gao, and Z. Jiang, "Double-Layer Temperature-Sensitive Hydrogel Fabricated by 4D Printing with Fast Shape Deformation," *Colloids Surfaces A Physicochem. Eng. Asp.*, p. 129307, 2022, doi: https://doi.org/10.1016/j.colsurfa.2022.129307.

[436] S. Shanthamma, R. Preethi, J. A. Moses, and C. Anandharamakrishnan, "4D Printing of Sago Starch with Turmeric Blends: A Study on pH-Triggered Spontaneous Color Transformation," *ACS Food Sci. Technol.*, vol. 1, no. 4, pp. 669–679, May 2021, doi: 10.1021/acsfoodscitech.0c00151.

[437] X. Huang *et al.*, "4D printed TPU/PLA/CNT wave structural composite with intelligent thermal-induced shape memory effect and synergistically enhanced mechanical properties," *Compos. Part A Appl. Sci. Manuf.*, vol. 158, p. 106946, 2022, doi: https://doi.org/10.1016/j.compositesa.2022.106946.

[438] M. Ali, F. Alam, Y. F. Fah, O. Shiryayev, N. Vahdati, and H. Butt, "4D printed thermochromic Fresnel lenses for sensing applications," *Compos. Part B Eng.*, vol. 230, p. 109514, 2022, doi: https://doi.org/10.1016/j.compositesb.2021.109514.

[439] N. Namvar, A. Zolfagharian, F. Vakili-Tahami, and M. Bodaghi, "Reversible energy absorption of elasto-plastic auxetic, hexagonal, and AuxHex structures fabricated by FDM 4D printing," *Smart Mater. Struct.*, vol. 31, no. 5, p. 55021, 2022, doi: 10.1088/1361-665x/ac6291.

[440] H. Ouyang, X. Li, X. Lu, and H. Xia, "Selective Laser Sintering 4D Printing of Dynamic Cross-linked Polyurethane Containing Diels–Alder Bonds," *ACS Appl. Polym. Mater.*, Apr. 2022, doi: 10.1021/acsapm.2c00565.

[441] M. C. Biswas, S. Chakraborty, A. Bhattacharjee, and Z. Mohammed, "4D Printing of Shape Memory Materials for Textiles: Mechanism, Mathematical Modeling, and Challenges," *Adv. Funct. Mater.*, vol. 31, no. 19, p. 2100257, May 2021, doi: https://doi.org/10.1002/adfm.202100257.

[442] A. Zolfagharian, M. Denk, M. Bodaghi, A. Z. Kouzani, and A. Kaynak, "Topology-Optimized 4D Printing of a Soft Actuator," *Acta Mech. Solida Sin.*, vol. 33, no. 3, pp. 418–430, 2020, doi: 10.1007/s10338-019-00137-z.

[443] M. Quanjin, M. R. M. Rejab, M. S. Idris, N. M. Kumar, M. H. Abdullah, and G. R. Reddy, "Recent 3D and 4D intelligent printing technologies: A comparative review and future perspective," *Procedia Comput. Sci.*, vol. 167, pp. 1210–1219, 2020.

[444] M. F. Pucci, P.-J. Liotier, and S. Drapier, "Capillary wicking in flax fabrics–effects of swelling in water," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 498, pp. 176–184, 2016.

[445] S. Tibbits, "4D printing: multi-material shape change," *Archit. Des.*, vol. 84, no. 1, pp. 116–121, 2014.

[446] M. Rüggeberg and I. Burgert, "Bio-inspired wooden actuators for large scale applications," *PLoS One*, vol. 10, no. 4, p. e0120718, 2015.

[447] A. Holstov, B. Bridgens, and G. Farmer, "Hygromorphic materials for sustainable responsive architecture," *Constr. Build. Mater.*, vol. 98, pp. 570–582, 2015.

[448] F. Momeni and J. Ni, "Nature-inspired smart solar concentrators by 4D printing," *Renew. Energy*, vol. 122, pp. 35–44, 2018.