Chapter 1
Advances in 4D Printing of Shape-Memory Materials: Current Status and Developments

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1.1 Introduction

Additive Manufacturing (AM), typically referred to as rapid prototyping or three-dimensional (3D) printing, was introduced in the late 1980s and since then, it has rapidly emerged as a sustainable, efficient, and intelligent tool. With 3D-printing methods, researchers can fabricate complex designs [1], drug delivery systems [2], remotely actuated robots [3], multi-material designs, and even bio-inspired designs [4, 5]. Moreover, recent developments in novel materials and software tools have synergistically expanded the stage for additive manufacturing. Conventional AM technologies are designed to produce static structures using a single material, which is not capable of fulfilling the demands of dynamic functions needed for applications such as adaptive wind turbines, self-folding packaging, and soft grippers for surgery. This kind of dynamic transformation incorporation in the object fabricated with AM gave the advent to the four dimension printing. This idea of additional dimension

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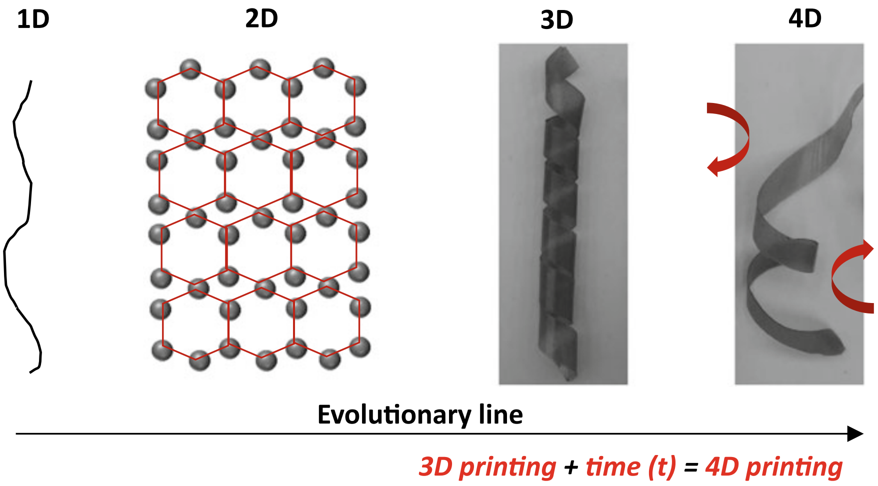

Fig. 1.1 Schematic illustrating the concept of 1D, 2D, 3D, and 4D

introduced a new branch of AM and is known as four-dimensional (4D) printing. The term 4D printing was first introduced by Tibbits in a 2013 TED talk, where 3D-printed static structures would transform their shape over time. Followed by this, report dealing with 4D-printing was published, demonstrating a printed sheet of active composite getting transformed into complex designs based on the phenomenon of shape-memory effect [6]. Thereafter, 4D printing received the attention of smart material and 3D-printing field research communities [7]. Initially, 4D printing was defined as 4D printing = 3D printing + time as shown in Fig. 1.1.

The 4D printing needs to be defined properly to have a clear differentiation between 4 and 3D printing. According to Tibbits et al., 4D printing is a new technique, in which customized material systems or multi-material structures can be printed with the ability to change from one shape to another or can transform over time, directly off the print bed [8]. The transformation over time was described as the fourth dimension, stressing that printed structures are no more dead objects or static; instead, they can transform independently and are active. The 4D printing was suggested as the AM technology where material with varying properties or stimuli-responsive composite material-based physical objects are printed by laying down successive layers appropriately [9]. The printed objects respond to the manually applied stimuli or from the environment, leading to a chemical or physical transformation of the state, over time. Thus, the main difference between the two definitions is that Tibbits et al. considered the shape changes only, while 4D printing was suppose to induce either a chemical or physical change of state [9]. Later, the concept was evolved, and researchers redefined the definition as 3D-printed objects that show intended targeted property, shape, or functionality transformation with exposure to a predetermined stimulus, such as light [10], water [11], heat [7], and pH [12]. The Gartner hype cycle looks into the evolution of emerging technologies and predicts their potential for possible practical application in a business ecosystem with a highly competitive advantage over the next few years. Along with other new technologies, such as artificial intelligence, quantum computing, and autonomous mobile robots, 4D printing is in the stage of development triggering and is expected to reach its mainstream in a decade [13].

For effective designing in 4D printing and better results, it is necessary to adopt the following steps:

- Individualization.
- Smart shape-memory lightweight materials.
- Integrated designing.
- Overall product efficiency.

For the successful 4D printing of the objects, these elements are essential and provide technological and economical improvements.

Currently, it is the initial development stage of 4D printing, and within a short time, it has evolved as a vibrant branch of AM and has grabbed the interest of industries and researchers. The extensive ongoing research on the active topic of 4D printing is indicated by the increased number of scientific publications in the past years [14]. Thus, before adopting fully the 4D printing technology, it is important to understand the concept of 3D printing which is one of the essential parts of 4D printing. The section below gives detailed information about the techniques involved in 3D printing.

1.2 3D Printing

Recent advances in 3D-printing techniques have shown a surge for future additive manufacturing, and extensive ongoing research in this area can be gazed at based on the number of publications [14]. There are more than 50 AM technologies that are recognized by the American Society for Testing and Materials (ISO/ASTM 52,900:2015). These common 3D-printing technologies can be classified into seven categories that include direct energy deposition, sheet lamination, binder jetting, material jetting, powder bed fusion, VAT photopolymerization process, and material extrusion. A brief description of their deposition method, materials used, and associated techniques is listed in Table 1.1.

1.2.1 Binder Jetting

The printing of 3D structures by jet deposition of binding agent and powdered material mixture is known as binder jetting. This technology prints materials like ceramics, polymers, and metals. The developers of this technology are 3D Systems (USA), ExOne (USA), and voxeljet (Germany).

Table 1.1 Different additive manufacturing techniques

Process category	Materials	Description	Technologies
Sheet lamination	Paper, Metals	3D object is formed by the bonding of materials layer in form of sheets.	UC, LOM
Material jetting	Waxes, Polymers	3D object is formed by selective deposition of material droplets	MultiJet, PolyJet, MJM, etc.
Binder jetting	Ceramic, metals, Polymers	Powder materials are selectively joined by a liquid bonding agent and are finally cured to achieve the structure.	PBIH, PP, BJ
Vat photopolymerization	Photo-polymers	Ultraviolet light is used to selectively cure (polymerize) the liquid photopolymer in a vat.	DLP, SLA
Material extrusion	Polymer-based materials	Heated nozzle is used to selectively extruded material and get deposited layer by layer	FDM
Direct energy deposition	Metals	Focused thermal energy is used to fuse materials by melting as the material are being deposited.	LDD, DMD, DALM, LMD
Powder bed fusion	Ceramic, Polymers, Metals	Regions of a powder bed are selectively fused by thermal energy.	SHS, DMLS, SLM, SLS, EBM

Note: AM = additive manufacturing; UC = ultrasonic consolidation; LDOM = laminated object manufacturing; MJM = multijet modeling; PP = plaster-based 3D printing; PBIH = powder bed and inkjet head; BJ = binder jetting; SLA = stereolithography; DLP = digital light processing; FDM = fused deposition modeling; LDD = laser direct deposition; DMD = direct metal deposition; DALM = direct additive laser manufacturing; LMD = laser metal deposition; SHS = selective heat sintering; EBM = electron beam melting; DMLS = direct SLS = selective laser sintering; metal laser sintering; and SLM = selective laser melting

1.2.2 Material Jetting

In this, small droplets of filaments are allowed to settle down and be carved by exposing to UV radiation as per the design instruction. The layer resolution by this printing is about 16 µm. For this type of printing, the materials used are wax and photopolymers. The technology was invented by Luxecel (Netherlands), 3D systems (USA), and Stratasys (USA).

1.2.3 Direct Energy Deposition

In this process, direct deposition of the fused material takes place, which is assisted by the focused thermal energy. The suitable materials for this type of feeding mechanism are in the form of wires and powders. The technology was implemented by TRUMPF (Germany), NRC-IMI (Canada), DM3D (USA), and IREPA LASER (France).

1.2.4 Powder Bed Fusion

In this technology, regions of a powder bed are fused based on the time dimension, and the deposition process is assisted by thermal energy. The materials employed for deposition consist of metals, ceramics, and polymers. This technology was developed by the 3D systems (US), Renishaw (UK), ARCAM (Sweden), EOS (Germany), Phoenix Systems (France), and Matsuura Machinery (Japan). The various processes used in the powder bed fusion technology are listed below.

- *Direct metal laser sintering*
  This process uses a highly focused laser beam to melt and fuse material in an inert atmosphere to generate desired 3D structures.
- *Electron beam melting*
  This technology employs high-intensity electron beam to melt the material power inside the vacuum chamber, and successive cooling of the processed material results in the final shape of the design.
- *Selective heat sintering*
  This method incorporates heating of thermoplastic powder inside the thermal print head, followed by layer-by-layer deposition of the processed material.
- *Selective laser melting*
  Here, a pool of melted metal powder is created inside an inert gas chamber by using a laser beam. The final product is generated by repeatedly rolling the melt in the form of layers.

- *Selective laser sintering*

In this process, a laser beam is employed to sinter the material powder and then rolled to produce the final shape. The process is similar to the laser melting, except that instead of heating material above the melting point, the material is heated below the melting point to allow particle fusion.

1.2.5 Light Photopolymerization

This process is based on creating objects by selectively curing materials using light. The technique uses materials like photopolymers and was developed by 3D Systems (US), DWS SRL (Italy), EnvisionTEC (Germany), and Lithoz (Australia). The technique employs either digital light processing or stereolithography during the printing of 3D structures.

- Digital light processing

  The CAD image of the object is projected layer by layer into the VAT of photopolymer, and with the simultaneous projection of light, the material gets cured to form a desired 3D part.

- Stereolithography
  This technique uses a laser source for irradiating UV light in a defined pattern over a liquid photopolymer. With the exposure of light, solidification of resin takes place and desired 3D structure is created.

1.2.6 Extrusion

Material is fed through a heated nozzle whose output is repetitively deposited layer by layer on a printing bed, where material instantly becomes hard to permit next layer deposition. Mainly thermoplastic material and thermosetting polymers are used for the printing process, and technology was implemented by Stratasys (US), 3D Systems (US), and Delta Micro-factory (China).

1.2.7 Sheet Lamination

In this process, sheets of printable material are trimmed and joined layer by layer to create 3D structures. The technique incorporates laminated and ultrasonic additive manufacturing. Materials like metallic sheets, ceramics, and hybrid materials are used in this process. This technology was developed by Fabrisonic (US) and CAM-LEM (US).

- Laminated object manufacturing
  In this process, the desired geometry of material is cut in the form of sheets by the laser cutter and then bonded layer by layer using plastic, metal, or adhesive paper.
- Ultrasonic additive manufacturing
  In this process, ultrasonic welding is used for laminating thin metallic sheets to form objects, and excess material is trimmed by an integrated CNC mill.

Among all these methods, material extrusion technologies and VAT photopolymerization process are being mostly utilized. The various material extrusion-based printing methods include fused deposition method (FDM) or fused filament fabrication (FFF) and direct ink writing (DIW). In both these deposition techniques, the 3D structure is printed layer by layer; the major variation is that DIW deposits a viscous ink composed of thermosetting polymers that needs to be cured, whereas in FDM the solid thermoplastic filament is melted in the heated nozzle and doesn't require a further curing step. Using extrusion-based technique, a wide range of materials and composites can be printed into 3D objects, where resolution is governed by the diameter of the nozzle an 100–200 μm [15]. Both FDM and DIW printing methods have limitations in printing multiple materials. The involvement of multiple materials in FDM can result in poor interface bonding due to a mismatch between their printing temperatures, and DIW suffers from the issue of polymer resin compatibility. On the other hand, using inkjet printing, multiple polymer resins can be printed by incorporating multiple nozzles for simultaneous spray, followed by UV curing. As a result, multi-material 3D objects can be fabricated easily with a relatively high resolution. For single-material inkjet printing, the resolution is about 30–40 μm, and for multi-material printing, the typical resolution is 200–400 μm [15]. Another polymer-based 3D-printing method is called VAT photopolymerization. Compared to material extrusion, the VAT photopolymerization process can be operated at higher printing speeds and can achieve better resolutions. The last major group of 3D-printing techniques is multijet fusion (MJF) and selective laser sintering (SLS). SLA and FFF printing techniques are most extensively used followed by DIW, inkjet, and DLP. In the DLP method, the introduction of continuous liquid interface production (CLIP) allows fast printing that can match with production level. Moreover, using optical lens setup, a high resolution of micro and nanoscale can be achieved, and this technique is called Projection Micro-Stereolithography (PμSL). A schematic illustration of a few conventionally used 3D-printing technologies is shown in Fig. 1.2.

1.3 4D Printing

The advancement in smart material and their incorporation in cost-effective 3D printing have triggered the AM technology to the next level, known as 4D printing. 4D printing is the next-generation version of 3D printing, which has the potential to

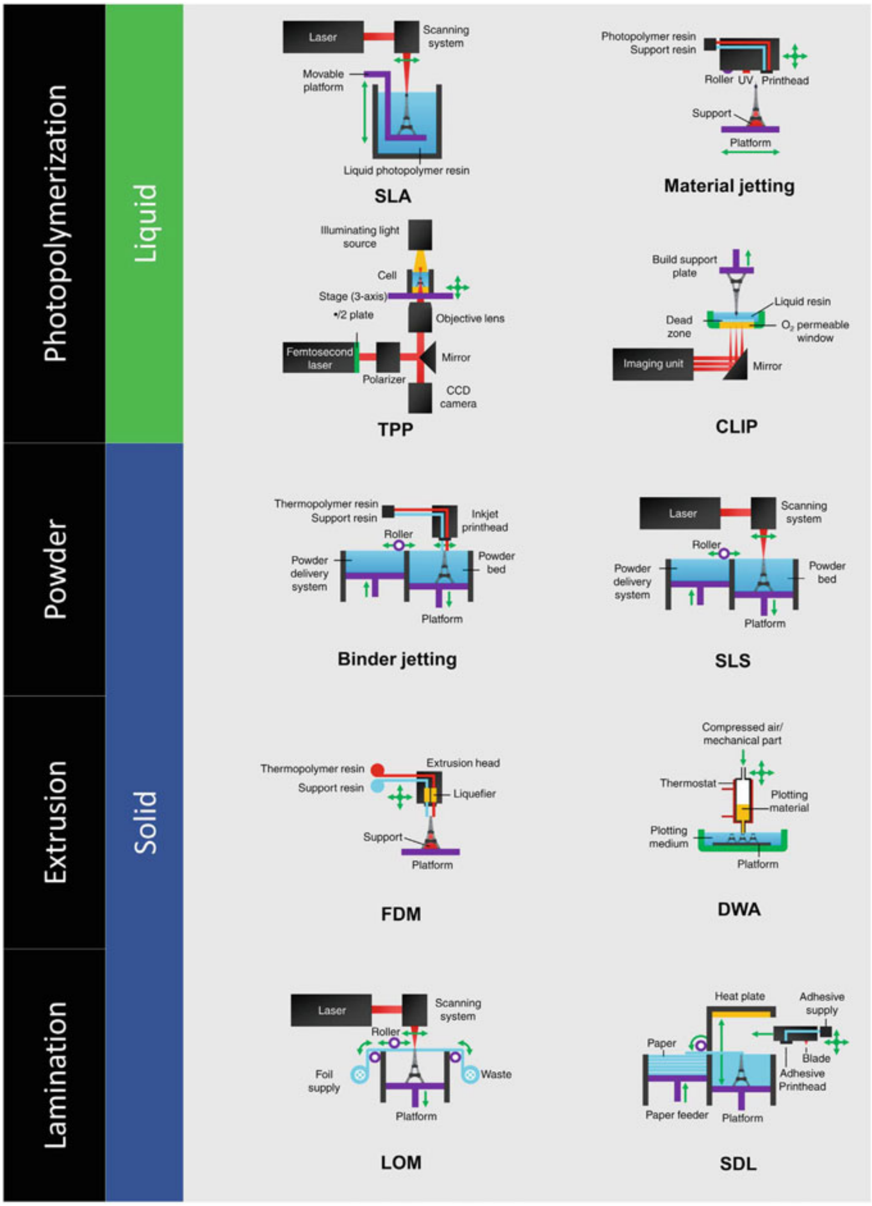

Fig. 1.2 Schematic illustration of conventionally used additive manufacturing techniques. Reproduced from [16], originally published under a CC BY 4.0 license, https://doi.org/10.1016/j.memsci.2016.10.006

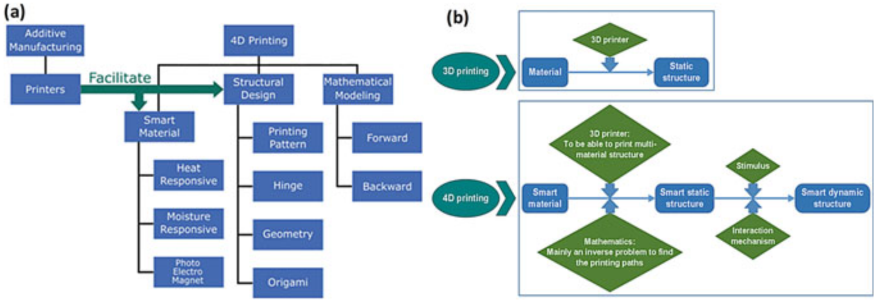

Fig. 1.3 **a** Schematic showing the research features of the 4D printing. Reproduced from [17], originally published under a CC BY 4.0 license. Copyright ©2019 Zhang et al. Published by Informa UK Limited, trading as Taylor & Francis Group. Taylor & Francis. https://doi.org/10.1080/19475411.2019.1591541. **b** Schematic for comparison between 4D and 3D printing. Reprinted from [18] Copyright © (2017) with permission from Elsevier Ltd.

realize self-repair, self-assembly, and multifunctionality. 4D printing feeds on technology related to 3D printing, with the extra feature of getting transformed over time under external stimuli [17, 18]. The salient features of the 4D printing are shown in Fig. 1.3a, and the technical difference between the printing process of 4D and 3D printing is illustrated in Fig. 1.3b.

Compared to 3D printing, 4D printing uses smart material with added features like interaction parts, stimulus, and mathematics. These elements facilitate the predictable and targeted progression of 4D-printed objects over time which is listed below:

- *3D-printing resource:* Generally, an appropriate distribution of different materials forming a single composite material is used for 4D-printing objects. The synergetic effect of materials properties, such as thermal expansion coefficient and swelling ratio, results in shifting behavior, transforming to a new desired shape. Therefore, to fabricate the simple and complex geometry of these smart materials, 3D printing is essential.
- *Stimulus-responsive material:* They are the most essential element of 4D printing. The capability of these materials is governed by the properties like self-repair, multifunctionality, self-adaptability, self-sensing, shape memory, responsiveness, and decision.
- *Stimulus:* 4D-printed structures are triggered to transform their shape/functionality/property by applying an external stimulus. Various stimuli like light, heat, different solvent, and even their combination can be used for 4D-printed objects. The stimulus selection depends on the types of smart materials used during 4D printing and desired application.
- *Interaction mechanism:* The interaction mechanism is referred to as a process by which the desired shape of 4D-printed objects is achieved by exposing them to an external stimulus in a defined sequence, over a period. This process is generally required for the materials that don't transform simply by exposing them to external stimulus.

- *Mathematical Modeling:* In 4D printing to achieve the desired functionality or property and change in shape, it is necessary to study the material distribution. Thus, numerical and theoretical models need to be studied to ascertain the relation between elements like material properties, desired final shape, material structure, and stimulus properties.

During the early breakthrough of 4D-printing technology, structures were designed to display one-way transformation, which means that structures need to be programmed (temporary shape setting by human interference) before every single cycle of stimulus. Thus, the need to eliminate the manual interaction to achieve two-way or reversible 4D printing arises. This kind of two-way reversibility can be realized by employing materials that can respond to an external stimulus and attain their parent properties back, by exposing them to another external stimulus. This allows reversibility into 4D-printed parts where the phenomenon is fully dependent on the external stimuli. Further, it eliminates the necessity of reprogramming, which is time-consuming. Moreover, after every recovery, the structure can be reused, which allows its usage over continuous cycles. Conventionally, this type of reversibility is termed "two-way memory" since it allows the two permanent shapes of material. Figure 1.4 illustrates the mechanism of one-way (irreversible) shape memory and two-way (reversible) shape memory with stimuli. Reversibility or repeatability is referred to as the capability of 4D-printed objects to replicate the complete cycle without any significant alteration to the permanent shape or fracture.

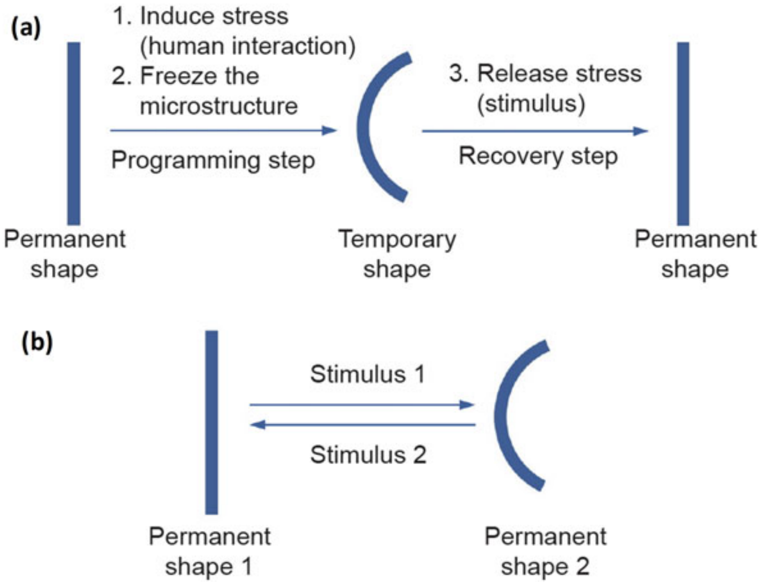

Fig. 1.4 Mechanism of one-way (irreversible) shape memory and two-way (reversible) shape memory with stimuli. Reproduced from [19], originally published under a CC BY 4.0 license, https://doi.org/10.1016/J.ENG.2017.05.014

The transformed geometry of the 4D-printed objects can be classified based on the structures and steps involved in the deformation (Fig. 1.5). The single deformation comes in the category of basic shape where a single step or process results in the desired transformation of the object. This includes contraction, topographical change expansion, curving, buckling, helixing, rolling, bending, folding, and twisting. The deformation geometry that involves multiple steps comes in the category of sequential shifting process, where stepwise transformation occurs at specific points of time. Such type of shape-changing behaviors comprises of multiple topographical, multiple helixing, multiple buckling, multiple twisting, multiple rolling, multiple bending, or multiple folding. Further, more complex and complicated geometry changes include curling and waving. Another category is the combined form, whereby printed objects are programmed to have two or more shape-changing behavior within the component.

Materials, those consists of two-way reversible ability are promising candidates for the future development of 4D-printing technology. Under the context, materials with shape-memory effect get the attraction of the researchers. To address such issues, shape-memory alloys (SMAs), shape-memory polymers (SMPs), and their composites are the rational choice for 4D printing to perform desired functions. An understanding of the shape-memory effect and a brief introduction to the concept are provided in the next section.

1.4 Fundamentals of Shape-Memory Effect

Shape-memory materials belong to a particular group of smart materials that can attain their original shape under external stimuli. Shape-memory materials are conventionally subjected to a programming process between different transformation phases which is initiated by the stimuli, and the phenomenon is termed as the shape-memory effect (SME). To achieve 4D printing of shape-memory materials, it is necessary to understand the functioning mechanisms of these materials.

1.4.1 Mechanisms of Shape-Memory Alloys

Shape-memory alloys (SMAs) are one such choice that can be transformed to a new shape upon cooling and while heating attains its original shape.

1.4.1.1 Thermal Shape-Memory Effect

SMA can attain different crystal structures and can exist in different structural phases. SMAs generally exist in three crystal structures (austenite, twinned, and detwinned martensite) having two different phases, which give rise to six possible transformations. As compared to the austenitic phase (stronger phase occurring at a higher

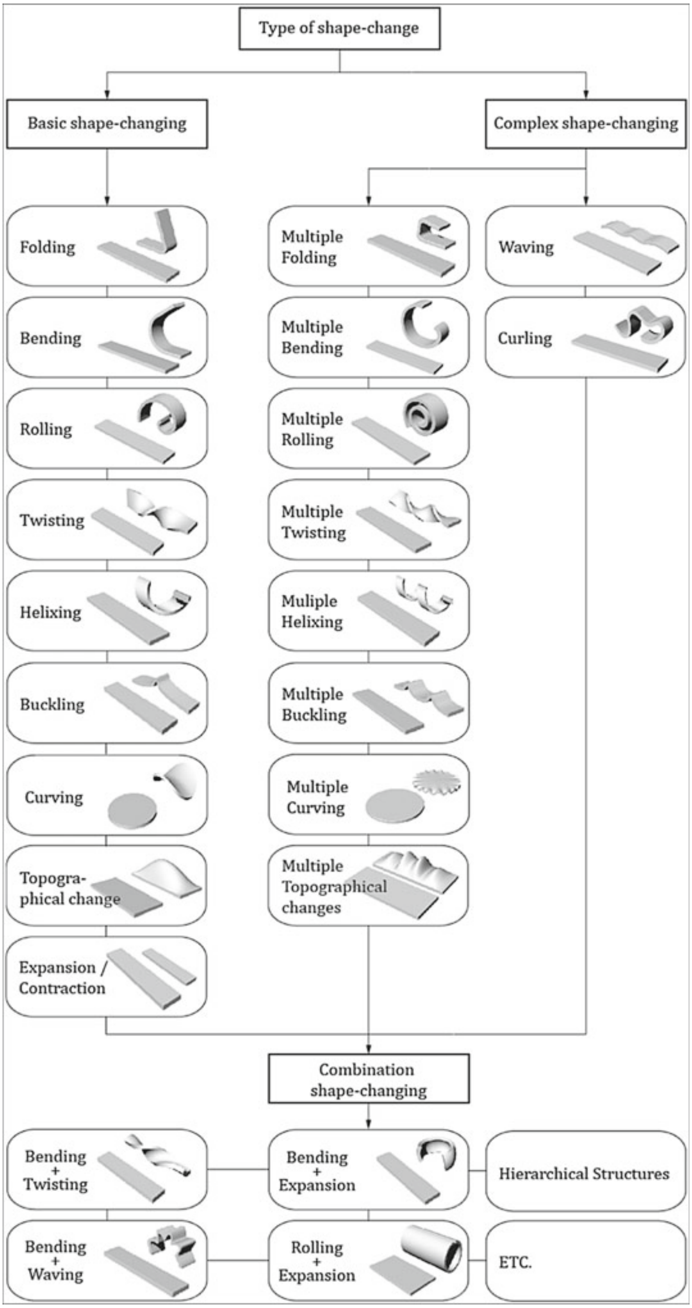

Fig. 1.5 Classification of shape-change geometry and their taxonomy. Reproduced from [20], originally published under a CC BY 4.0 license, Copyright © 2019, Seokwoo Nam et al. https://doi.org/10.1007/s40964-019-00079-5

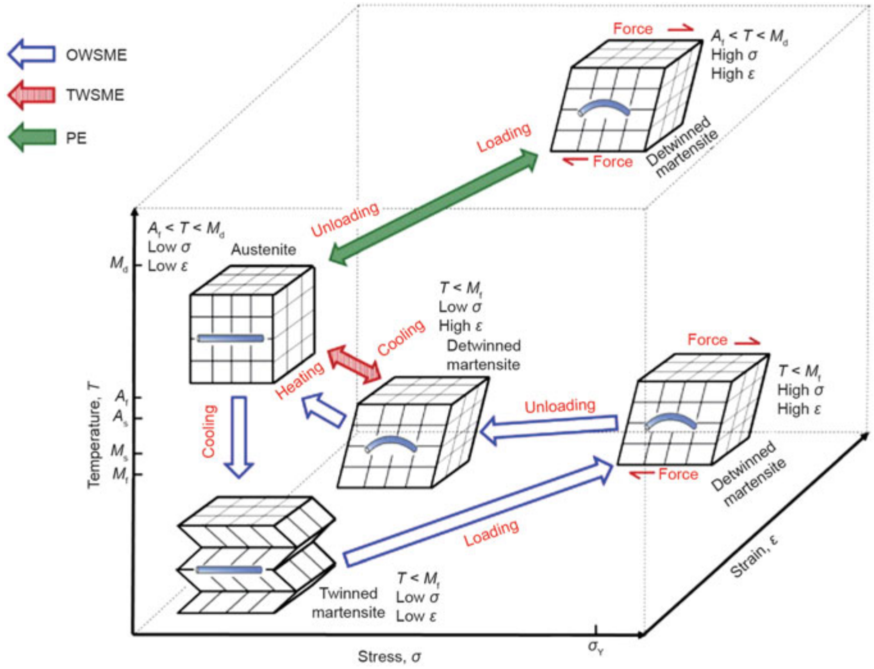

Fig. 1.6 Crystal structures and phases of SMA. Reprinted from [21] Copyright © (2013) with permission from Elsevier Ltd.

temperature), the martensite phase is soft, can be easily deformed, and exists at a lower temperature. Moreover, heating of alloy above its transformation temperature range results in its transformation from martensitic phase to austenite. A remarkable point in austenite phase is metal retains memory and "remembers" pre-deformation shape. There are three categories of SMAs, one-way shape-memory effect, two-way shape-memory effect, and pseudoelasticity as shown in Fig. 1.6.

- *One-way shape-memory effect*
  In this process, after removing the external force, the material retains its deformed shape, and upon heating, it comes to its original shape. Above the austenite start temperature (A_S), crystallographic phase reversibility is assisted by the difference in chemical free energy. At higher temperatures, the austenite structure is stable, but at lower temperatures, the martensite structure is more stable. Naturally, SMA exists in the form of a twinned martensite state, and under load, it forms a detwinned martensite structure that remains after unloading. When detwinned martensite material structure is heated above the austenite phase start temperature, it contracts and converts into the austenite phase, resulting in shape recovery. On further heating at a particular temperature (M_d), a stage reaches where martensite cannot be recovered and SMA will be permanently deformed.
- *Two-way shape-memory effect*

In this, the SMA will transform between two phases, which are generally the detwinned martensite phase at low temperatures and the austenite phase at high temperatures. Thus, these alloys can remember shapes at both low/high temperatures, and unlike one-way shape-memory alloy, it does not require any external mechanical stress. This type of functionality is achieved by tailoring one-way shape-memory alloys at the structural level.

- Pseudoelasticity

  In the mechanism, when the load is removed between austenite final temperature and M_d, without any heat, the SMA reverts to its original shape completely. This functionality is more like that of elastic solid; hence, it is less important in the context of smart materials.

1.4.2 Mechanisms of Shape-Memory Polymers

Shape-memory polymers (SMPs) contain molecular switches and net points that are either chemical or physical cross-links and behave as switching domains during the thermal transition. Conventional light (photo-responsive), chemical (chemo-responsive), or temperature changes (thermo-responsive) are used as a stimulus.

1.4.2.1 Thermo-Responsive Shape-Memory Polymers

In polymeric materials, the shape-memory effect induced by heat is based on a two-element system in which one element (metric) remains elastic during transformation while the other element (fibers) responds to temperature by a reversible change in the stiffness. To achieve a change in stiffness of polymer, melting glass transition temperature is commonly used. Based on the programming and recovery cycle, the working strategy of thermo-responsive SMPs can be classified into three mechanisms as shown in Fig. 1.7a.

- *Dual-state mechanism (DSM)*

  In this, polymers attain a more flexible rubbery stage above the glass transition temperature (T_g) and can be easily deformed. Below T_g, micro-Brownian motion in the polymer is frozen, and as a result, it becomes harder and exists in a glassy state. Thus, by cooling below T_g, the polymer attains a distorted shape and even retained this transformation after removing the applied constraint. On the other hand, micro-Brownian motion can be reactivated by heating above T_g and polymer recovers its shape. Usually, all polymers and their composites show a glass transition phenomenon; therefore, the thermal shape-memory effect is their intrinsic property.

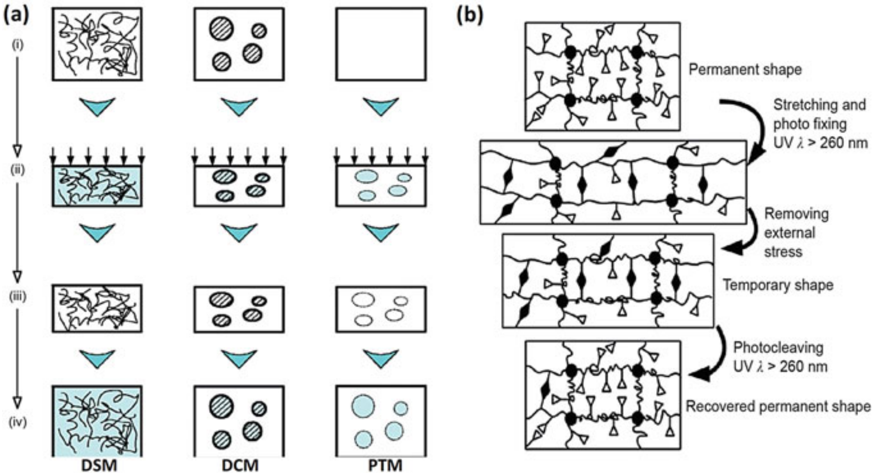

Fig. 1.7 **a** Thermo-responsive SMPs working mechanisms. (i) Original shape at low temperature; (ii) with compressing and heating; (iii) upon constraint removal and cooling; and (iv) Shape recovery upon heating. Reprinted with permission from Springer Nature: Springer Science Business Media B.V.: Journal of Polymer Research [22]. Copyright © 2012. **b** Molecular mechanism of a photo-responsive SMP. Reprinted with permission from Springer Nature: Nature Publishing Group: Nature [23] Copyright © 2005

- *Dual-component mechanism (DCM)*

  In this, polymer usually has two or more elastic transition/matrix elements or has soft/hard elements as an inclusion. During programming, the elastic matrix or hard element stores static elastic energy and retains its parent behavior throughout the transformation process. Whereas, upon heating, the stiffness of the soft element changes and is considered as the transition component. At low temperatures, the stiffness of these elements is high and prevents shape recovery. While heating reactivates the stored elastic energy of the transition element and polymer gets soft enough to return to its original shape.

- *Partial-transition mechanism (PTM)*

  Unlike DSM or DCM, in this, the polymer is heated within the transition range that lies between the glass transition and melting temperature. During the phenomenon, the softened component serves as a transition element and the un-softened component serves as the elastic element where elastic energy is stored.

1.4.2.2 Chemo-Responsive Shape-Memory Polymers

Here, appropriate chemicals are used to initiate plasticizing behavior in the polymer, which in turn decreases the glass transition temperature of the polymer, and transition can be triggered below T_g. This phenomenon is observed as swelling, softening, and dissolving of the polymer, which depends on the quality of the chemical, ionic strength, and pH value. The chemo-responsive shape-memory effect is widely observed in the hydrogel and gel polymers.

- *Swelling*

  The swelling can be exaggerated by allowing alteration in the miscibility and by inducing a change in the degree of cross-linking between solvent molecules and polymeric segments. The swelling amount is inversely proportional to the cross-linking density, which can be tuned by adjusting the pH of the solvent.

- *Softening*

  In this, the actuation of the polymer is initiated by gradual softening of the materials, and it attains its original shape. For example, in polyurethane (PU), transformation can be initiated through water or moisture as a stimulus.

- *Dissolving*

  This phenomenon is observed in the extreme case of softening, where, due to excess material softening the outer layer, the transition element starts dissolving into the solvent.

1.4.2.3 Photo-Responsive Shape-Memory Polymers

These polymers respond to light, and the corresponding molecular change is reflected in their shape transformation. A cinnamic group-containing polymer was reported by Lendlein et al. with the ability to attain modified transform shape upon exposure to UV light as shown in Fig. 1.7b [23]. The new transformed shape remains stable, and the original shape can be recovered under ambient conditions or by exposing it to lights of different wavelengths.

1.5 Development in Shape-Memory Material-Based 4D Printing

Integration of shape-memory materials in 4D printing has opened the possibility of systems for self-assembly, self-healing, and changes in material properties. SMAs, SMPs, and their composites are widely studied in this regard. The SMAs have a unique characteristic; they can remember their original shape prior to the deformation and return to their original shape after deformation, once they are heated. Only a few

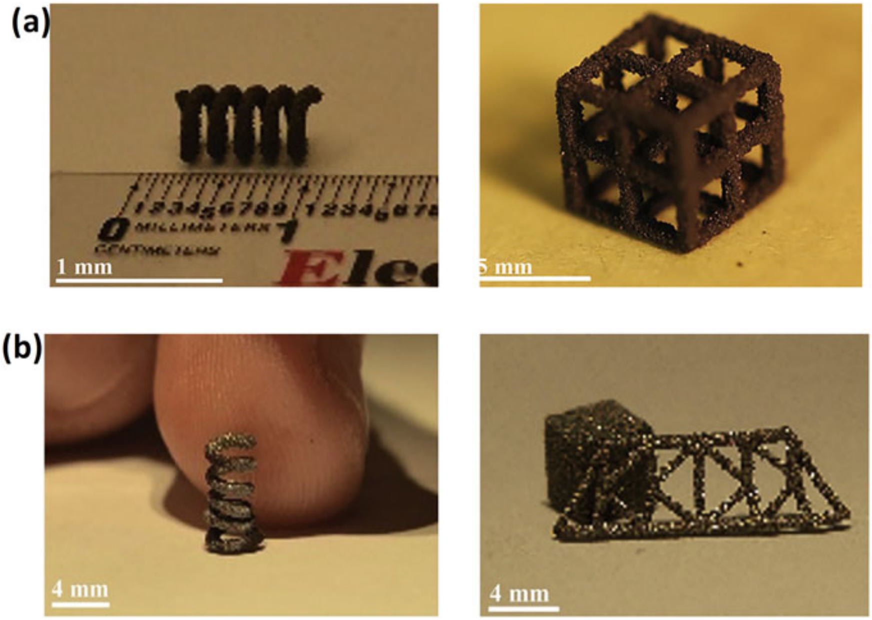

Fig. 1.8 **a** Spark eroded Ni–Mn–Ga 3D-printed parts after curing. **b** Ball-milled Ni–Mn–Ga 3D-printed parts after sintering. Reprinted from [24], Copyright © 2018 with permission from Elsevier B.V.

alloys systems like Au–Cd, In–Tl, Au–Cu, Cu–Al, Cu–Zn, Cu–Al–Be, Fe–Pd, Fe–Pt, Ni–Ti, Ni–Mn–Ga, etc. exhibit shape-memory effect. Recently, Caputo et al. fabricated 4D parts of Ni–Mn–Ga alloy by incorporating predictable changes in 3D printing as a function of time. Ni–Mn–Ga powders-based net-shaped porous structure was produced by binder jetting 3D printing [24]. The fabricated object showed good mechanical strength after curing and sintering. Figure 1.8a, b shows spark eroded Ni–Mn–Ga 3D-printed parts after curing and ball-milled Ni–Mn–Ga 3D-printed parts after sintering.

In particular, SMP materials with the ability to change their shape in response to stimuli have made remarkable progress in the 4D-printing research field. These materials are suitable alternatives for SMAs due to their flexibility, lightweight, biocompatibility, and high-strain capacities. A DLP-printed reversible and free-standing origami geometry was reported by Zhao et al. via swelling and desolvation of film and in acetone (Fig. 1.9a) [25]. Direct 3D printing of liquid crystal elastomer was demonstrated by Yuan et al. that can have high 4D-printing potential [26]. On the other hand, pure SMP exhibits lower modulus and recovery forces, when compared to shape-memory alloys and/or shape-memory ceramics. Due to the high density of cross-linking, most of the polymers suffer from the issue of large stretchability, and this hinders their employment in 4D printing. For efficient high-strength and high-recovery force-related applications, these unreinforced pure

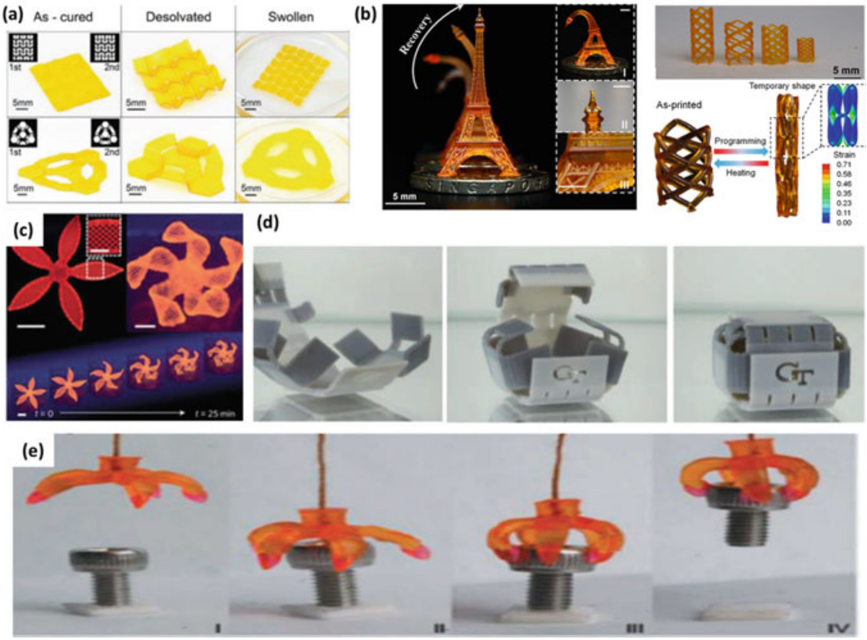

Fig. 1.9 4D-printed structures. **a** The as-cured 3D origami object, the folded desolvated, swollen shape, and flat sheet folded for application as an LED device. Reproduced with permission from [25] Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. **b** Dimension tunable ability of PμSL-printed stent. Reproduced from [27], originally published under a CC BY 4.0 license Copyright ©2016 Qi Ge et al., https://doi.org/10.1038/srep31110. **c** Biomimetic 4D printing by anisotropic swelling printed by DIW technique. Reprinted with permission from Springer Nature: Nature Publishing Group: Nature Materials [28] Copyright © 2016. **d** 4D-printed box showing the self-locking mechanism. Reproduced from [29], originally published under a CC BY 4.0 license Copyright © 2015 Yiqi Mao et al. https://doi.org/10.1038/srep13616. **e** 4D-printed grippers using PμSL 3D-printing technology. Reproduced from [27], originally published under a CC BY 4.0 license Copyright ©2016 Qi Ge et al., https://doi.org/10.1038/srep31110

SMPs are not suitable. To overcome these issues, materials with specific performance are essential to diversify their utilization in various applications. This can be achieved by using the incorporation of various reinforcing fillers within SMPs, where its pristine mechanical properties (high strength and high Young's modulus) can be improved. Under this context, shape-memory polymer composites have emerged as an attractive substitute. The shape-memory polymer composites (SMPCs) have additionally improved high recovery stress and novel functions. In a study by Ge et al., several difunctional acrylate oligomers and benzyl methacrylate were used to improve the stretchability [27]. High-resolution PμSL was used to print different geometry stents and displayed appreciable recovery (Fig. 1.9b, e). Multi-material printing can assist the complex shape formation and recovery. Figure 1.9c shows a biomimetic 4D-printed programmable bilayer structure reported by Gladman et al. [28]. Viscoelectric composite hydrogel ink was used, and printing was done by the

DIW technique. The anisotropic stiffness in the transverse and longitudinal direction of printed objects enabled the localization of the swelling, resulting in the transformation of structure from 2D to complex 3D structure. A hydrophobic swelling rubber-based 4D printing was reported, where bending deformation was triggered by the Eigenstrain induced in the hinge during hydrogel expansion. A deformed hyperbolic structure was observed when the grid was immersed in the water as stimuli [11]. By altering the spatial distribution materials, the folding angle could be controlled precisely. Thus, multi-material printing gives freedom to have multiple sequential shape transformations and shifting. In a study, Mao et al. controlled the printed object shape-changing sequence and demonstrated sequential folding of the hinges that resulted in the self-locking of the printed box, as shown in Fig. 1.9d [29].

1.6 Challenges in 4D Printing of Shape-Memory Materials

Smart materials should posses desirable properties for employing in the 4D-printing methods. Figure 1.10 shows the properties of the 4D-printing material. 4D printing of shape-memory materials has opened up the possibility of systems for self-assembly, self-healing, and changes in material properties. Currently, 4D-printing technology that is used for printing smart materials has a major challenge with the use of multi-material printing.

The various other challenges for the advancement of next-generation 4D-printing technology are listed below.

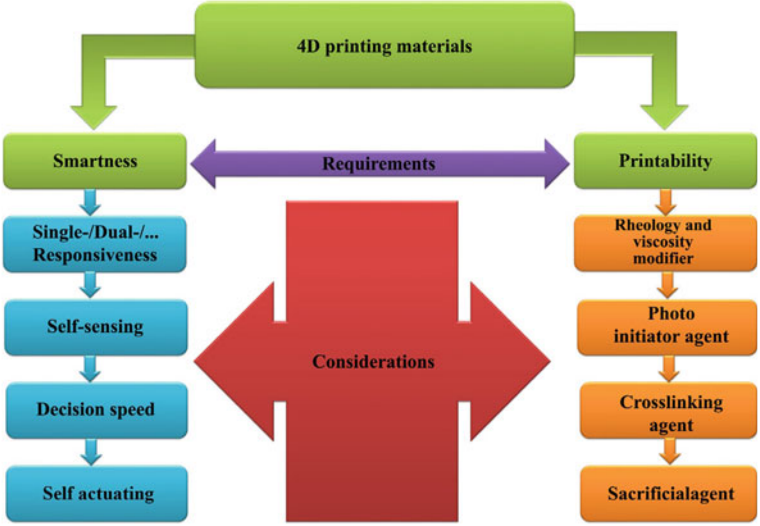

Fig. 1.10 Required properties of the 4D-printing material. Reprinted from [30] Copyright © (2020) with permission from Elsevier Inc.

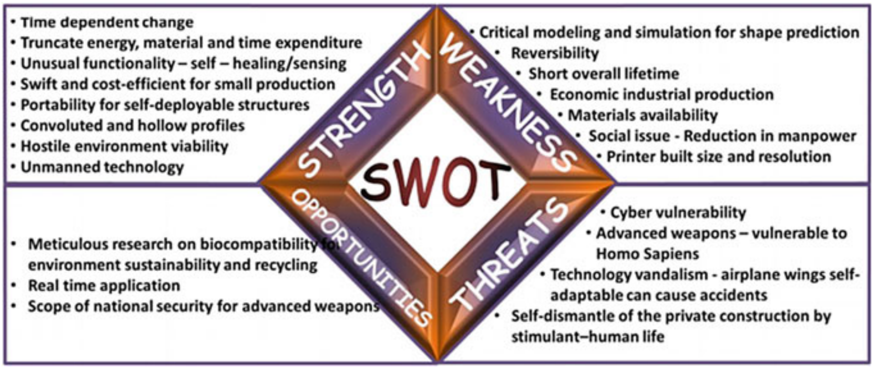

Fig. 1.11 SWOT analysis of 4D printing. Reprinted from [31] Copyright © (2019) with permission from Elsevier B.V.

- Integration of 3D printing with other hybrid technologies for 4D printing.
- Develop new advanced properties of materials for 4D printing.
- Improve scale size (e.g., nanoscale) and accuracy of the 4D-printed structure
- Improve resolution and printing speed to reduce cost and energy consumption.

Apart from this, the SWOT analysis of 4D printing is shown in Fig. 1.11.

1.7 Application and Future Prospective

4D printing has opened up the possibility of systems for self-assembly, self-healing, and changes in material properties. Shape-memory materials are active smart materials that can change from a deformed state to their original shape or vice versa under the external stimulus. These materials have attracted researchers due to their wide range of potential applications in various fields like aerospace, biomedical equipment, morphing structures, deployable structures, biomaterials, smart textiles, 4D printing of active origami structures and self-healing composite systems, etc. [32–37]. 4D printing technology will offer benefits to biomedical engineering especially in areas not covered by 3D-printing technologies [38]. Findings have proven to enhance the credibility of technology and it can provide extensive support in the medical field, especially with better smart medical devices of polymer composites, implants, and tools so that medical researchers can explore this with 4D-printing technology to provide improved service to a patient. 4D printing of organic foams provides additional functionalities such as the partial recovery of damages from impacts or volume reduction for long-time storage. For this reason, organic foams have big potential to be used in the aerospace and biomedical field mainly as light actuators, expandable and self-deployable structures, and environmental-sensitive structures. Superelasticity and pseudoplasticity are the most important mechanical properties that exhibit SMAs.

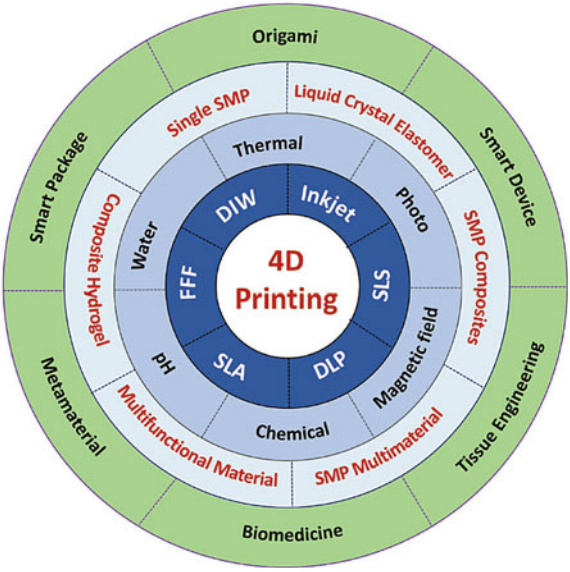

Fig. 1.12 Applications of 4D-printed shape-memory materials. Reproduced with permission from [15]. Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

The above-mentioned properties make these materials unique for structural applications, automobiles, and actuators in micro-electromechanical systems (MEMSs) [39, 40]. A schematic showing the possible application of 4D-printed shape-memory materials is shown in Fig. 1.12.

The endless application possibility of the 4D-printed shape-memory materials will increase further improvement in the properties listed below:

- Improving structural complexity of printed objects.
- Improve printed programmed cycle capability, and product lifespan.
- Research on self-reacting and self-growing controllable function.
- Improvement in stimulus response.
- Synthesis of novel shape-memory materials with advanced properties.

1.8 Book Chapter's Outlook

The invention of new technology and materials has always been a stringent challenge to scientists and engineers to address its applications in various sectors. 4D printing along with shape-memory materials have opened the possibility of systems for self-assembly, self-healing, and changes in material properties. Integration of these smart materials with 4D printing to perform suitable functions needs systematic analysis of technology and associated material. To understand the material's behavior in a better way and utilize them for specific applications, it is crucial to use characterization techniques for materials testing. Chapter 2 covers the detailed description of conventional techniques that are used in the characterization of shape-memory alloys and polymers. In this chapter, characterization techniques like Dilatometry to measure the thermal stress, Differential Scanning Calorimetry (DSC) for describing recoverable strain parameters, Electrical Resistivity probe (ER) to study the dependence of various phases on heat treatment, Nano-indentation tool for characterizing the local mechanical properties and to study the pseudoelastic behavior, Dynamic mechanical analyzed (DMA) for mechanical and thermal study, Thermogravimetric Analysis (TGA) to demonstrate the stability of the material, Thermo-Mechanical Analyzer (TMA), etc., are covered in detail.

Metallic alloys consist of shape-memory alloys (SMAs) that demonstrate twin unique properties, i.e., shape-memory effect and pseudoelasticity. With the rise of new technological developments and modern production techniques, demand for new materials with highly functional, specific, and special properties has increased. Thus, to have a more elaborate and clear understanding of the SMA state of the art, key materials in the field of the SMA need to be covered. In this regard, Chap. 3 discusses the processing and performance analysis of Nitinol (Ni–Ti alloys)-based SMA. Other advantages of Nitinol including high power to weight ratio, large deformation, large actuation force, high damping capacity, and high frequency response lead to a faster response in the micron-size actuators. Nitinol has gained significant interest as a micro-electromechanical system (MEMS)-based micro-actuators which are precision control devices that work based on mechanical forces at the microscale level. In the book, Chap. 3, dependency of the transformation and shape-memory behavior of Nitinol on composition, annealing temperature, sputtering pressure, sputtering power, and growth temperature has been explained. Further difficulties arise during the fabrication process of near-equiatomic Ni–Ti shape-memory alloy with stable ductility due to the strong tendency of oxidation, and cracking that takes place during co-sputtering has also been explained. The shape-memory effect is due to the microstructural changes occurring at the atomic level. Thus, it is difficult and expensive to monitor through in situ experimental studies. In this scenario, molecular dynamics (MD) simulations provide significant insight into atomic-level details of the structural changes during loading or thermal treatment. Chapter 4 provides a comprehensive review of the usage of MD simulations for a better and deeper understanding of the transformation and deformation behavior of SMAs. The related MD simulations studies like austenite–martensite–austenite transformation, micro-mechanisms of deformation, crack propagation, twinning and de-twinning, shear deformation, superelasticity, pseudoplasticity, nano-indentation, etc., are covered in this chapter. The 4D-printing techniques have been implemented to produce SMAs with complex geometries such as U-shaped parts, layer-structured parts, and lattice-based and hollow structures. Chapter 5 discusses the influence of powder size distribution of Fe–Mn/ Alloy 625 for 4D-printing conceivable applications. In Chap. 6, copper (Cu)-based SMA and their possibilities to be prepared by 4D printing are outlined and emphasized. In addition, viewpoints on current challenges and future research directions for the high performance of 4D-printed Cu-based SMA are also covered. Apart from SMA, shape-memory polymers (SMP) and their composites are a new class of smart polymer materials gaining wide attention due to their multifunctional applications. The past decade has seen an impressive development in SMPs and shape-memory polymer composites (SMPCs). These materials undergo significant macroscopic deformation upon the application of an external stimulus and provide a cheap, efficient alternative to well-established shape-memory alloys. As a result, it is essential to have a grasp of various synthesis methods of SMPs and SMPCs. Various techniques employing numerous composite materials for synthesis SMPCs have been reported till date. The SMP- and SMPCs-related important literature are covered in the successive book chapters. Chapter 7 discussed the synthesis techniques of SMPCs using different materials such as reinforcement fillers (such as Si–C fiber, Ti–Ni fiber, chopped fiberglass, woven fiberglass, Kevlar fiber, and carbon fiber), carbon nanotubes, polyurethane nanocomposites, and nanoclay. Chapter 8 covers a detailed description of the techniques used in the preparation of shape-memory polymer composites like in situ polymerization, melt mixing, solution mixing, precipitation, sol–gel process, and electrospinning. Apart from the preparation methods, the conventional SMPCs like thermoplastic polymer, thermoset polymer, their composites with cross-linkers and one-step synthesis of phase-segregated block copolymer composites are reviewed. Understanding the relationships between the composition and structure of an SMP and its SM properties as well as its limitations enables one to better define the development areas for high-performance SMPs. Thus, recent progress in synthesis techniques of SMPCs and their proposed applications is presented in Chap. 9. Literature reports that SMPs structure, properties, and functionality can be affected with the addition of various fillers/particulates of different sizes, scaffolds, and fibers. The effect of nano and hybrid fillers on SMPs properties is illustrated in Chap. 10. The addition of different sizes of particulates impacts the phase separation process and material properties of polymer composites. Thus, it is important to have an understanding of the synergetic effect of the particulates doping that enhances various mechanical, optical, magnetic, functional, and shape recovery properties of SMPs. In Chap. 11**,** emphases are given on the incorporation of particulates such as meso, micro, and nanostructures to polymers, and their behavior is discussed. Further, the fiber and fabric shape materials act as a crucial role in enriching the shape-memory properties. In Chap. 12, we examined the reinforcement of carbon fiber, natural fiber, and conductive fiber in SMPs along with its potential applications. Another class of SMPs is organic shape-memory foams (OSMFs). They have advantages of lightweight, low cost, high shape deformability, high shape recoverability, tailorable switch temperature, and are easy to manufacture. In Chap. 13, literature on OSMFs is reviewed, highlighting synthesis and characterization of different materials, challenges and applications in technical fields, and future expected developments and perspectives. The possibility to manufacture OSMFs by 4D-could open new scenarios for in-space manufacturing and colonization missions. Thus, some conceptual evaluations on 3D- and 4D-printing feasibility are reported. Moreover, a combination of stimuli-responsive metal alloys and polymers significantly change their properties like shape, mechanical properties, optical properties, and electrical properties upon a small variation of environmental conditions. Chap. 14 gives an extensive review of the recent progress of combined shape-memory polymers and metal alloys composites with design feasibility and fabrication by various methods. The outcome of research, the challenges in this field, and its prospects are highlighted and concluded in this chapter. All these chapters together give a broad and systematic outlook of the SMAs and SPMs, related to their synthesis, characterization, property enhancement, and recent development. These details are very valuable to combine these materials with newly emerging 4D-printing technology. 4D printing of SMAs and SMPs is still in its initial triggering stage. Extensive research is being conducted to explore its application in aerospace, biomedical equipment, morphing structures, smart textiles, self-healing composite systems, etc. To give an overview of the SMP 4D-printing application, one such study is reported in Chap. 15. This study demonstrated the 4D material which can be easily fabricated with different loadings of thiophene-based polymer with localized smart actuation behavior. It encompasses the mechanisms, sensor response, repeatability, and also potential research involved in the development of thiophene polymer in 4D printing and shape-memory polymer thin-film transistors (SMPTFTs). Further Chap. 16 covers the applications of 4D printing in various fields like aerospace, biomedical devices, morphing structures, deployable structures, biomaterials, smart textiles, 4D printing of active origami structures, self-healing composite systems, soft robotics, wearable sensors, transportation, etc. 4D-printing technology is a new branch of research that originated from 3D printing (which involves the printing of complex geometries with smart materials). The development in synthetic smart materials, deformation mechanisms, novel printers, and mathematical modeling has enhanced the research area of 4D printing. In Chap. 17, the progress in additive manufacturing and 4D printing is discussed with the help of bibliometric analysis. Smart materials developed with 4D printing are explained with their morphing mechanisms for Industry 4.0. The chapter also includes a discussion about emerging industries in 4D printing, challenges, and future scope in terms of manufacturing and business perspective.

1.9 Conclusion

The advancement in the smart material and their incorporation in 4D-printing technology have triggered additive manufacturing technology to the next stage, and arguably a valuable technology in the current era. Compared to conventional printing technology, it has transformed the additive manufacturing technology by reducing manual intervention and manufacturing time. 4D-printing technologies are emerging and require a considerable amount of research to convey and deliver up to their actual potential. Additionally, the incorporation of shape-memory materials in 4D printing can be beneficial in numerous ways (reduction in labor, cost, and time).

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References

1. Gu GX, Libonati F, Wettermark SD, Buehler MJ |(2017) Printing nature: unraveling the role of nacre's mineral bridges. J Mech Behav Biomed Mater 76:135–144. https://doi.org/10.1016/j.jmbbm.2017.05.007
2. Firth J, Gaisford S, Basit AW (2018) A new dimension: 4D printing opportunities in pharmaceutics. In: 3D printing of pharmaceuticals, pp 153–162. https://doi.org/10.1007/978-3-319-90755-0_8
3. Gul JZ, Sajid M, Rehman MM, Siddiqui GU, Shah I, Kim KH, Lee JW, Choi KH (2018) 3D printing for soft robotics—a review. Sci Technol Adv Mater 19:243–262. https://doi.org/10.1080/14686996.2018.1431862
4. Gu GX, Takaffoli M, Hsieh AJ, Buehler MJ (2016) Biomimetic additive manufactured polymer composites for improved impact resistance. Extreme Mech Lett 9:317–323. https://doi.org/10.1016/j.eml.2016.09.006
5. Sullivan TN, Pissarenko A, Herrera SA, Kisailus D, Lubarda VA, Meyers MA (2016) A lightweight, biological structure with tailored stiffness: The feather vane. Acta Biomater 41:27–39. https://doi.org/10.1016/j.actbio.2016.05.022
6. Ge Q, Qi HJ, Dunn ML (2013) Active materials by four-dimension printing. Appl Phys Lett 103:131901. https://doi.org/10.1063/1.4819837
7. Quanjin M, Rejab MR, Idris MS, Kumar NM, Abdullah MH, Reddy GR (2020) Recent 3D and 4D intelligent printing technologies: A comparative review and future perspective. Procedia Comput Sci 167:1210–1219. https://doi.org/10.1016/j.procs.2020.03.434
8. Tibbits S (2014) 4D printing: multi–material shape change. Archit Des 84:116–121. https://doi.org/10.1002/ad.1710
9. Pei E (2014) 4D Printing: dawn of an emerging technology cycle. AssemAutom. https://doi.org/10.1108/AA-07-2014-062
10. Yang H, Leow WR, Wang T, Wang J, Yu J, He K, Qi D, Wan C, Chen X (2017) 3D printed photoresponsive devices based on shape-memory composites. Adv Mater 29:1701627
11. Raviv D, Zhao W, McKnelly C, Papadopoulou A, Kadambi A, Shi B, Hirsch S, Dikovsky D, Zyracki M, Olguin C, Raskar (2018) Active printed materials for complex self-evolving deformations. Sci Rep 4:1–8. https://doi.org/10.1038/srep07422
12. Nadgorny M, Xiao Z, Chen C, Connal LA (2016) Three-dimensional printing of pH-responsive and functional polymers on an affordable desktop printer. ACS Appl Mater Interfaces 8:28946–28954. https://doi.org/10.1021/acsami.6b07388
13. Gartner Gartner Hype Cycle. https://www.gartner.com/en/newsroom/press-releases/2018-08-20-gartner-identifies-five-emerging-technology-trends-that-will-blur-the-lines-between-human-and-machine
14. Ahmed K, Shiblee MN, Khosla A, Nagahara L, Thundat T, Furukawa H (2020) Recent progresses in 4D printing of gel materials. J Electrochem Soc 167:037563. https://doi.org/10.1149/1945-7111/ab6e60
15. Kuang X, Roach DJ, Wu J, Hamel CM, Ding Z, Wang T, Dunn ML, Qi HJ (2019) Advances in 4D printing: materials and applications. Adv Funct Mater 29:1805290. https://doi.org/10.1002/adfm.201805290
16. Low ZX, Chua YT, Ray BM, Mattia D, Metcalfe IS, Patterson DA (2017) Perspective on 3D printing of separation membranes and comparison to related unconventional fabrication techniques. J Membr Sci 523:596–613. https://doi.org/10.1016/j.memsci.2016.10.006
17. Zhang Z, Demir KG, Gu GX (2019) Developments in 4D-printing: a review on current smart materials, technologies, and applications. Int J Smart Nano Mater 10:205–224
18. Momeni F, Mehdi Hassani M, NS, Liu X, Ni J (2017) A review of 4D printing. Mater Des 122:42–79. https://doi.org/10.1016/j.matdes.2017.02.068
19. Lee AY, An J, Chua CK (2017) Two-way 4D printing: a review on the reversibility of 3D-printed shape-memory materials. Engineering 3:663–674. https://doi.org/10.1016/J.ENG.2017.05.014

20. Nam S, Pei E (2019) A taxonomy of shape-changing behavior for 4D printed parts using shape-memory polymers. Prog Addit Manuf 4:167–184. https://doi.org/10.1007/s40964-019-00079-5
21. Jani JM, Leary M, Subic A, Gibson MA (2014) A review of shape-memory alloy research, applications and opportunities. Mater Des (1980–2015) 56:1078–1113. https://doi.org/10.1016/j.matdes.2013.11.084
22. Huang WM, Zhao Y, Wang CC et al (2012) Thermo/chemo-responsive shape-memory effect in polymers: a sketch of working mechanisms, fundamentals and optimization. J Polym Res 19:9952. https://doi.org/10.1007/s10965-012-9952-z
23. Lendlein A, Jiang H, Jünger O, Langer R (2005) Light-induced shape-memory polymers. Nature 434:879–882. https://doi.org/10.1038/nature03496
24. Caputo MP, Berkowitz AE, Armstrong A, Müllner P, Solomon CV (2018) 4D printing of net shape parts made from Ni-Mn-Ga magnetic shape-memory alloys. Addit Manuf 21:579–588. https://doi.org/10.1016/j.addma.2018.03.028
25. Zhao Z, Wu J, Mu X, Chen H, Qi HJ, Fang D (2017) Desolvation induced origami of photocurable polymers by digit light processing. Macromol Rapid Commun 38:1600625. https://doi.org/10.1002/marc.201600625
26. Yuan C, Roach DJ, Dunn CK, Mu Q, Kuang X, Yakacki CM, Wang TJ, Yu K, Qi HJ (2017) 3D printed reversible shape changing soft actuators assisted by liquid crystal elastomers. Soft Matter 13:5558–5568. https://doi.org/10.1039/C7SM00759K
27. Ge Q, Sakhaei AH, Lee H, Dunn CK, Fang NX, Dunn ML (2016) Multimaterial 4D printing with tailorable shape-memory polymers. Sci Rep 6:1–11. https://doi.org/10.1038/srep31110
28. Gladman AS, Matsumoto EA, Nuzzo RG, Mahadevan L, Lewis JA (2016) Biomimetic 4D printing. Nat Mater 15:413–418. https://doi.org/10.1038/nmat4544
29. Mao Y, Yu K, Isakov MS, Wu J, Dunn ML, Qi HJ (2015) Sequential self-folding structures by 3D printed digital shape-memory polymers. Sci Rep 5:1–12. https://doi.org/10.1038/srep13616
30. Deshmukh K, Houkan MT, AlMaadeed MA, Sadasivuni KK (2020) Introduction to 3D and 4D printing technology: State of the art and recent trends. 3D 4D Print Polym Nanocomposite Mater 1:1–24. https://doi.org/10.1016/B978-0-12-816805-9.00001-6
31. Rastogi P, Kandasubramanian B (2019) Breakthrough in the printing tactics for stimuli-responsive materials: 4D printing. Chem Eng J 366:264–304. https://doi.org/10.1016/j.cej.2019.02.085
32. Rayate A, Jain PK (2018) A review on 4D printing material composites and their applications. Mater Today: Proc 5:20474–20484. https://doi.org/10.1016/j.matpr.2018.06.424
33. Khoo ZX, Teoh JE, Liu Y, Chua CK, Yang S, An J, Leong KF, Yeong WY (2015) 3D printing of smart materials: a review on recent progresses in 4D printing. Virtual Phys Prototy 10:103–122. https://doi.org/10.1080/17452759.2015.1097054
34. Gao B, Yang Q, Zhao X, Jin G, Ma Y, Xu F (2016) 4D bioprinting for biomedical applications. Trends Biotechnol 34:746–756. https://doi.org/10.1016/j.tibtech.2016.03.004
35. Zarek M, Layani M, Eliazar S, Mansour N, Cooperstein I, Shukrun E, Szlar A, Cohn D, Magdassi S (2016) 4D printing shape-memory polymers for dynamic jewellery and fashionwear. Virtual Phys Prototy 11:263–270. https://doi.org/10.1080/17452759.2016.1244085
36. Zhang W, Zhang F, Lan X, Leng J, Wu AS, Bryson TM, Cotton C, Gu B, Sun B, Chou TW (2018) Shape-memory behavior and recovery force of 4D printed textile functional composites. Compos Sci Technol 160:224–230. https://doi.org/10.1016/j.compscitech.2018.03.037
37. Jian B, Demoly F, Zhang Y, Gomes S (2019) An origami-based design approach to self-reconfigurable structures using 4D printing technology. Procedia CIRP 84:159–164. https://doi.org/10.1016/j.procir.2019.04.184

38. Javaid M, Haleem A (2019) 4D printing applications in medical field: a brief review. Clin Epidemiol Glob Health 7:317–321. https://doi.org/10.1016/j.cegh.2018.09.007
39. Rafiee M, Farahani RD, Therriault D (2020) Multi–material 3D and 4D printing: a survey. Adv Sci 7:1902307. https://doi.org/10.1002/advs.201902307
40. Chua CK, Yeong WY, An J (2017) 3D printing and bioprinting in MEMS technology. Micromachines 8:229. https://doi.org/10.3390/mi8070229