

## 18 4D Printing of Nanostructure Modified Shape Memory Polymer Composites

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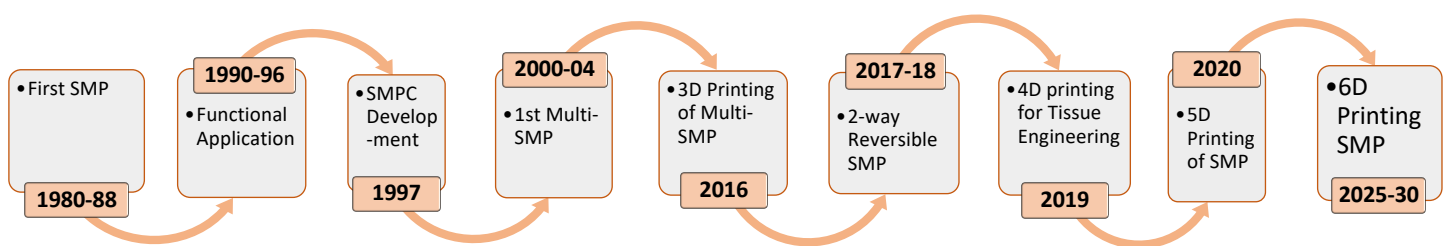
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### **Abstract**

Four-dimensional (4D) printing and nanostructure have introduced the possibility of having systems for self-assembly, self-healing, and material properties changes. Layered printing allows creating compound and complex geometry previously in the general production path. The present chapter reviews and presents several recent and relevant studies on current additive manufacturing (AM) or 3D and 4D printings of nano and micro-structured polymer composites. These smart materials respond to external stimuli. Perspective on their possible use in all areas, including nanostructures of the implant, is considered. There are promising applications for 4D printing in the medical field. The need is to identify the research state and explore where this new set of technologies can be effectively implemented. Hence, this chapter outlines more on the practical application of AM/3D and 4D printings of nanostructured polymer composites in the medical field. This study further elucidates 4D printing as the latest technology that creates innovation and solves complex medical problems. It briefly describes 4D printing, details its difference from 3D Printing, and identifies five steps required to develop a medical model, using this technology and its possible medical applications implementation. Extensive studies carried out on 4D printing technology, and their detailed discussion is reported in this compendious review. But, there are decidedly fewer publications available in the medical field that clarify this quest. Finally, nine critical 4D Printing applications in the medical field, the main limitation of its requirement of significant investment and support for transformation, are stated in this informative report. The emerging applications of 4D printing and its advantages to biomedical engineering, especially in areas not covered by 3D printing technologies, are explained. Summarily, findings have proven that enhancing this technology's credibility provides extensive support in biomedical engineering. Especially with better smart medical devices of polymer composites, implants, tools, and how

innovation and new materials for the production of additives. Future trends suggest that there will be significant investments in the 3D printing market in the next ten years [1-3]. Recharge production will impact all industrial sectors, including aerospace and construction, medical and military, among others. 3D Printing provides significant design flexibility, considerable material savings, customization, and individuality. Four-dimensional (4D) Printing allows the use of *smart material* that can be pre-programmed in response to external stimuli. This is called '4D representation', and the fourth dimension refers to time. The structural change itself is evident in all sectors of the medical, defense, and aerospace industries, including in space with integrated solar panels - hinges and composite antennas.

The use of shape-memory materials in the production of additives is widely useful [3-5]. Many corrections illustrate the variety of shape memory polymers (SMP) and compounds that have shape memory polymers or only shape memory polymer composite/compound (SMPC). A specific review of SMP and SMPC in the aviation sector, such as antenna hinges, has been conducted. This reflects the transformation in the nanostructure of the moon's habitat and the reticular band. One after-one passes around, making the thermostat very popular with more strength and durability for the environmental area [5-7]. Materials that have shape memory or simply shape-memory materials (SMM) can regain their shapes after deformation due to the stimulation used. This is called shape memory effect (SME), unique resistance in shape memory alloy (SMA) and viscoelasticity. Informing memory polymers, shape memory hybrids (SMH) are observed, and other form compounds are also emerging. With the development of 4D Printing and AM's rapid growth, SMMs have significant potential in many industries. SMP has the advantages of being light and is more likely to recover from stress than SMA. They can also be enabled to work with many stimuli at the same time [7-9]. In addition to many activation incentives, SMP can also be modified to be biologically compatible and biodegradable according to the application's requirements. For example, SMP thermoplastic polyurethane is an open-cell foam designed for therapeutic areas and applications [6-8]. The emergence of AM techniques in the 1980s allowed scientists to explore and develop different types of SMP. SMP has since garnered intense interest and ongoing efforts from scientists since then as schematically illustrated in Fig. 18.1 [8-10].



**Fig. 18.1** Progress and advancement of AM techniques

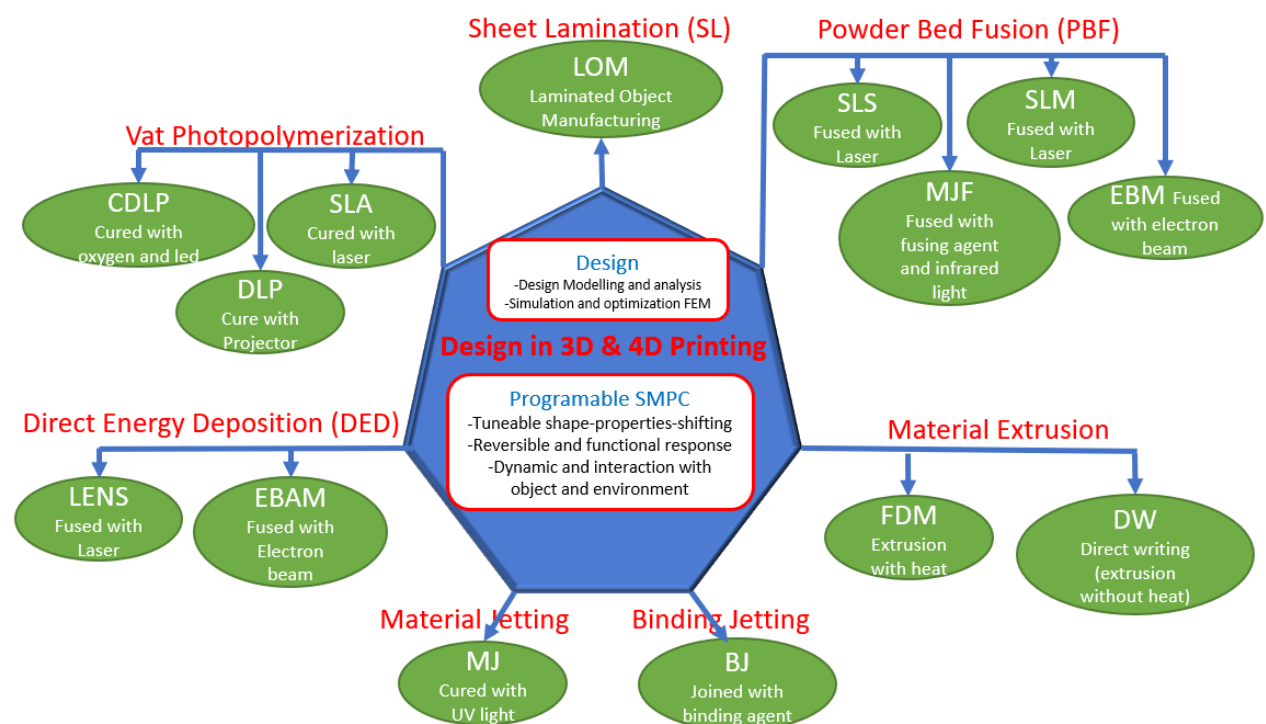
### 18.1.1 Revolution of 4D Printing

It is impressive how human beings continually question the challenges achieved. Without a doubt, human deoxyribonucleic acid (DNA) has a curious gene, which advances without justification. In this view, some concepts about 4D printing are subsequently shared. The industry could at first think that 3D printing was the end of the road. 3D printers were sent into space, thus reducing the weight of all the parts that would probably never be used. With these machines, precisely what is needed can be built, making the vehicle's payload more efficient

[10-12]. But, coming from what it is the dream factory, thought, why not be even more efficient? 3D prints need assembly, then without the intervention of a third party, they help, but they are not final. A group of researchers commenting on the video have added the fourth dimension: temporal. This implies that they can print a nanostructure and provide it with the necessary functions such that once printed, they adopt the shape and properties for which they have been programmed. Depending on the material, it uses humidity, light, or ambient temperature to evolve. Thus far, this is the theory and research. Now, the business and industry have begun. As is evident, the possibilities are endless. Some ideas focus on clothing that fits the body, seats that take the driver's exact shape in a vehicle, or smart packaging that protects the product, even becoming part of the work upon receipt [12-14]. The tool already exists, and the materials required with it. It is about making materials intelligent until they could now perform actions by themselves. 3D Printing has technically evolved. Researchers are trying to keep up and develop their minds searching for applications and businesses that use this technology. How many sectors are linked to electronic commerce, the volume of shipments/transportation, consumer items? Companies like Autodesk are already on the path of creating business [13-15].

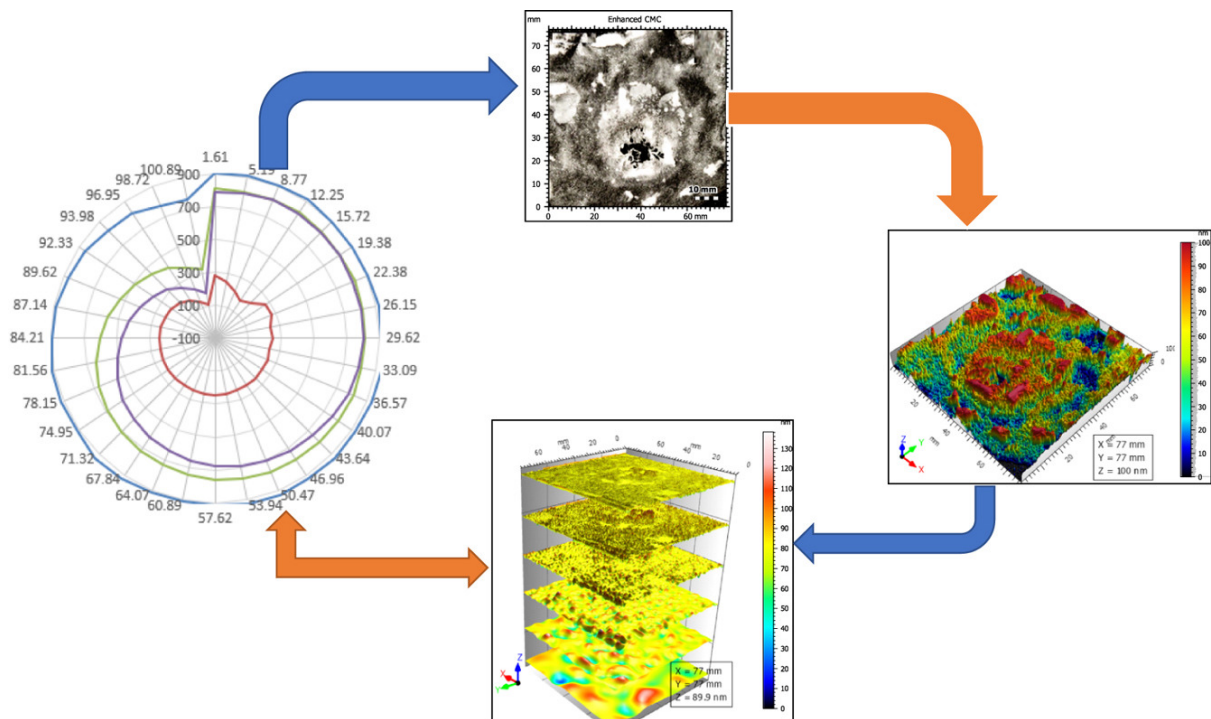
In 4D printing, digital light from a commercial printer is used to irradiate Sandwiched between two slides separated by a spacer, the printable solution. With these set-ups, it was reported that light could attenuate along the gradient or the difference in thickness, thus allowing to produce different curing conditions. The selection of planar light patterns permitted Fast access to complex permanent forms that can be turned into temporary forms and recovered after reheating. This was since certain SMP hydrogels could undergo specific structural arrangements according to the degree of swelling when exposed to certain stimuli [14-16].

Since 3D printing hinges on using different materials with glass transition temperatures ( $T_g$ ), adaptive designs capable of self-folding were created. They responded rapidly to a heat stimulus and controlled shape-changing in succession (Fig. 18.2). The image of a 4D printed self-folding box that combined different materials at different hinges. The schematic diagram for self-locking during heating with a separate external environment [16-18] is shown in Fig. 18.2.



**Fig. 18.2** Common fabrication and Classification of 3D and 4D Printing with composite materials and illustration of the SMP composite process: Digital fabrication of complex permanent shapes and proof of their shape memory behavior

Moreover, the 4D-printed self-construction nanostructure of a self-folding cubic container printed from SMPs has been investigated [18-20]. It was adapted from a self-rolling tube container printed from smart polymers and actuated by acetone. The complex curved surface deformed from a balanced state was published, using moisture-responsive polymers (hydrogels) with a gradient distribution, adapted from and sequentially folded stipe that can lock itself, as explained by [20-22]. The joints were printed with different combinations of SMPs, which is further illustrated by [23-25]. The joints of the self-nested boxes were printed with SMPs in different colors. The cross-folding test specimens with and without a stress release hole, with the conceptual design of material with tunable lattice nanostructure. This permit bandgap control and multifunctional material with tunable Poisson's ratio was explained by [25-27]. The simulation related to the gradient distribution of material nanostructure red indicates the rigid material, and purple shows the active material. The results of its immersion in water over time were explained by Bankole et al. [28], as depicted in Fig. 18.3.



**Fig. 18.3** An illustration of a multi-material AM system of pulp-CMC composite films, illustrating the improvements in dispersion as a result of optimized mixing strategies ultra-sonication. An original scale value of SEM ultra-sonication of surface view of KL transform of the threshold has  $-69.8$  nm;  $39.1$  nm of surface luminance Gaussian filter. The waviness filter of Daubechies and Motifs analysis of KL transformation have roughness wavelet filter of Daubechies with extract filter profile across the surface roughness

The 4D-printed medical devices for photolithographically fabricated polymeric containers, intended for drug delivery, with different patterned porous faces outlined in red of scale bar is  $250 \mu\text{m}$  according to [28-30]. Thermo-

responsive shape change demonstration is demonstrated, as the gripper is gripping a clump of cells, and 4D-printed stent, using 4D-printed robotic devices. The Soft McKibben type actuator is made from porous silicone elastomer with the pores filled with ethanol. Demonstration of 4D-printed thermo-responsive liquid crystal elastomer used for adaptive optics and 4D-printed polylactic acid braided tube preform has demonstrated a thermo-responsive shape memory behavior. Also, as a gripper with 4D-printed SMP gripper and 3D-printed hydraulic robot using liquid support for bellow actuators [31-33].

### ***18.1.2 Polymers with Shape Memory and 3D Printing***

Shape memory polymers can be transformed into traditional forms from distorted shapes when stimulated by temperature, humidity, or light using radiation. Therefore, SMP can induce magnetic fields combining nanoparticles with thermoplastics [33-35]. SMPs are often used, due to their biodegradability and biological compatibility, primarily if they are derived from renewable energy sources. They are produced at a low cost. SMPs have found complete attraction and great relevance in biomedical applications [34-36], small electrical and mechanical systems, and manual nanostructure. The possible disadvantages of SMPs are lower tensile strength and stiffness when compared with SMA [36-38]. Lots of memory forms are developed to improve electrical conductivity in response to electrical and mechanical properties.

Heat sensitive SMP is characterized by cross-linking, chemical and physical changes related to the transition temperature, which may be  $T_g$  for SMP after each phase change climate. The shape can be programmed to activate the SMP. The original form deforms under a voltage higher than  $T_g$ . If the resulting stress persists when the polymer cools below the SMP's  $T_g$ , it remains deformed until the heat exceeds  $T_g$ . Once again, [39-41] show that SMPs have a clear advantage of low density and high elastic deformation, although the slight recovery effort limits the size of the light-sensitive SMP components. Heat is a catalyst; therefore, the correct wavelength is used to prevent other SMP materials from being exposed to the temperature required for SMP activation. The direction and intensity of the polarization of the light can be controlled without heating. Form memory is influenced by chemical composition, processing method and material design [42-44]. The control of 3D printing in each layer allows the production of complex geometry with various materials, creating multiple parts. In general, thermosetting materials have more extensive use of heat and have better mechanical properties than thermoplastics. The SMP has more advantages than SMA, such as high-pressure recovery, low density, and price, secure processing, biological compatibility, and biodegradability. Shape memory alloys for metal parts are original materials that can directly convert thermal energy into mechanical work.

### **18.2 4D Printing of Nanostructured Polymer**

The latest breakthrough in inkjet 3D inkjet printing is Stratasys, which uses curable ultraviolet (UV) resins to create multi-layered material as a new platform for 4-dimensional stimulus sensitive substrates. At this moment, the following discussion focused on the latest development in 3D printing and current 3D printers' capabilities, looking to the future for possible use. Recently, 3D4MD, a printing company named Medical 3D has completed medical instruments, surgical splints for fingers, and other dental tools at the International Space Station [44-46]. It can perform an accurate laser scan on the floor. 3D files are sent directly to the International Space Station for Printing. 4D Printing is now a viable option, and transformable web printing [46-48] explained its future

possibility in space. Direct production by strategy created the first 3D-printed parts for use outside of satellites. Six satellites were launched in 2018 as a part of COSMIC-2 project of the National Aeronautics and Space Administration (NASA). The antenna array is an integral part of the satellite, which was previously made of astroquartz and a high-strength engineering thermoplastic, using fused deposition modeling (FDM). Light model to protect the polymer from oxygen, atoms and UV rays has been experimented [48-50]. The stars' color is used to create a glassy layer that can reflect a high percentage of sunlight. Significant advances in computer-based design, AM, and materials science have opened up the possibility of self-assembly systems, self-healing properties and shape changes.

A block from blocks that are not connected can be created or use a programmable nanostructure to print the unique transformation nanostructure to build a large nanostructure. This can be changed to the desired construction with multiple hinges or electronic components. To include examples in an environment would be tensegrity nanostructures that could be reconfigured on satellites. When they reached orbit, Campbell and his team combined nanotechnology with 4D printing, creating materials that altered electromagnetic waves' properties. This can be very useful for eventual detection, blood pressure testing or insulin levels, or in space. The satellite's surface can alter the absorption of radiation of the material when necessary [50-52]. Like two-dimensional (2D) pixels, a voxel is a graphical data unit that points in a 3D space. Kurman describes it as a necessary component, similar to a biological life [52-54]. The voxel can be programmed to be a sensor, conductor, or insulation, as required. For use, if voxels are processed together to create a system, it can be reversed - disassembled and reused to make something else so that survival and production in remote locations can be managed. In-depth research is being conducted on deformed materials, medical devices, self-repair surfaces, and self-assembled nanostructures in all environments.

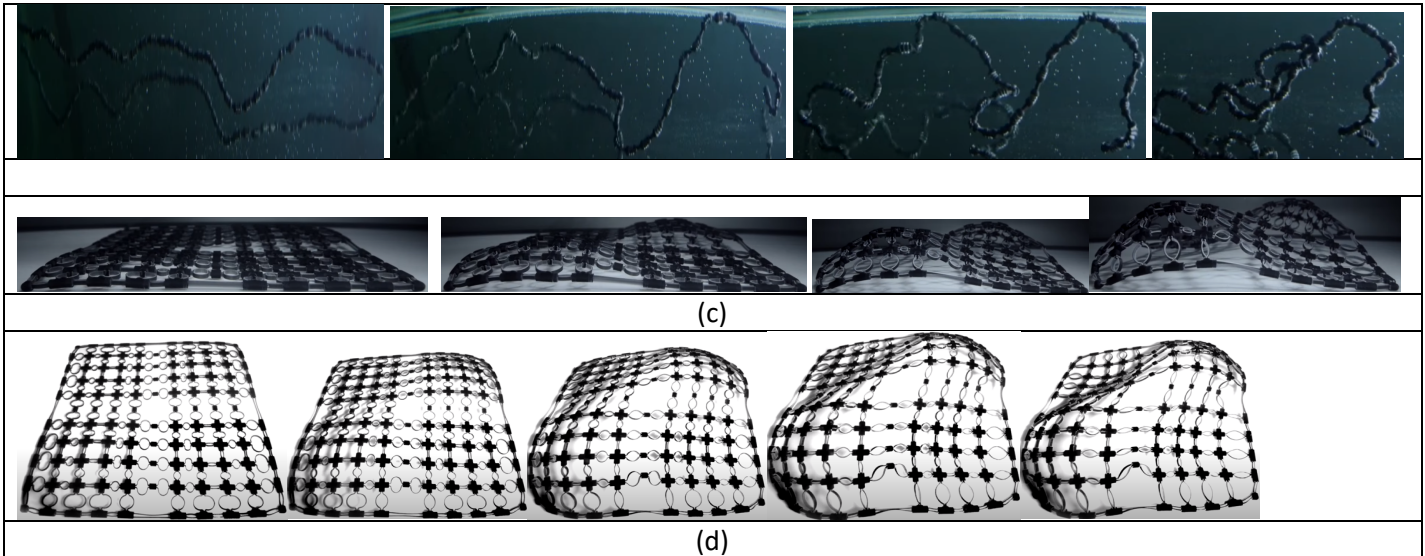
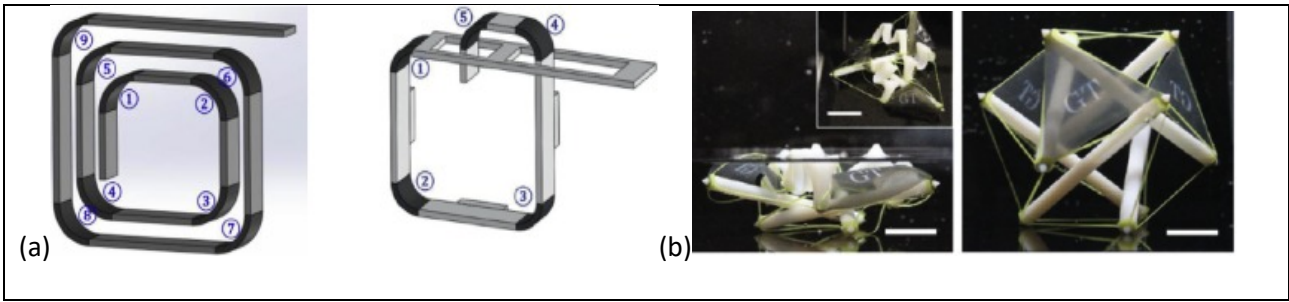
**Table 18.1** Some 4D-printed materials and their potential applications

3D Printer	Material	Stimulus	4D application	Reference
Stratasys Connex 500 multi-material 3D printer, UV photopolymerizing.	Hydrophilic acrylate monomers, UV curable. (Vinyl caprolactam of 50%, polyethylene of 30%, epoxy diacrylate oligomer of 18%, iragcure 819 of 1.9% and wetting agent of 0.1%).	Water	Multiple hinges, folds, and curls from a flat sheet.	[20-24]
Stratasys Objet Connex 260, UV Photopolymerizing.	Tangoblack: A rubbery material at room temperature - polymerized with a spot of ink containing urethane acrylate oligomer, Exo-1,7,7-trimethylbicyclo [2.2.1] hept-2-yl acrylate, methacrylate oligomer, polyurethane resin and a photoinitiator. Verowhite: A rigid plastic at room temperature - polymerized with a spot of ink containing isobornyl acrylate, acrylic monomer, urethane acrylate, epoxy acrylate, acrylic monomer, acrylic oligomer and a photoinitiator.	Temperature	Hinges, box, plane from a flat sheet, among others.	[25-29]
Prusa i3 Rework, maximum printing area of 19 × 19 cm <sup>2</sup> , nozzle temperature of -210 oC, heating plate of 70 oC and pinting speed of 18 mm/s.	Supplied by ColourFabb wood fill fine - a mix of poly (lactic acid) and poly(hydroxy alkanoates) reinforced with recycled wood fibers.	Water	Actuators, Hinges.	[30-35]
Makerbot Replicator 2× 1.75 mm inlet diameter, nozzle temperature of - 220 oC, platform temperature of	Poly (2-vinyl pyridine) (P2VP).	pH	Flow regulating devices, catalytic supports.	[36-40]

90 °C and speed of 100 mm/s.				
Freeform Pico 2 SLA Digital Light Processing Printer. The wavelength of the UV-LED light source was 405 nm.	Semicrystalline methacrylate polycaprolactone (PCL).	Temperature	Medical devices.	[41-44]
Microdepositing robot I&J2200-4 I&J Fisnar, a dispensing apparatus HP-7X EFD, two 365 nm UV LEDs.	Semicrystalline thermoplastic poly lactic acid (PLA) pellets 4032D from Natureworks LLC, Fe3O4 nanoparticles of 30 nm average diameter.	The magnetic field, temperature.	Medical devices.	[45-48]
Air-powered fluid dispenser Ultimius V EFD, printed using x-y-z 3 axis positioning stage ABL 9000 Aerotech.	Varying ratios of Epoxidized soybean oil (ESBO), with Bisphenol F diglycidyl ether. Incorporated carbon nanofibers.	Temperature	Medical device, conductive hinges.	[49-52]
Polyjet Objet 500 Connex Jets microscopic layers of liquid photopolymer directly onto a build platform at 70 °C, cured with UV light.	Tangoblack plus is a soft and flexible material obtained in the polymerization of an acrylic oligomer, 2-Propenoic acid, 1,7,7-trimethylbicyclo [2.2.1] hept-2-yl ester, exo-, photoinitiator, xylenes (o-, m-, p- isomers), benzyl alcohol, acrylic acid ester, propylene glycol monomethyl ether acetate, isoamyl acetate, n-Butyl acetate, carbon black, ethylbenzene, citral, dipentene, 2,6-Di-tert-butyl-p-cresol, geraniol. Verowhite is a stiff material obtained in the polymerization of an acrylic monomer, 2-Propenoic acid, 1,7,7-trimethylbicyclo [2.2.1] hept-2-yl ester, exo-, acrylic oligomer, photoinitiator, titanium dioxide, acrylic acid ester, propylene glycol monomethyl ether acetate, phosphoric acid.	Temperature	Self-expanding/shrinking nanostructures	[53-56]
Materialize	Polyvinyl siloxane and polyurethane.	Pressure	Mechanical Metamaterials.	[57-62]
Object 260 Connex and a Fused Filament Fabrication printer HYREL.	Verowhite Plus, and digital materials DM9895 and DM8530. For the FFF printer, a rubbery material Filaflex was used; a thermoplastic elastomer-based polyurethane.	Temperature	Tensegrity deployable nanostructures.	[63-69]

Furthermore, the SMP is modeled using CAD for each hinge with different T<sub>g</sub>. The radius of each hinge is 5 mm, the thickness of the cable is 0.8mm and the depth is 6 mm. The edge is 5 mm, as shown in Fig. 18.4(a), among others. Polymer 1 has a minimum T<sub>g</sub> of 32 °C, assigned in hinges 1 and 2 [56-59]. Polymer 7 has a maximum value of T<sub>g</sub> 65 °C. For hinges 8 and 9, hinges 3–7 are determined with 2-6 polymers, increased to T<sub>g</sub>. After printing, it is heated and then transformed into a straight form in hot water at 100 °C. The sample is immediately transferred to an environment with a temperature of 10°C, allowing all hinges to be transferred to a state of Form A of the glass, which is temporary and stored for approximately 10 minutes. Form recovery occurs when the SMP is at a temperature higher than T<sub>g</sub>, as shown in Fig. 18.4 [59-61].





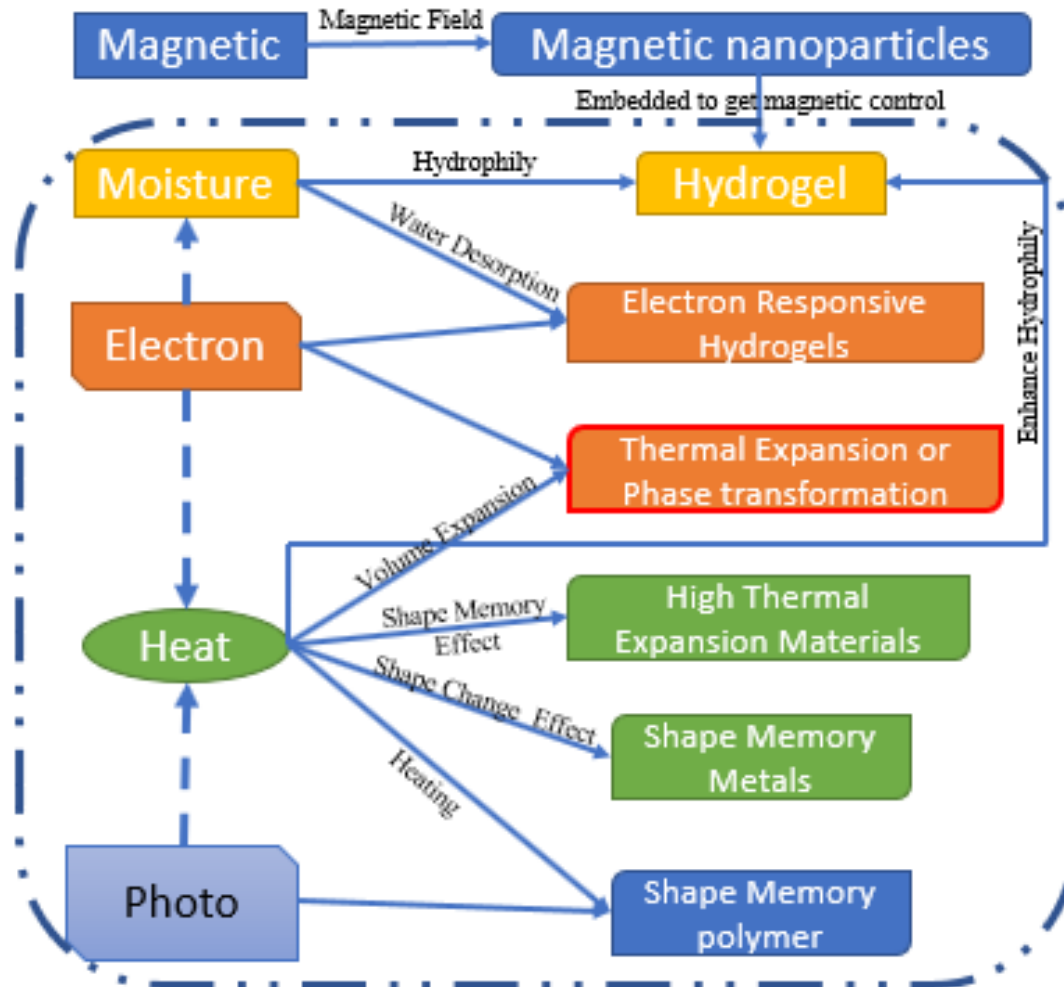
**Fig 18.4** Deployment of (a) SMP component, each active hinge is formed from a different polymer, (b) 6-strut spherical tensegrity, (c) snapshots of the free shape recovery process of a Smart Composite Polymers (d) initial shape of the 3D printed composite sheet of final flower 3D printed shape after immersion in water, mechanical treatment, and complex lightweight nanostructure after removal of the paper [61-63]

A researcher uses internal tension when using PLA material in a 3D form. The flat strip produced exhibits a 3D shape after cooling. After heating, it returns to the initial shape so that the previous formation results from heat deformation through heat [64-66], as previously illustrated in Fig. 18.4. Current developments in 3D printing allow the determination of a wide variety of materials in microscopic resolution. Compounds that specify an architecture, fiber, size, shape, and direct direction have been printed to control the compound's mechanical, thermal and mechanical behaviors. Within the 3D-printed nanostructure, the fiberglass shows shape memory effects [66-70]. The Objet Connex 260 Stratasys 3D printer is used. The polymer ink is put at 70 °C in a thin film and then the UV cures the film layer in layers. The resolution is 32 to 64 microns. They are elastomers, and fibers are polymers with mechanical and thermal behaviors that have shape memory.

The polymeric elastomers used have  $T_g$  of -5 °C and act as a coarse solid between 10–100 °C and 0.7 MPa at 15 °C. The glass fibers have moduli between 3.3 and 13.3 MPa, depending on the composite layer's temperature being printed with a thickness of 2 mm with a single row fiber with a volume of 0.28. The shape memory effect is obtained by changing the sample's shape at 60°C, above the  $T_g$  of the digital material's fibers. This maintains the tension used in While cold at 15°C, 2°C/min at 15°C, the samples are stored for 5 to 10 minutes. The stress is recovered by heating the model from 2 °C/min to 60 °C [70-72]. The difference in orientation of the fiber results

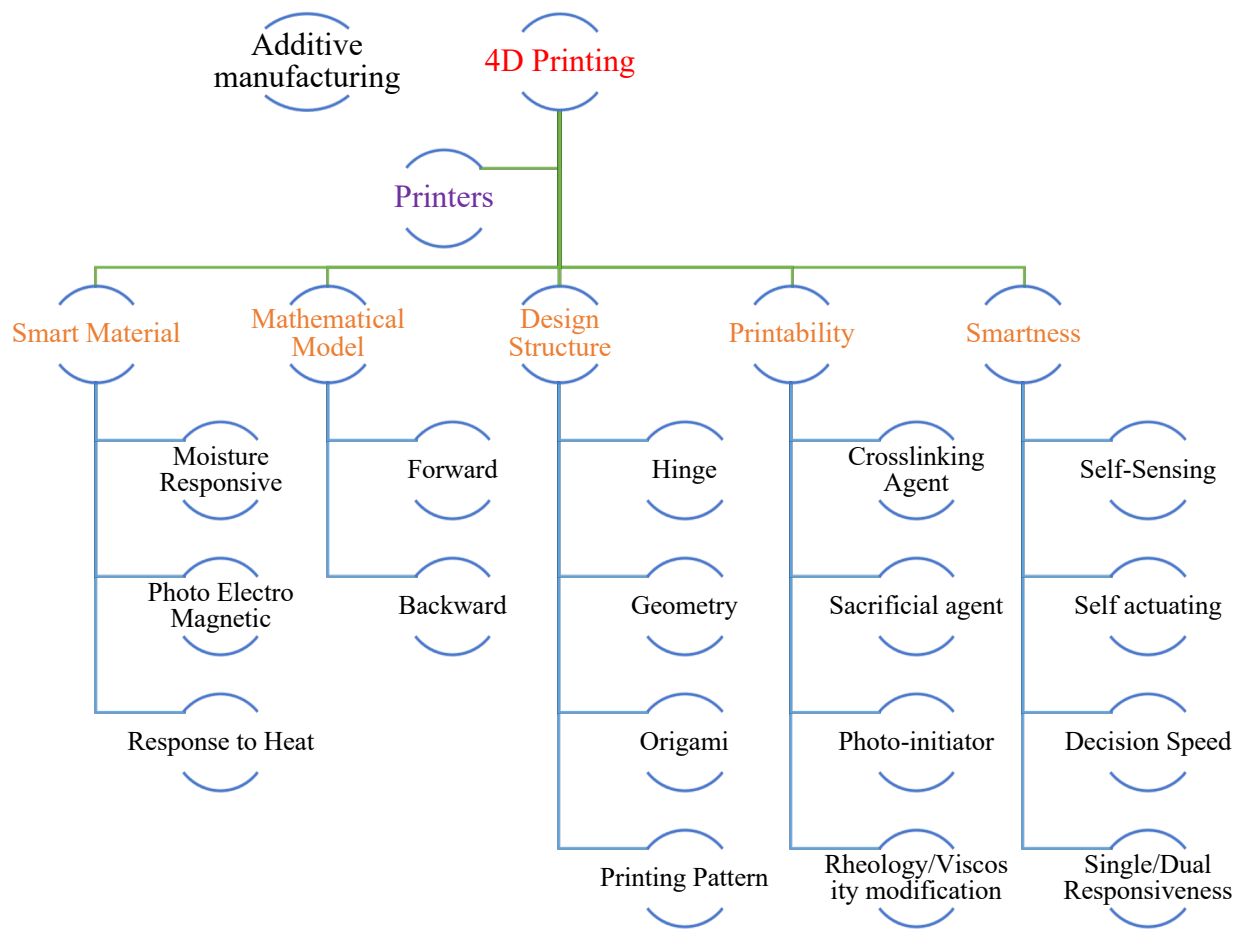


in behavior different from the shape of the memory. With various fiber orientations, traditional shapes can take many forms. 4D printing materials have been classified according to their environmental and temporal stimuli, as shown in Fig. 18.5. Various stimuli are discussed, including temperature, moisture, electricity, light, current, and magnetic fields.



**Fig. 18.5** Classes of smart materials that can respond to different types of stimuli, including heat, moisture, light, electricity and magnetic fields [72-74]

Moving forward, the various research topics in 4D printing fall into the categories of development of equipment, deformation mechanisms and mathematical modeling (Fig. 18.6). Equipment production includes the synthesis of new materials characterised by various types of responses [74-76] and advancing printing technology, both of which are the foundations for 4D printing. The degree of deformation of the state depends on the compound's shape and properties, the mechanical load, and heat history. The printing of fibers at various angles in the two layers leads to changes in curvature demonstrated [77-79]. After activation, the strip with the threads in the coil of 30° on the propeller is successfully printed. The fibers *bd* have alternate areas of the segment. One with volume fraction ( $v_f$ ) of 0.25 and another without  $v_f$  (of 0.00), the fibers are laid. They are in the top layer with a center in the bottom layer of the strip. The two layers of a compound can also be printed as hinges attached to a rigid plastic sheet that is not intended to deform the proposed mechanism of expansion/contraction through the 4D printing of many materials [80-82].



**Fig. 18.6** Research directions in 4D printing encompassing development of equipment, deforming mechanisms and mathematical modeling and meta cube reveal its precisely programmed surface texture under uniaxial compression

This developed process creates a self-expanding and contracted nanostructure. It shows the experiment that the printing process brings anisotropy into the printed part. The print design is a two parallel straight beam fixed at the center and the manufactured parts can be folded in two opposite directions. The design uses the vitreous phase and the rubber of SMPs with  $T_g$  changes [82-84]. The rubber step is preferable to the temperature, changing the state of the glass. The primary mechanism of action depends on the SMP fibers carefully placed at low and high temperatures. The project was modeled using the finite element method (FEM) to analyze SMP materials' thermal and mechanical behaviors [85-87]. The equation of the printed nanostructure is obtained from the nonlinear transformation model. Green-Lagrange and modified by FEM, along with Newton Raphson's incremental outlines and verified by experimental data.

The composite material is also heated above the  $T_g$  of SMP materials, causes change in the thermo-elastomeric form. Then, the nanostructure is stretched to create tension. The composite nanostructure is corrected in a deformed state and cooled below  $T_g$ ; less than  $T_g$  of both SMP materials. The polymer in the rubber phase gradually becomes glassy, creating the first temporary form. Mechanical constraints are released and during the release, elastic stress is recovered, while the significant primary stresses remain in the polymer compound. After heating, the previous tension is removed, and the permanent pressure is recovered [88-90]. Stress recovery without stress, the compost heats up and opens the nanostructure's space and reduces heat to maintain the original diameter.

Researchers have used the Polyjet Objet 500 Connex system [90-92]. The 3D printer uses a liquid photometer directly on the construction platform at 70 °C and is treated with UV immediately. Combining the two materials used in the composite production are Tango Black Plus and Vero white Plus. The composition of these polymers has been described in Table 2. The Objet 500 can combine the two materials with different proportions to obtain new digital materials. Therefore, in the study in question, Tango Black Plus and Vero White Plus are mixed to create high and low Tg of 30 and 60 °C, respectively, known as DM8510 printer material library [92-94]. Dynamic mechanical test and Tg analyzed digital materials for DM8510 are 64°C. During the measurement of anisotropy in the printed parts, 12 different thermal and mechanical parameters are tested. Each polymer specimen is printed in six different directions. The samples are prepared in accordance with ASTM D638 standard. Tensile and thermodynamic data show Young and cutting moduli. The Poisson ratios differ in three directions in the glass phase, similar to the rubber phase [94-96].

Recently, another method for creating deformation in 3D printing materials using the Stratasys J750 multi-strand printer, unlike other printed memory polymers, has been developed [97-99]. The printed pattern is temporary, and the permanent way changes all the time according to the temperature. When printing a rigid bilayer SMP with elastomer, the thermal expansion coefficient does not bend the material. Internal print compression efforts can be created in elastomers controlled by the light intensity layer's printing time and treatment time. When outside the construction sheet, the 3D printed part retains its shape until it is heated above the Tg, which turns into a programmed pattern. The increased temperature helps reduce stress in the room. This process has many advantages, allowing producers to print and store nanostructures for collection. A single core can be changed into a nanostructure. This makes it possible to produce assemblies that are much larger than the production plates. Significant savings have been reported in terms of time and material usage when printing flat, packaged parts that can be changed [100-102].

Thermoplastic fibers are widely used in melting modeling (FDM) models. Economical, reliable and straightforward processes make 3D FDM printers top-rated for small cooperatives and home users. Therefore, many types of research are developing new materials for FDM printers [103-104]. Steven and the Faculty of Radiation Sensitivity blended SMP acrylate polymers and molded materials for accepting FDM (especially rubber). Hence, they studied the use of SMP with FDM printing. DiAPLEX MM-4520 granule is the SMP material used from SMP technology. The 3D printer used in their study is Makerbot Replicator 2x (Makerbot Industries, LLC). The material is extruded at 220 °C, and the temperature of the construction plate is 45 °C. SMP is a thermoplastic polyurethane. The removal of polymers from injection molding materials has been studied [105-107].

Also, crystal material molecules are systematically managed to develop crystals when it cools down below Tg. Therefore, they are more sensitive to thermal shrinkage than amorphous materials. Because of rubber materials' heat sensitivity, there is a cooling mechanism designed for 3D printers to reduce shrinkage. Although it is unnecessary for acrylonitrile butadiene styrene (ABS) or PLA, the heat transfer from the printed nanostructure to the external environment is enough to reduce the extruded temperature SMP to cool down below its Tg during the extrusion. Additional airflow is needed. To help the filling be fed correctly, one roller is activated by one motor and the other is in the extruder material. To ensure that the roller's temperature is still lower than the Tg of the material is essential. Otherwise, the device will be blocked. An infrared thermometer accuracy of + -1.5 °C

has been used [108-110], and if the temperature is higher than  $T_g$  of the polymer, the printing process will be interrupted.

The relationship between partial density and extruded temperatures has been studied and discovered that SMP nanostructure's higher density helps create recovery stress during recovery. When the nozzle's scanning speed increases, the target's density decreases slightly to 30–150 mm/sec during the test [110-112]. The temperature of the construction plate is also vital in any printing. Therefore, it is recommended to print any SMP materials, provided the heat of the construction plate is adjusted to  $T_g$  of the material. The nozzle scanning speed of 60 mm/sec during extrusion leaves a small room to find a Printing mistake, though is too slow. Hence, SMP dissipates heat and the printing layer is soft and unstable. But, if printing is too fast, extrusion may not be enough. Another vital part of the observation is the increase in surface roughness of printed parts when the extruder's temperature increases [112-114].

### 18.3 Stimulus: Mechanical

Complex shapes can be quickly printed with 3D printing as opposed to traditional production methods. . For instance, a set of irregularly shaped cube blocks was designed, the internal nanostructure is an isometric type. Each block is freely adjusted to allow complex nanostructures [116-119]. Deformed blocks are assembled like a brick in the form. Each tablet is a form of programmable when it classifies itself. The design of mechanical free material and mechanical truffle is possible (Fig. 18.7). 4D Printing is basically about creating smart objects. The traditional 3D printer has helped in this capacity. Adding something else; the secret of 4D printing is not the printer but the material with which it is printed [118-120]. 3D printing turns digital blueprints into physical objects by building them layer-by-layer. 4D Printing is practically the same technology, but with one big difference: it uses special materials and digital designs to generate objects capable of changing their shape and adapting to the environment.

This capacity can be exploited for printing objects through materials that respond to thermal, kinetic, gravitational, magnetic, pneumatic or other stimuli. The invention consists of making impressions using a gel composed of several substances, also known only as a *compound* that prints flat objects and alters their shape when subsequently immersed in water. The project was developed by a some scientist, they wanted to add to the hydrogel the tiny fibres of cellulose, an organic compound found in plants. The ability of flora to alter its shapes according to external stimuli was a crucial aspect in developing 4D printing. The study aimed to develop a printing substance capable of mimicking how plants respond to rain and sun. This gel was the result of the research [120-124]. "By using a composite ink printed in one pass, the printing of changing geometric shapes on the hydrogel, which contain greater complexity than any other technique is possible, and this is realistic by modifying the printing path. It is also interesting that different materials can be exchanged by adding properties, such as conductivity and biological compatibility".



**Fig. 18.7** 4D printing of polymer composites for smart textile industry

The printer adjusts the hydrogel ink to add the precise point of hardening and thickness to the cellulose by aligning the cells. This characteristic allows the team to accurately predict how the object changes its shape when exposed to water, allowing researchers to develop a mathematical process that will enable them to program and design any desired type of impression. The most important and impressive output from this advance is that it allows the design of any transformation in various forms with different materials, properties, and applications. It also establishes a new platform to print products that build themselves and dynamic nanostructures on a micro-scale that can be applied both in the industry and in medicine. Different research groups have been conducting tests on using the 4D technique to print living tissue [124-126]. Although 3D printers can print organs, the new advances in 4D printing can make it possible to create cells that adapt to changes in the body with the support of the leading 3D printing techniques (Table 18.2).

**Table 18.2** A summary of the leading 3D printing techniques

Technique	3D Printer	Process	Material	Advantage (Adv)/ Disadvantage (Disadv)	Companies
Material extrusion	Fused deposition modeling (FDM) / Fused filament fabrication (FFF), Contour Crafting (CC).	The filament form material is extruded through a nozzle at a temperature, deposited onto a heated build plate, and then deposited layer-by-layer. CC: Using high pressure and large nozzles, materials can be extruded for large nanostructures.	Thermoplastic filaments, typically ABS, nylon, PLA, PC, composites, nano-fillers. CC: Concrete, soil,	Adv: Low cost, simplicity, low maintenance, CC: Large construction. Disadv: Voids, the challenge of printing complex nanostructures, Accuracy is low.	FDM: Stratasys, Ultimaker, Makerbot, Zortrax, BEEVERYCREATIVE, Markforged CC: Contour Crafting Corporation.
Vat photopolymerization	Stereolithography (SLA), Digital light processing (DLP).	A platform moves downwards after each layer of liquid resin is cured. SLA– cured with a laser. DLP– fixed with a projector.	Liquid photopolymers (acrylic or epoxy-based).	Adv: High accuracy- microns. Disadv: Limited materials to use, relatively expensive, requires significant support nanostructures.	SLA – 3D Systems, Formlabs, DWS Systems DLP- EnvisionTEC, B9 Creations.
Sheet lamination	Laminated object manufacturing (LOM)	Continuous layers in sheet form are cut using a mechanical cutter or laser and then bonded together.	Polymer composites, ceramics, paper, metal-filled tapes.	Adv: High speed, low cost. Disadv: Depending on the material, post-processing might be needed, limited material use.	EnvisionTEC, Mcor Technologies.
UV Laser	Ultrasonic additive manufacturing (UAM).	A rotating sonotrode applies ultrasonic vibrations to a foil, creating roughening friction between the foil and the welded material. This displaces the surface oxides and other contaminants; under a compressive force, the materials are bonded. A CNC stage allows for selective removal and machining to final dimension.	Metals - aluminum, copper, electronics, polymers and other materials can be embedded.	Adv: Low-temperature processing allows electronics, sensors and polymers to be embedded. Disadv: Early stages of development. More research is needed into titanium and stainless steel.	Fabrisonic.

### 18.7.1 Application of SMPC in Space

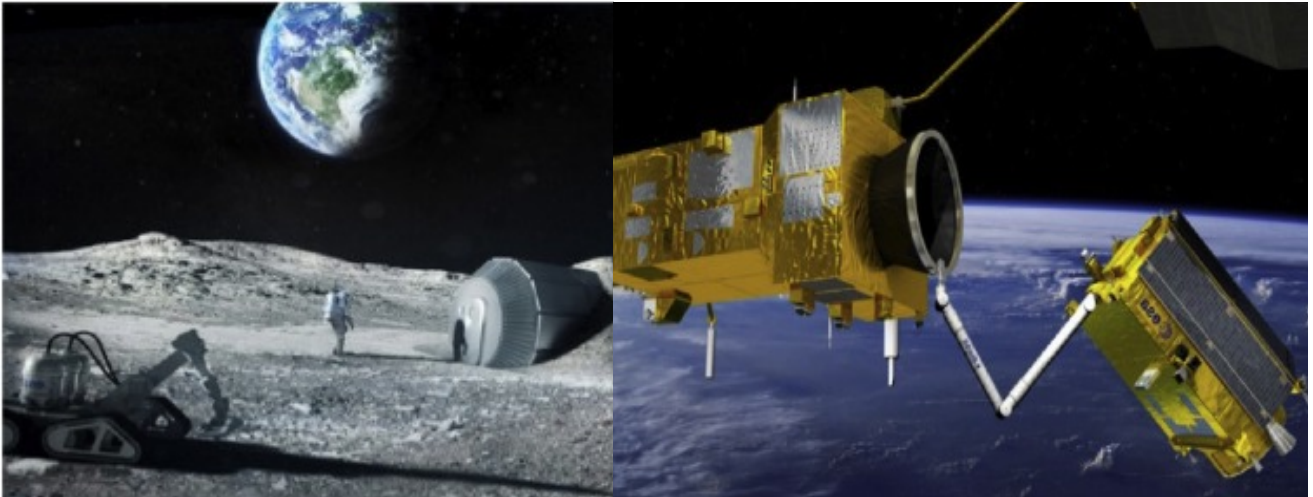
NASA's in-house production team has developed a technology-based action plan, from earth-based production technology to exploration by 2040, which can focus on Mars. The European Space Agency (ESA) also considers it a basis and sees the moon as the next step [149-151]. ESA has partnered with the Manufacturing Technology Center (MTC), based in Coventry, the UK's largest manufacturing center. Prototypes can be reproduced in state-of-the-art facilities to test the suitability of space applications. Research on product innovation contributes to the

development of green technologies. As previously discussed, there is a significant waste reduction compared with the conventional production methods, in addition to a decrease in production stages, energy consumption and widespread environmental impacts. All businesses have a duty to consider the space's layout to manage waste and residual pollutants. The immediate objective is the 3D printing of plastics, metals and the reuse of printing parts. Finally, the key is self-confidence in open and remote areas, with a large additive building (artistic surface) and the use of planetary resources. In 2018, NASA unveiled the next step in space extraction and sustainability. The remanufacturer converts raw materials into recycled materials, all in the same order [120-125]. Currently, only plastic parts can be recycled and reused. However, NASA plans to build a large, fully recyclable industrial laboratory, including steel, by the end of 2020. 3D Printing allows producers to avoid the usual nanostructures of production, where a dozen of small Logga produce the necessary, using less energy and materials.

The resources of Logga needed outside the local environment are essential. The weak earthquake (LEO) is 200 to 2000 km above ground level. The most commonly used polymer on the surface of LEO air is Kapton. Kapton is a polyimide of 50 to 150 kDa, formed from dianhydride vapor and a diamond monomer. It has strong UV ray resistance and is stable from -270 to 395°C [101-105]. For thermal stability, Kapton has been used as a flexible film to convert sunlight, heat transfer, and high-performance nanostructures in air-conditioned buildings. After six years of LEO, Kapton has the potential to be extremely poor. The leading causes of its erosion are UV radiation from high-intensity waves from 100 to 200 nm, the temperature range from 175 to 160 °C, the effects of collisions in air and micrometeoroids, radiation and oxygen saturation (ATOX) [121-126]. At LEO, ATOX is considered the leading cause of erosion. The photo-dissociation of oxygen triggers ATOX by an intense UV light. Material conflicts will cause oxidation and corrosion if they are not yet in their highest production state. Conflicts with oil-based polymers such as Kapton can break the C and C-H bonds and cause burns, resulting in the loss of fatty acids and gases, such as CO<sub>2</sub> and CO [128-130]. Current devices capable of 4D Printing provide compelling evidence for future satellite design concepts—progress in identifying and using Logga outside of the required atmosphere.

Fig. 18.8 illustrates the implementation of MARSIS; multimeter bars are released and locked in place. Very low-frequency radio waves are sent to the planet and reflected on the surface they find. According to the seventh exploration ground of ESA, Operation Marine, the importance of concrete nanostructures to succeed in the mission is unprecedented, which will begin in 2020. The mission will provide important information about the circumstances. This will develop our knowledge of the global carbon cycle. The 637-6666 km long-range biomass device consists of a P-band of 435 MHz synthetic-aperture radar (SAR), based on a large-scale observer (Fig. 18.8). The large antenna will be folded, opened to the Vega and sent to space. The antenna will consist of a concrete arm and a folding mirror with an expected 12 m.





**Fig. 18.8** Lunar base constructed via AM - An inflatable dome is extended from one end to provide nanostructure support for construction. To produce a protective shell, layers of regolith are built up over the dome using 3D printer base, made by 3D Printing with Biomass mission - Concept B deployed configuration with NG reflector [159]

Potential applications for low-dimensional 3D printing include the antenna for radio communications, radar surveillance, equipment upgrades and solar air [116-118]. Typically, three types of deployment systems are used, the architecture is based on the cluster nanostructure. The pantographic nanostructure is made of solid materials with a spring compressor, which uses its locking mechanism. It is usually caused by drag from the ground. If the engine speed must be controlled or reversed, techniques for moving the motorcycle will be used. Flexible nanostructures require a higher speed volume and are more substantial, although they offer greater geometric precision. Examples of highly deactivated systems are reliable bridges, where all components are integrated to save a number and increase reliability. Dedicated systems are a bit heavy, although they do require gas storage. Recruitment tools, if printed in 3D, can be part of the solar navigation operation. The solar boats were printed and placed in a house, previously prepared to respond to environmental stimulation. With solar panels, scratching can be a problem. Therefore, the operation must be precise, considering the stable nanostructure, ensuring that the membranes are tightened in each line. It can be challenging to guarantee the correct accuracy of many circuits. If the whole deposition process depends on the combined heat generated by the sun's flow, problems can arise [119-122].

Today, about 750,000 items with more than 1 cm of active waste disposal circle are essential to stabilize the waste dump's growth. Any newly manufactured product must follow the guidelines for post-waste disposal. At a typical collision speed of 10 km/s in the lower corners of the earth, the impact of 1 cm objects can destroy a satellite, while a ruin of about 10 cm can cause damage to the satellite. Any possible collision creates an additional accumulation of waste that increases the percentage of other effects, leading to Kessler syndrome's independent mapping process. In 2015, ESA Integral and Cluster-2 satellites saw their orbit change to ensure that the two satellites safely returned to Earth's atmosphere over the next decade. Populated regions of 1000 km long are selected for large-scale ecosystem operations. The ESA Dealbit will be on its first flight in 2024 to eliminate large objects owned by ESA on its current planet and bring it back into the atmosphere. Several independent indicators and adaptations have been proposed [122-125]. Accuracy and speed are of great importance to avoid the Logga

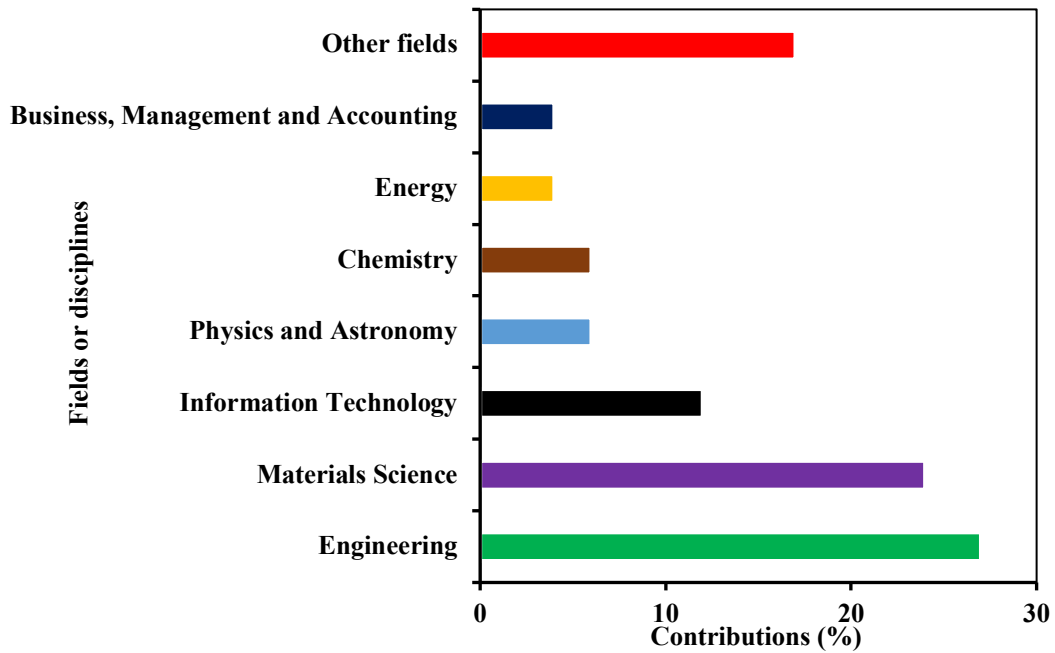
trigger and, consequently, accidents. In the future, the weapons and robotics kits from the company may print 4D areas to avoid likely Logga with the elaborate packaging and regions (Fig. 18.9).

## 18.8 Research Status in 4D printing

Innovative studies on 4D printing are increasing, as evident from the Scopus data by searching for the keyword - 4D printing. There are 171 published articles on this technology up to September 2018. The first research article on 4D printing was published in 2007. In the same year, only one article on this technology was published. There was no article published in from 2008 to 2011. In 2012 and 2013, an article was published annually. In the year 2014, there was an increase in publications.

Additionally, 55 articles were published on 4D Printing between January and September 2018. Therefore, it is evident that research on this technology has started developing rapidly, especially from 2016 to the current year 2020. Currently, several journals and other sources have published research articles on 4D Printing[125-128]. These include, but are not limited to, magazine publications, International Journal of Precision Engineering and Manufacturing-Green Technology with the highest publications of nine, Magazine of Intelligent Materials and Nanostructures and the Periodic Publications of Virtual and Physical Prototyping with eight published articles.

Also, American Chemical Society (ACS) Applied Materials and Interfaces published 6 articles, Assembly Automation, and Materials and Design, have two publications, each. The 3D Printing and AM and Materials Magazine published four articles. Scientific Reports has published three research articles. Besides, magazines and other sources have also published articles on 4D printing. Summarily, various fields of study or disciplines have contributed immensely to 4D printing technology advancement in different ways [128-131]. The percentage of their involvement is represented in Fig. 18.9. It is observed that the Engineering field provides the maximum or leading contribution of 27%, followed by Materials Science contributes with 24%. These two results depict the most relevant of both disciplines to 4D printing. Information Technology has 12%. It is quite interesting that Chemistry as well as Physics and Astronomy provide same contribution of 6%, each. Similarly, Energy as well as Business, Management and Accounting contribute 4%, each. There is also a multidisciplinary and collective contribution of 17% from other fields, which include **Chemical Engineering**, Mathematics, Biochemistry, Genetics and Molecular Biology, Medicine, Arts and literature, Environmental Sciences, Social Sciences, Decision Sciences, Pharmacology, Toxicology and Pharmaceuticals.



**Fig. 18.9** Percentage of contribution to the advancement of 4D printing technology by various fields or disciplines

### 18.9 4D Printing Applications in the Medical Field

4D bioprinting is an emerging technique, where a time of use is also integrated with 3D bioprinting and the printed medical model changes its shape and functionality. This time-dependent model also offers high potential for biomedical scaffolding and several other essential purposes. It has several emerging applications in the field of medicine. Both Tables 18.1 and 18.2 have previously analyzed the actual definitions or applications. In treatment, it is necessary to obtain precise details about anatomy. It is to improve the clinical results, reduces the effective length, reduces the donor site's morbidity, and decreases the operation's general complications. 4D printing has a suitable applications in biomedical such as self-folding stents and other self-retracting and clamping clips. 4D printing technology can change the surgeon's approach to plan diagnosis and treatment in orthopedics [131-134].

### 18.10 Future Outlooks and Prospects

4D Printing futuristic applications will increase in the medical industry/field to meet innovative requirements. It will become a ubiquitous and essential technology for the surgeon to manufacture smart and personalized implantable medical devices that provide significant performance. Using an intelligent multiple print model includes blood loss information, blood clots, infection in the chest wound, and difficulty breathing [135-138]. Due to its greater flexibility in the manufacture of medical models, the surgeon can produce intelligent anatomy of each patient at any time, which was impossible before. In the next decade, it is obvious and predictable that 4D printing technology will bring essential and more innovative improvements to the medical, engineering and related fields with advancing smart materials. The objects printed through this technology can be used in engineering, large auto parts and adjusted according to the necessary environmental conditions and energy required. These

products can change the pipes' diameter in the plumbing system, depending on the flow and demand for water. The tubes may have the ability to heal automatically in the event of a break or crack. This technology can also become the best solution for smart buildings and bridges that can change shape depending on weather conditions, to mention but a few potential innovative and futuristic applications.

### 18.11 Concluding Remarks

4D Printing has advanced in recent years and promises to be relevant to many areas. In this comprehensive review that focused on 4D printing and its applications, multiple useful 4D printing technology cases have been discussed. In particular, case studies in three areas were studied: home-built nanostructures, electronic robotics and medical devices, pressing innovative tools into 4D printing to perform functions that are impossible or too expensive to manufacture using traditional manufacturing methods. 4D-printed devices are suitable for unusual environments due to their high adaptability and lack of mechanical elements. 4D-printed devices have great potential in the medical field, where medical devices' patient-specific designs are significant. Surgical treatments with 4D printing have already been performed and successfully demonstrated the extent to which 4D printing enhances its effect. Intelligent printable materials, mathematical models and advances in printing technologies enable 4D Printing to develop further surgical treatments, targeted drug management, electronic robotics and other unthinkable technical domains. Therefore, 4D Printing offers an exciting future for manufacturing and products. Significant budgets and savings can be realized through this innovative technology.

The 4D printing is proof of concept phase, which has taken a big step forward to prove the teaching capacity of programs that respond to different motivations. Carriers may have the potential to revolutionize the airline, healthcare and defense industries over the next decade. For example, space printing precision is required over long distances, saving weight, especially at the initial cost of \$10,000 per kg and possible waste. Integrated adaptive devices can incorporate different motivations to achieve different response patterns in complex environments. To date, 4D metal printing has often involved memory devices' design, while several studies have emerged, which indicate other incentives for bikers and campers. The development of new technologies, such as UAM, allows the synthesis of iron and polymer in complex geometries. The next step is developing large print runs combining production and robotics with the printing of various materials. As well as advances at the nanoscale, focusing on the delivery of drugs to the body.

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