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Recent Progress in Materials

Review

Emerging Advances in 3-D & 4-D Printing of Polymeric Nanoarchitectures & Multifacet Applications

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Abstract

3-Dimension printing (3-DPT) or additive manufacturing (AM) technology has been utilized for a while in the construction of customized 3-D objects utilizing computer software such as computer-aided design (CAD). However, the emergence of an innovative and new four-dimensional printing (4-DPT) has enabled the synergy of AM technology with programmable materials in transforming digital processes virtually into physical entities, thereby providing innovation and advanced functionalities. 4-DPT is a procedure facilitating 3-DPT components to undergo programming in order to enable the transformation of their shape with time on exposure to external stimuli such as physical stimuli, including light-responsivity, chemical responsivity, magnetic/electrical responsivity, pH response, thermo-sensitive as well as biological stimulation such as biomolecular responsivity. The inherent difference between 3-DPT and 4-DPT is premised on the shape-changing material (SCM) utilized during

manufacturing, depicting the advanced material exhibiting the specified changes in responsivity to external parameters. Therefore, this elucidation presents emerging 4-DPT technology in manufacturing polymeric nanoarchitectures and applications. Furthermore, insight into 4-DPT techniques, including extrusion, direct ink writing (DIW), fused filament fabrication (FFF), and vat photo-polymerization strategies (digital light processing (DLP), stereo-lithography (SLA), and multi-photon polymerization (MPP), are also presented.

Keywords
4-D printing technology; polymeric nanoarchitectures; applications

1. Introduction

AM, also called 3-DPT, has garnered escalating attention from industrial engineers and academic investigators due to its enchanting attributes, including freedom of prototyping and susceptibility to achieving intricate architectures at an elevated resolution [1]. The 3-DPT of deformable and innovative materials has resulted in the construction of emerging 4-DPT, referring to the material propensity in altering their form post-printing with time in the fourth dimension regulated through designing dynamic architectures [2]. 4-DPT offers added functional features and performance-propelled uses in vast segments, such as automobile, aerospace, maritime, biomimetic, construction, biomedical, civil engineering, electronics, acoustics, industrial food, textiles, fashion, oil and gas, mechanical, defense, retail, and other industrial applications as elucidated in Figure 1 [3].

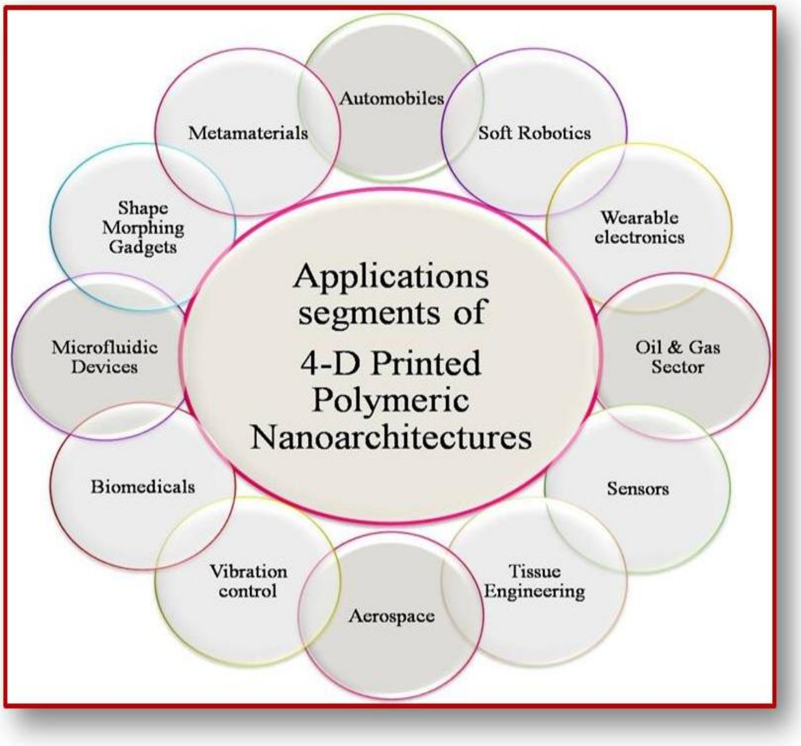

Figure 1 prospective application of 4-DPT materials and gadgets.

The acronym "4D" combined with "printing" *ab initio* emanated in a conference proceeding in 2012, where it was referred to as a 4-D barcode (color + 2D + time) [4]. In a subsequent publication, the initial term was formed by 3-DPT, whereas the programmed polymeric activity created a time-based configuration termed the 4-D perspective [5]. The 3-DPT component exhibits a single static architecture, whereas the 4-DPT bright part exhibits at least two smart phases vis-a-vis static and dynamic architectures. 4-DPT technology, as an emerging AM technique, facilitates further shape variation, features, or functionalities of printed objects on subjection to external stimuli [6].

Nowadays, 4-DPT of materials prone to programming and deforming, like thermo-responsive shape-memory polymers susceptible to varying shapes when exposed to heat, has garnered attention. 3-D objects premised on shape memory polymers (SMPs) have been propounded for varying prospective uses in differing segments, such as soft robotics, biomedical, electronics, and smart actuators. Thus, to facilitate the manufacturing of intricate multi-functional 3-D objects, SMPs are regularly synergized with other functionalized polymeric matrices or nano-fillers before or after-3-DPT [7].

Innovative materials, also called programmable materials, wherein the printed shape or features are not the final state. When the final geometry is required, they can undergo shape-shifting into the pre-programmable form on exposure to external stimuli. Instances of environmental stimuli include temperature, light, pH, moisture and magnetic field [8, 9]. These stimuli cause physically or chemically affiliated reactions like phase variations, stress relaxation, or molecular motions, which induce geometrical deformation or reformation. The materials programmed, thus, garner high attention in multifacet segments from up-scale manufacturing to micro/nanometric level for a vast range of applications in biomedicals or soft robotics [10]. Hence, materials susceptible to responding to differing external stimuli over time have been widely investigated for application in tissue regeneration procedures. Stimuli-responsive biomaterials have been utilized in conceptualizing 4-D bioprinting, in which 3-DPT scaffolds are constructed for transformation over time according to one or more environmental stimuli [9, 10].

Therefore, this elucidation presents a novel 4-DPT of PNC with insight into AM techniques (extrusion, direct ink writing (DIW), fused filament fabrication (FFF), and vat photo-polymerization strategies (digital light processing (DLP), stereo-lithography (SLA), and multi-photon polymerization (MPP)), for 4-DPT of smart polymeric architectures and multifacet applications.

2. Insight into 4-D Printing

4-DPT utilizes AM strategies in synergy with innovative materials. These are known as materials undergoing variations in geometry, and at times functionalities on subjection to the suitable external stimuli (light, solvent, temperature, magnetic, pH, and so on) [11, 12]. From this synergy, 4-DPT enables the construction of dynamic and adapting components in negative to inactive parts garnered via 3-DPT. Innovative materials capable of recovering their configuration (SME) on exposure to external stimuli are the most effortless preference when considering materials to be manufactured via 4-DPT [13].

The movement of a 3-D printer is three-dimensional and geared towards fabricating 3-D architectures. 4-DPT entails the integration of a 4th dimension and time, implying that 3-D printed items undergo transformation and shape variation in time on exposure to external stimuli like magnetic fields, water, light, pH, heat, electricity, and so on [14-16]. Garnered objects are termed

4-D printed entities printed using 3-D printers but utilizing 4-DPT materials [14]. Hence, a 4-D printing material can transform or change its geometry or configuration over time on exposure to external stimuli. This geometry transformation can be achieved by utilizing multiple materials within the printer, each representing differing responsiveness to external stimuli.

The printing step for a 4-D printed item is similar to that of a 3-D printed object. However, the key difference lies in the premise that materials utilized in 4-DPT technology are prone to be programmed and subjected to transformation in contact with external stimuli (heat, light, or moisture). These materials capable of responding to external/internal stimuli are termed innovative materials. Hence, 4-DPT uses a 3-D printer to print innovative materials for required objects prone to architectural or feature transformation on exposure to external/internal stimuli [15]. Polymeric matrices, metals, ceramics, and biomaterials are materials susceptible to being used in differing AM procedures to construct multi-facet materials. Adaptive and shape-morphing features cannot be achieved using rigid, pre-arranged architectures garnered via 3-DPT. This is where 4-DPT comes in as a channel for attaining these features. An enchanting 4-DPT material that is responsive to solvent interaction is water [16].

4-DPT is the construction procedure of 3-D objects with capability of changing their shape/configuration over time or as a response to an external environmental stimulus thereby demonstrating a sharp shifting in AM and providing a streamlined route from idea to reality with performance-focused functionality in-built directly within the materials [17]. Using this strategy, a vast range of actively programmable materials is fabricated with the capability of self-transformation from one configuration to another [18]. The main differences between 3-DPT and 4-DPT are schematically elucidated in Figure 2 [18].

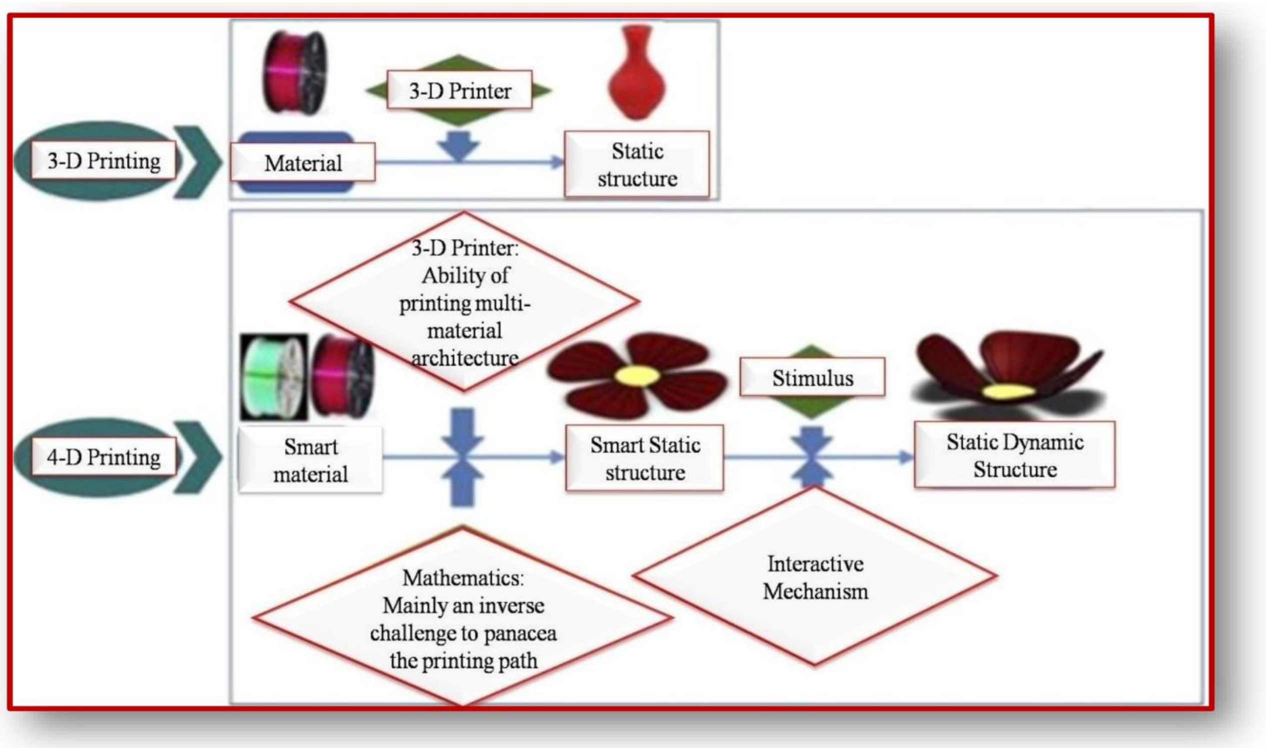

Figure 2 Differences between 3-DPT and 4-DPT [18].

The main differences between 3-DPT and 4-DPT are ascribed to material depositing into a pre-ascertained static configuration. On the other hand, 4-DPT entails the precise depositing of an innovative material into a pre-ascertained, smart static architecture. When this brilliant static architecture interacts with an internal or external stimulus, the material will undergo inherent shape transformation, becoming an innovative and dynamic architecture [18].

3. AM Techniques for 4-DPT

The 3-DPT/AM technology is utilized in generating 3-D samples, wherein sheets of material are continually formed under a computer-regulated program to construct a physical sample. According to ISO/ASTM52900-15, there are seven sets of AM procedures: binder jetting, directed energy deposition, material extrusion, powder bed fusion, vat photo-polymerization, material jetting, and sheet lamination [19]. The key principles of commercially available AM technologies are presented in Figure 3 (a-g).

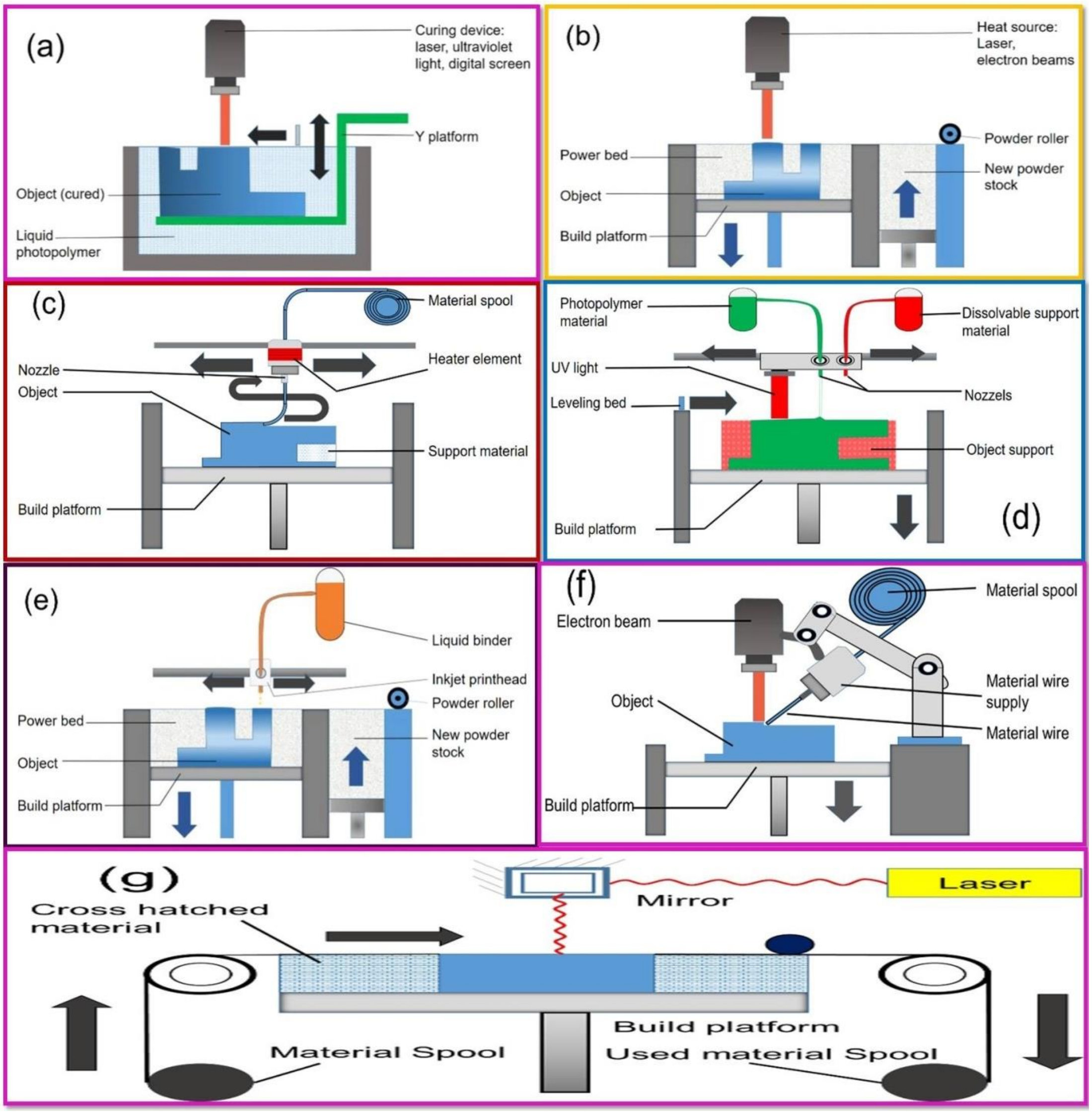

Figure 3 Varying Additive manufacturing (AM) technologies utilized in 3-DPT. (a) Photo-polymerization; (b) Power bed fusion; (c) Material extrusion; (d) Material jetting; (e) Binder jetting; (f) Direct energy deposition; and (g) Sheet lamination [19].

AM techniques presently utilized in 4-DPT includes fused deposition modeling (FDM); selective laser sintering (SLS); stereolithographic apparatus (SLA); and polyjet [19]. The key commercially available 4-D AM procedures have been mainly classified using their associated printing mechanisms; liquid solidification, powder solidification, and direct material extrusion. These strategies entail photo-polymeric light-curing; melt extrusion, and direct-ink printing [19].

The routes selected are premised on the innovative materials to be printed and the required features/functions of the end architecture. Parameters, including the speed of printing, frequency of the laser, and nozzle temperature, influence the preciseness of fabrication and are therefore susceptible to investigation and optimization to enable the feasibility of industrial scale-up [20]. The printing step can also be selected based on susceptibility to enhancing and facilitating the object shape-memory functionality. Despite the AM strategy utilized, constructing a 3-D architecture requires a comprehensive Computer Aided Design (CAD) model of the physical architecture [21]. The model design is primarily digitally cut into slim horizontal sheets, as the printer creates the architecture through sequential printing of individual layers of the material [22].

3.1 4-DPT of Mechanically Stable and Elevated Temperature Shape Memory Polymer with Good Irradiation Resistance

4D-printed shape memory polymers (SMPs) have aroused high attention in a vast range of segments. However, the development of elevated-temperature SMPs combining the elevated mechanical features and radiation inhibition remains daunting. Hence, in work, a novel photosensitive constitution (PSC) premised on elevated-performance heat stable poly-N, N'- (*m*-phenylene) isophthalamide (MPA), rigid photopolymerizable *tris* [2-(acryloyloxy) ethyl] isocyanurate (TAI), and a reactive solvent (N, N-dimethylacrylamide (DMAA)) was constructed [23]. The garnered PSC was used in fabricating elevated-temperature SMPs via a facile two-step LCD 3DPT and thermal post-curing step (Figure 4) [23].

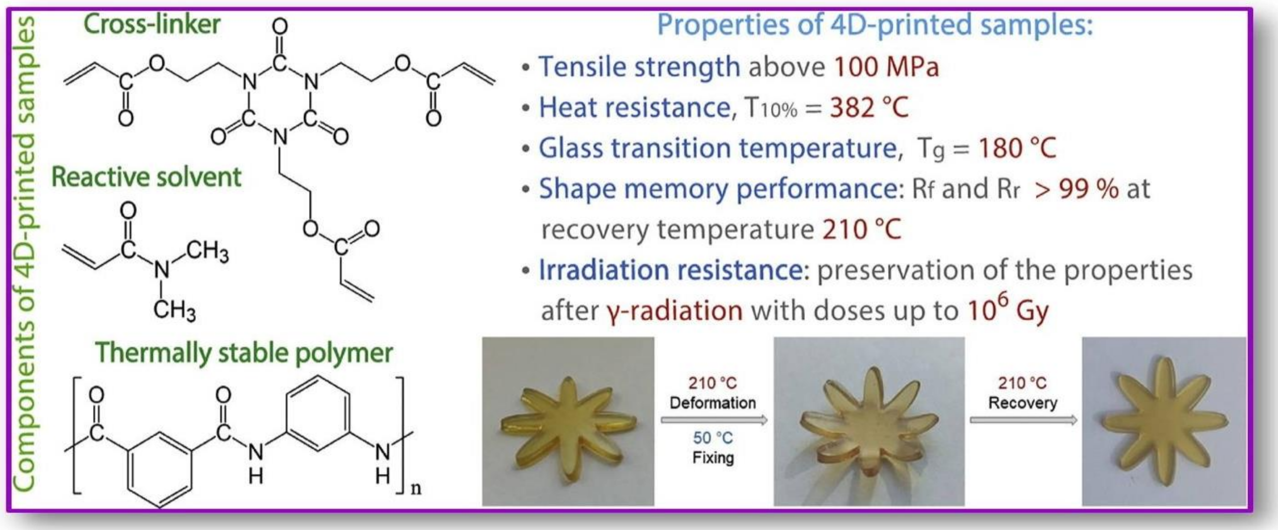

Figure 4 Components of 4-DPT SMPs and garnered properties [23].

As a result of their vast prospects in varying segments (energy conversion, bio-construction, adsorption, and catalysis), the construction of 4-DPT hierarchically porously architectures from the molecular degree to the macroscopic level has garnered great attention. Hence, comprehending the structural-feature linkage of innovative materials in 4-DPT is essential in designing novel constructs with a broader scope. Hence, work has been conducted on the construction of heat-responsive macroporous polymerized-elevated internal phase emulsions (poly-HIPEs) via 3DPT of Pickering-type HIPEs [24]. Garnered 4-DPT objects displayed elevatedly interconnected porous architecture exhibiting thermo-responsivity and elevated mechanical strength with exceptional self-recovery behavior, thereby depicting prospects of constructing a heat-responsive macroporous structure exhibiting shape memory features at varying temperatures through regulation of emulsion formulation [24].

Nevertheless, the printing disposition of PPH-0 ink also offered a better comparison between this specimen and the superior ink (i.e., PPH-8). Figure 5 (bottom) depicts the printed architectures of a 1-D zigzag architecture, 3-D square lattice, 3-D DNA helix, and a flowery appearance bearing 5 petals. The shape recovery attribute of the printed PPH-8 entered on subjection to heat stimulus was studied in accordance with its quantitative shape-memory attributes exhibiting satisfactory printability (Figure 6) [24].

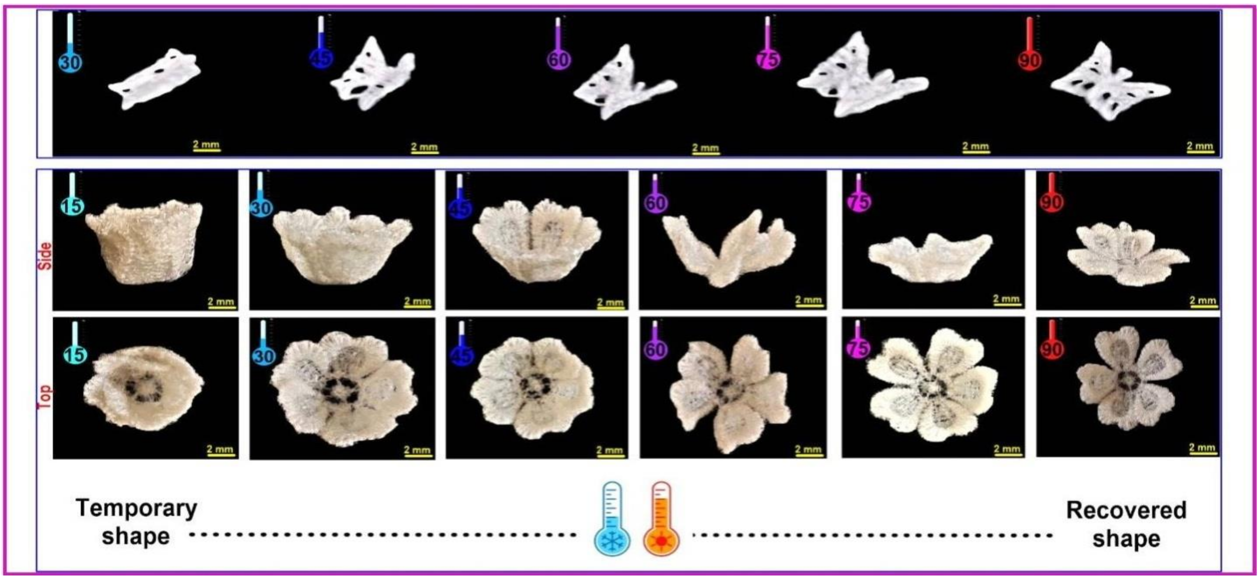

Figure 5 Sequential shape memory responsivity of 4-DPT PPH-8 figurines susceptible to temperature variations. (Top): The elevated transformation between permanency and temporary 3-D figurines of printed "butterfly" and (bottom): "5 petals flower". Individual constructs include a thermometric graphic monitoring atmospheric temperature [24].

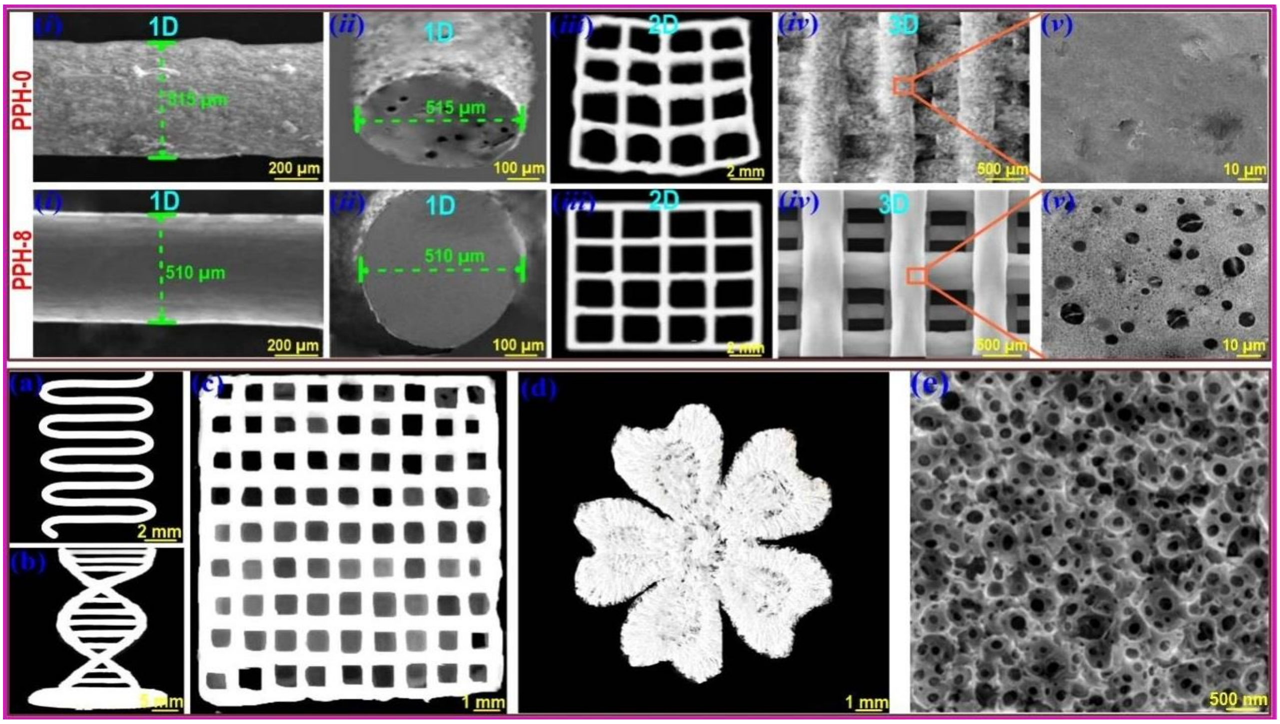

Figure 6 Printability of varying printed configurations from 1-D to 3-D constructed via PPH-0 and PPH-8 inking. (Up): FESEM images of (i) 1-D printed surface filaments, (ii) their significant cross-sectional rapture, (iii) 2-D square lattice, (iv) 3-D self-supporting scaffolds and (v) micro-architectures of 3-D self-supportive scaffolds. (Down): Printing quality of 3-D printed configurations constructed by PPH-8 inking. (a): 1-D zigzag pattern; (b): 3-D DNA helix; (c): 3-D square lattice, (d): 3-D flowery with 5 petals, and (e): magnified FESEM image of Figure 5 Up (v) for PPH-8 [24].

Through the integration of 3-DPT disposition with the shape-memory attribute of heat-stimulated printed PPH-8 architecture, varying printed figures with 3-D permanent configurations were garnered subject to structural restoration on exposure to temperature. A printed "butterfly" and "flowery" geometries were printed to entrench the transformation between permanency and temporary 3-D configurations (Figure 5).

3.2 4-DPT of Magnetic Responsive Shape Memory PLLA/TPU Blend

The combination of poly (L-lactic acid) (PLLA) with thermoplastic polyurethane elastomer (TPU) is capable of synergizing the benefits of outstanding biocompatibility with intrinsic shape memory capabilities of PLLA and elevated elasticity and exceptional shape memory features of TPU in use of minimally invasive surgery for bone tissue engineering. However, TPU creates a sea-island-appearing architecture in the PLLA matrix, decrementing shape memory features. Thus, in an investigation, a co-continual architecture of the TPU phase within the PLLA matrix was fabricated through the inclusion of Fe_3O_4 nanoparticles because of the varied interfacial tension and flowing disposition of TPU, which inculcated TPU/PLLA/Fe_3O_4 blend constructed via selective laser sintering (SLS) with outstanding shape memory features [25].

The construction steps of the composite blends are presented in Figure 7 (b). Lotus root-appearing blends were constructed via a self-formed SLS system composed of a computer-managing apparatus, a CO_2 laser equipped with 35-W power, and a dynamic focusing optical system based on the 3D model of a lotus root (Figure 7) [25].

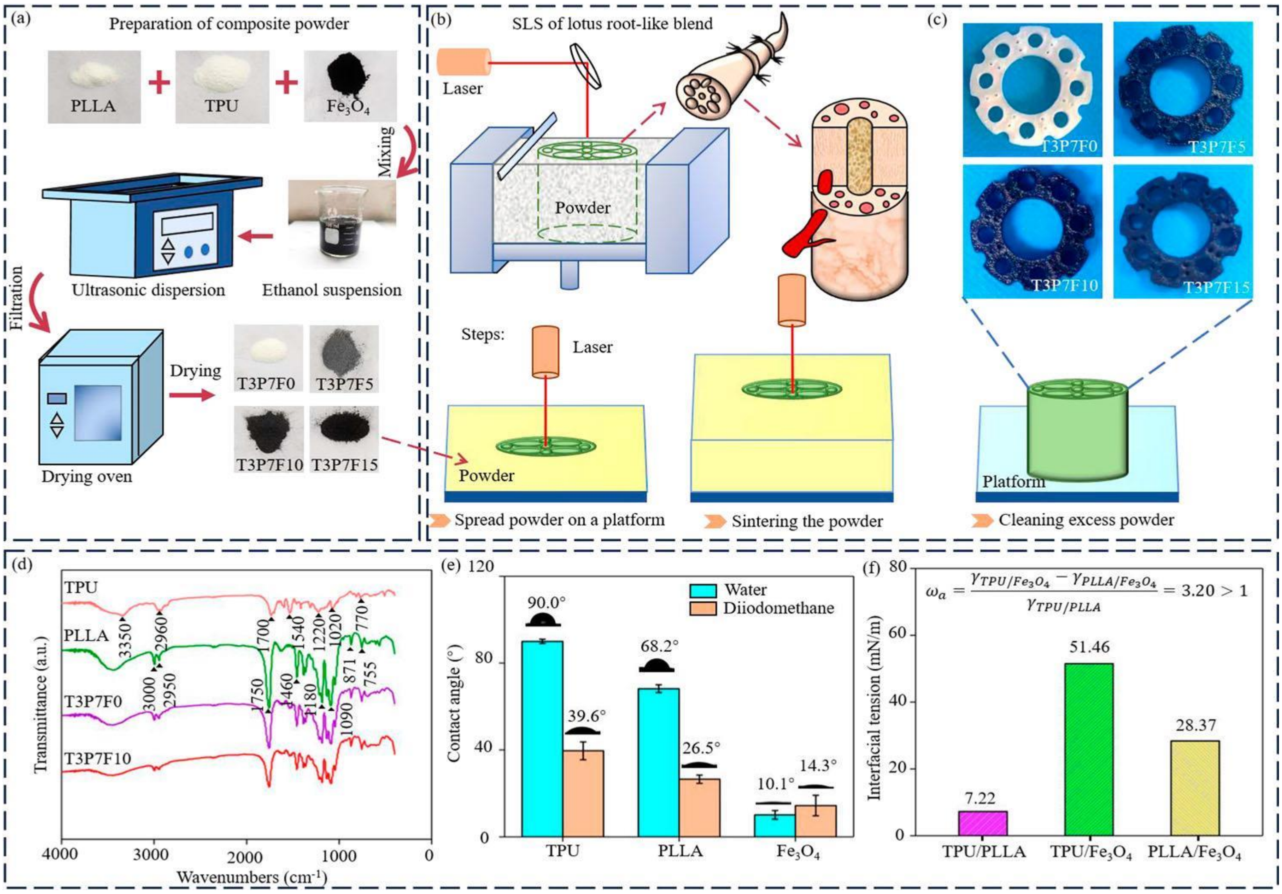

Figure 7 (a) Schematic elucidation of the construction of the T3P7F0, T3P7F5, T3P7F10, and T3P7F15 powders, (b-c) schematic illustration of the construction of the T3P7F0, T3P7F5, T3P7F10, and T3P7F15 lotus root-appearing blends, (d) FTIR spectra of the TPU, PLLA, T3P7F0, and T3P7F10 powders, (e) The contact angles of the TPU, PLLA, and Fe_3O_4 samples, (f) interfacial tension between differing pairs [25].

4. 4-DPT: Benefits and Disadvantages

AM has emerged as a prominent technology exhibiting great potential [26]. Despite 4DPT benefits similar to those of 3-DPT, 4-DPT performs better than 3-DPT relative to the dynamic features of fabricated products. Additionally, 4-DPT seems to be the following genre of AM [26]. The benefits entail energy conservation, time, money and materials [27]. Also, 4-DPT is advantageous for minimizing waste, errors, and loss of products in fabrication applications [27]. Differing reports depict the 4-DPT procedure as energy-proficient [27], with sustainability [27], and fast compared to other fabrication procedures.

Work has stated that 3-DPT entails object printing, while 4-DPT entails a creative procedure including topological modification or motion stimulation of the printed figurine [28]. These attributes are garnered by utilizing 4-DPT technology in fabricating the end product. Nevertheless, another work concluded that 4-DPT is a good material for biomedical scaffolds and micro-robotic construction premised on 4-DPT items affiliation with environmental variations in the system [27].

Inherent capabilities include elevated versatility as well as sensitivity, in addition to advanced designing and stimulation. Moreover, these parameters depict that 4-DPT facilitates the direct embedment of programming within a material devoid of external gadgets or systems usage [28].

4.1 Deficiencies of 4-DPT

Similar to its benefits, the deficiencies of 3-DPT may be identical to 4-DPT. Considering the added efforts essential for facilitating the mechanical behavior of printed figurines, 4D designing is more intricate than 3-D design [29]. The versatility of 4-DPT is still relatively limited, as 4-DPT shape-memory constructs are still within the early stages of maturation in comparison with 3-DPT [30]. A novel set of innovative materials has been constructed utilizing 4-DPT [31, 32]. Conversely, a 4-DPT deficiency has been seen as an uphill task in maintaining its exactness due to instability garnered during optimizing parameters that regulate the functionalities of dimension and geometry [33].

4.2 Stimuli Affecting 4-DPT Procedures

The basic difference between 3-DPT and 4-DPT is the materials fabricating some figurines. The change in the value of the mechanical behavior of material from static to dynamic is gingered by external stimuli or actuators. Various stimuli applied to 3-D figurines to enable improvement of their functions and dispositions have been outlined including light, temperature, water, pH, magnetic, humidity, and electric [34-36].

4-DPT figurines based on sensitivity to temperature have been constructed [37, 38]. A notable advantage of utilizing temperature as a stimulus involves the capacity to control the enhancements in a fabricated figure [39], performance capacity for mechanical enhancements [40], and operational ease [41]. The hindrances linked with temperature use as a stimulus include damage to cells [42], poor responsivity [43], usage complexities [31], as well as structural failures [35]. Most reports of temperature influence as the stimulus are based on temperature usage as an external triggering agent in generating shape-deforming bio-printed components [42]. Temperature as a stimulus has additionally been utilized for in vitro drug release [43] and tissue engineering [44].

Light is another notable stimulus greatly reported [45, 46]. Inherent benefits of light utilization as a stimulus include fast-switching [47, 48], precision [49], sustainability and biocompatibility [50], controlling wirelessly and remotely [51], modification of color [52], as well as mechanical features manipulation [53]. On the other hand, the use of light as an external source of stimulus for modifying 4-DPT objects structural modification also exhibits inherent deficiencies such as reduced geometrical transformation [54], potential toxicity [55], generation of heat generation [56], as well as complexities [57]. Because light cannot deteriorate cells, it can be applied in optical tools, micro-cantilevers, and the segment of in vivo biomedicine and drug conveying uses [58].

Numerous investigations have utilized water as a stimulus in actuating 4-DPT figurines [59]. Water utility in 4-DPT figurines has inherent benefits, including convenience, manipulability, and temperature minimization [59, 60]. Other inherent water benefits include gradual time of reaction and difficulty manipulating humidity-sensitive materials [61].

Magnetic fields utility in actuation has varying benefits such as fast response [62], inferior safety [63], remote guidance as well as capability of accelerating the mobility of specific 4-DPT figurines [64]. On the other hand, inherent deficiencies include elevatable reactive prospects and agglomeration affinity of magnetic-responsive materials, especially in biomedical applications [65], intricacies of magnetic nanoparticles within living structures [66], inferior temperature usage, and elevatable density of conventional magnetic absorbents [67].

pH is a veritable bank of stimulus for 4-DPT figures due to its susceptibility to causing swelling, shrinkage, degradation, and dissociation [68]. pH can also activate expansion, contraction, and torsion functionalities [69]. Moreover, pH facilitates biocompatibility, enhancements of responsivity, drug release controlling, self-mending, color variation and biodegradation [70-73]. Due to their inherent biodegradability as well as biocompatibility, 4-DPT of pH-responsivity polymeric systems displays notable prospects for biomedical uses. pH is utilized in drug delivery applications, soft robotics, medicine, food packaging, spinal cord regeneration, and tissue engineering applications [74-78].

The electric field is another notable form of stimulus investigated in various studies, and it exhibits capabilities including high speed and remote control [79]. Inherent deficiencies linked with electric field stimulus include membrane degradation, localized heating, or cell demise [80]. Electric stimulation is utilized for tissue regeneration, artificial muscle and drug conveyance. Another rarely utilized stimulus is humidity due to inherent prospects to swell, shrink, twist, bend, and expand. The advantages of humidity use as an actuator include low cost and harmlessness [81].

4.3 Materials for 4-DPT

Since the approach for 4-DPT is similar to 3-DPT, especially relative to productivity, the novelty in 4-DPT includes material selectivity and characterization for reactions to an active entity. Commonly prevalent 3-DPT substrates include plastics, ceramics, and metals. Nevertheless, these materials are not appropriate for 4-DPT [82]. Materials that have been utilized in constructing 4-DPT include shape-memory polymeric materials, shape-memory alloys, shape-memory metals, hydrogel-sensitive materials, shape-memory ceramics, and liquid crystal elastomeric substrates [82, 83].

Smart shape-memory polymers (SMPs) are commonly utilized materials for 4-DPT technology attributable to inherent features (inexpensiveness, low density, satisfactory strain recovery, elevated ratio of shape recovery, universality sustainability, biodegradability, biocompatibility and ability to manipulate molecular weights [84, 85]. Moreover, SMP features include their lightweight nature and capability to deform significantly [86]. Moreover, SMPs perform more than shape-memory alloys relative to the end-product quality as well as dimensional precision [87]. Inherent deficiencies of SMP materials include inferior modulus strength paucity, unwanted transitional temperature, gradual time responsivity, toxicity affinity, and lack of immune responsivity [88]. Application segments of 4-DPT SMP nanomaterials include biomedicals, aerospace, inner surfaces of automobiles, textiles, and industries [89, 90].

Shape-memory hydrogels (SMHs) are another set of materials used for 4-DPT objects due to inherent ionic conductivity, functionalization simplicity, biocompatibility, stretchability and transparency. Hydrogels are established for inherent elevated water content and capability of absorbing high water levels or other biological fluids [91]. Hydrogels' scope of expansion is hindered by some parameters, including elevated cost, constraints in loading handling, inferior mechanical strength, gradual responsivity, and minimized features attributable to the dryness in open-air feasibility [92]. Selected applications of smart hydrogels for 4-DPT include healthcare, tissue engineering, drug delivery and agriculture [93].

Other materials used for 4-DPT include shape-memory alloy (SMA), shape-memory composites (SMCs), and so on [94].

5. Manufacturing Technologies of 4-DPT

Notable manufacturing technologies used in 4-DPT figurines include fused deposition modeling (FDM), direct ink writing (DIW), stereo-lithography (SLA), digital light processing (DLP) and selective laser sintering (SLS) as depicted in Figure 8 [95-100]. These 4-DPT fabrication techniques are further elucidated in Figure 9 [96].

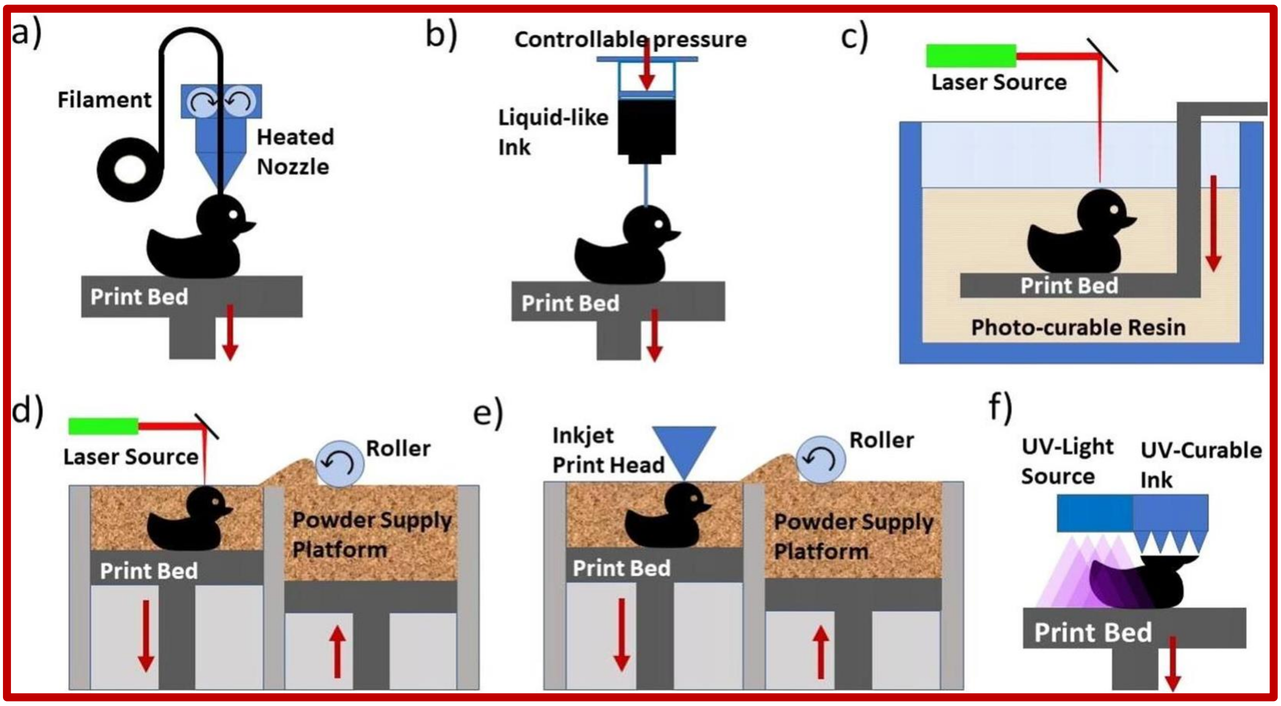

Figure 8 Schematic depictions of 4-DPT technologies. a) Fused Deposition Modeling (FDM). b) Direct Ink Writing (DIW). c) Stereo-lithography (SLA). d) Select Laser Sintering (SLS). e) Binder Jetting. f) Inkjet printing [95].

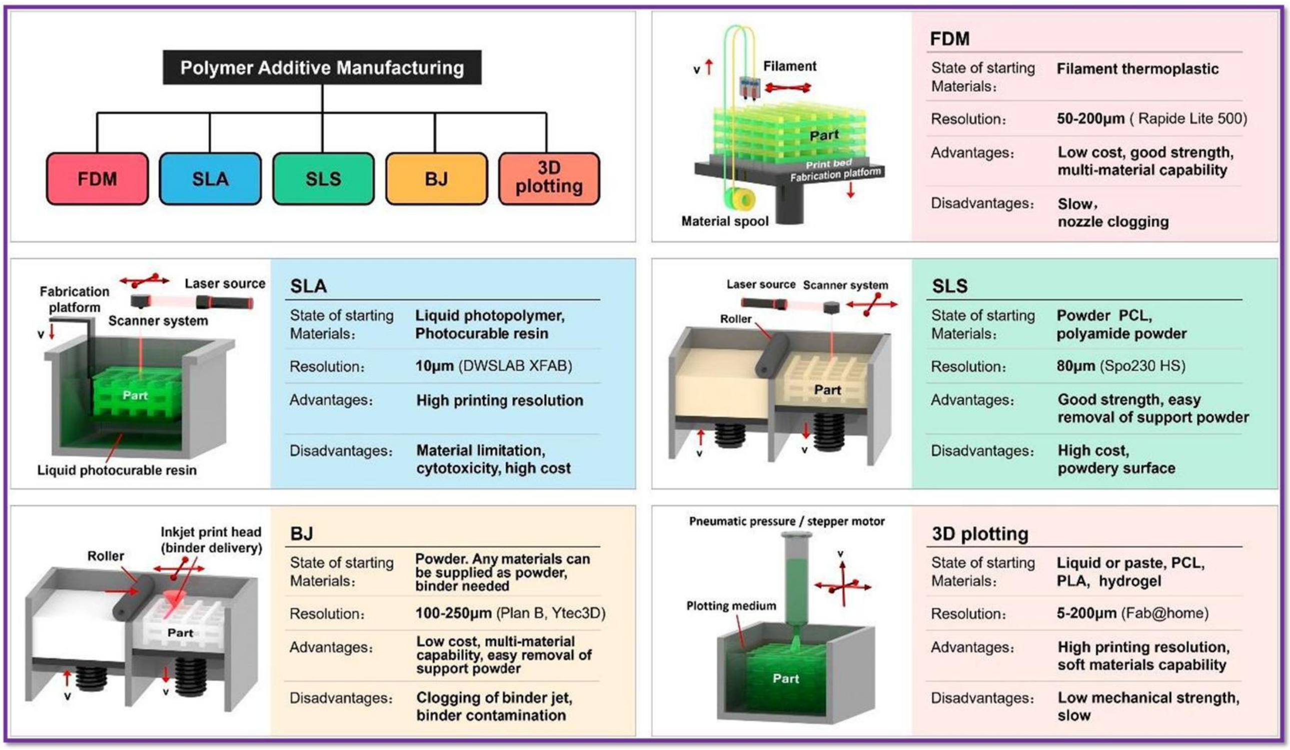

Figure 9 4-DPT techniques for polymeric nanoarchitectures [96].

FDM is commonly utilized in the fabrication of 4-D components, which are then followed by SLA, SLS, DLP, and DIW. Other techniques used in 4-DPT figure manufacturing include PolyJet printing, powder bed fusion, photolithography [101], directed energy deposition, and selective laser melting [101, 102]. Fused deposition modeling (FDM) is the most prevalent construction route for fabricating a 4-DPT object [103].

The FDM technique has utilized various stimuli (temperature, pH, light, and water) [103]. This relatively inexpensive method produces high-quality, elevated-resolution products, involving rapid printing procedures and easy accessibility [103]. FDM flaws include elevatable fragility, complexity, low printing speed, rough surface finishing, and greater materials wastage compared with other techniques [104]. The FDM techniques have been utilized for vast industrial uses (biomedical gadgets, aerospace components, origami architectures, drug conveyance, as well as optical gadgets [105]. Figure 10 depicts a schematic elucidation of the FDM technique [105].

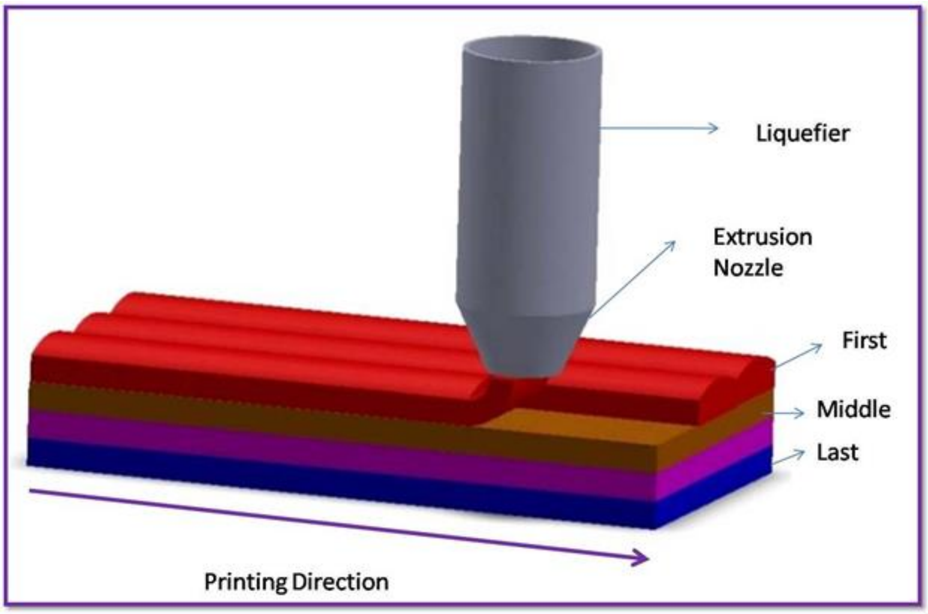

Figure 10 A schematic elucidation of the fused deposition modeling (FDM) technique [105].

Stereo-lithography (SLA) is another strategy utilized in fabricating 4-DPT objects. The benefits of SLA strategy utilization include rapid speed, high profiling, smooth surface finishing, as well as elevated resolution, and operating optimally with SMP at relatively low temperatures [106]. Despite SLA capability of printing polymeric components, the final component display inferior mechanical features [107]. Varying studies have been conducted utilizing SLA soft robotic segments, drug delivery, tracheal stents, biomedical scaffolds, and tissue engineering [108].

Selective laser sintering (SLS) facilitates component manufacturing without supporting materials [108]. Furthermore, this technique displays the benefits of elevated production volume and processing speed [108]. The SLS technique is utilized for biomedical gadgets, drug delivery, aerospace, and magnetism-responsive grippers [108].

The digital light processing (DLP) construction technique has been used to fabricate a 4-DPT figure. Texas Instruments found this strategy shortly after the SLA technology was invented in 1987 [107], offering benefits such as fast production time, elevated-quality resolution, and intricate structures [107]. DLP is limited by material selectivity, elevated cost of materials, and inferior mechanical features [108]. The DLP construction strategy has been utilized in several of applications including medication delivery, tissue engineering, and electronic gadgets [109].

Direct ink writing (DIW) is not as viable as other strategies. DIW displays minimal figurine precision of printed components in comparison with other printing strategies such as SLA [110]. However, the DIW technique is good for use in biomedicine and robotics, tissue engineering, electronic gadgets, and biomedical engineering [110].

5.1 Fabrication of Multiwalled Carbon Nanotubes/Halloysite Nanotubes Filled Heat Responsive Shape Memory Polymeric Nanocomposites for 4-DPT Applications

The shape-recovery and mechanical features of 4-DPT heat-responsive shape-memory polyurethane (SMPU) filled with multiwalled carbon nanotubes (MWCNTs) and Halloysite nanotubes (HNTs) were studied [110]. The HNTS-filled sample (1 wt.%) yielded elevated tensile, flexural, and impact strengths. However, the MWCNT-filled sample (1 wt.%) displayed rapid shape recovery.

Summarily, improved mechanical features were observed with HNT-filled samples, and a rapid shape recovery was observed with MWCNT-filled samples [110]. Garnered results revealed potential use for 4-DPT shape-memory polymeric nano architectures for continual cycles even after an extended bending deformation [111].

Figure 11 depicts the overall step of filament extrusion and 3-DPT. Parameters used (screw speed = 40 rpm, melting temperature = 210 C) utilized for filament extrusion in twin screws [111].

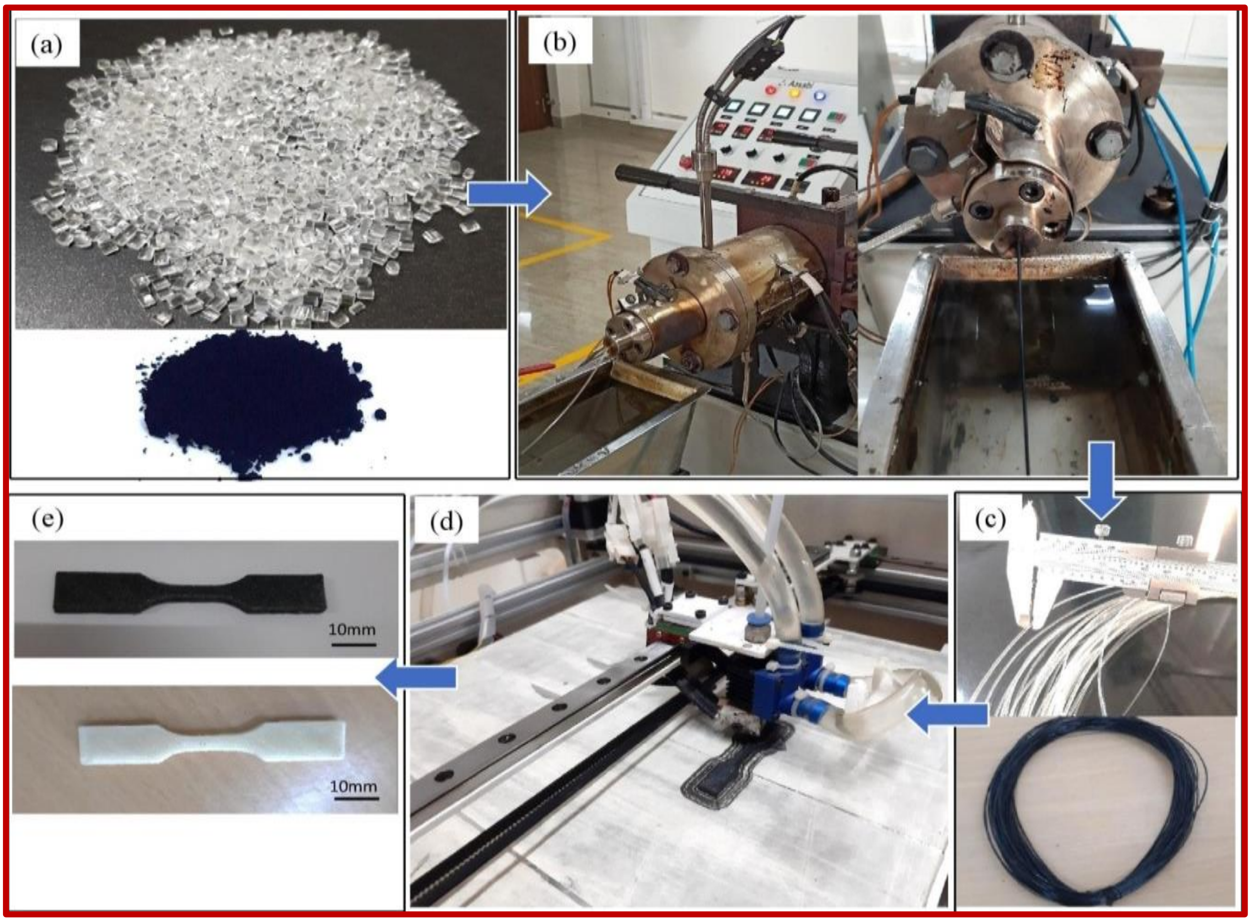

Figure 11 Elucidation of the procedure for 4-DPT of pristine SMPU and SMPU using nano-fillers: (a) SMPU pellets and MWCNT nano-fillers; (b) extraction of desired nanocomposite filaments constitution; (c) extruded filaments of pristine SMPU and filled with MWCNTs; (d) specimen 3-DPT; (e) tensile test specimens made of pristine SMPU and SMPU filled with MWCNTs [111].

The SMPU samples (125 × 15 × 5 mm^3) underwent printing for shape recovery examination. After heating above Tg (in hot water), they deformed to a U shape (as shown in Figure 12) [111].

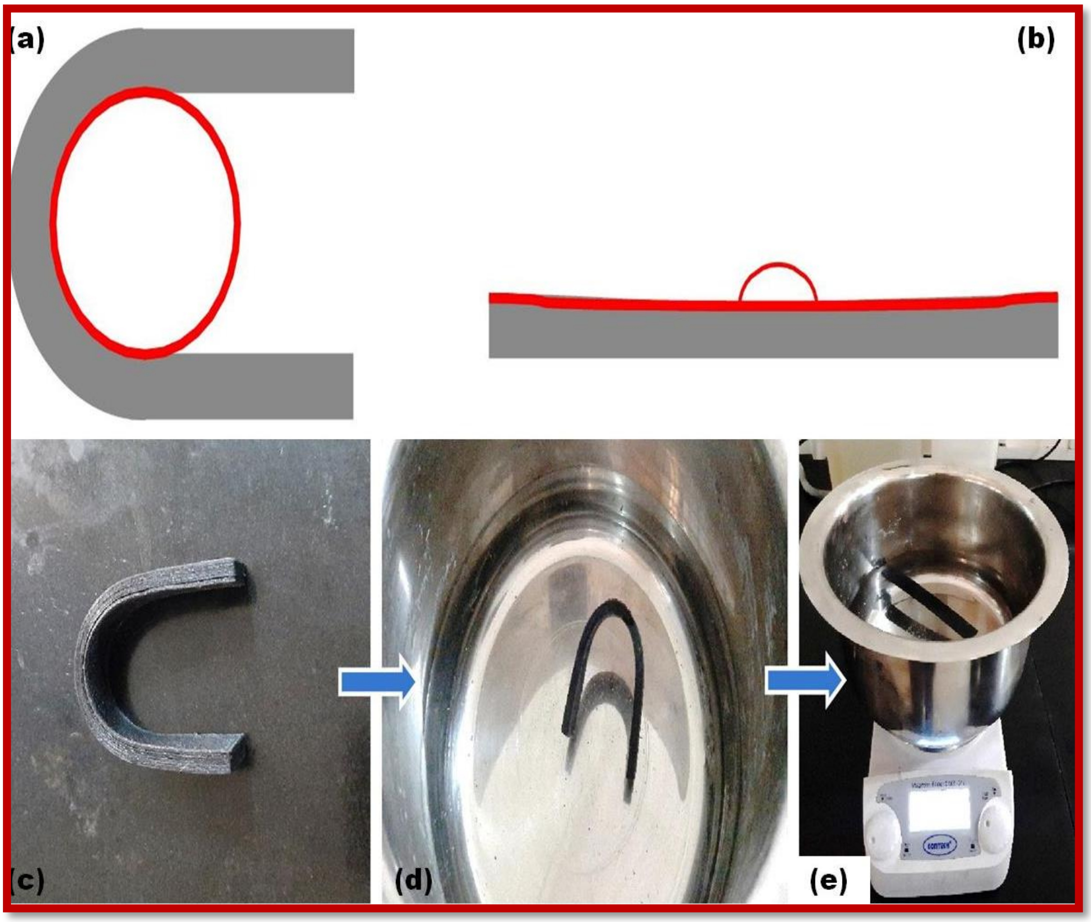

Figure 12 (a) Deformed and (b) permanent models of samples presented for shape recovery examination; (c) temporary deformed shape; (d) kept in a water bath above Tg; (e) shape recovery in a water bath [112].

6. Applications of 4-DPT

4-DPT is a potential technology capable of fabricating printed architecture at a minimal cost and labor duration [113]. 4-DPT has been vastly utilized for a vast range of applications (aerospace, military, healthcare, fashion, electronics, automobiles, agriculture, building and renewable energy) as elaborated in Figure 13 (a, b) [114].

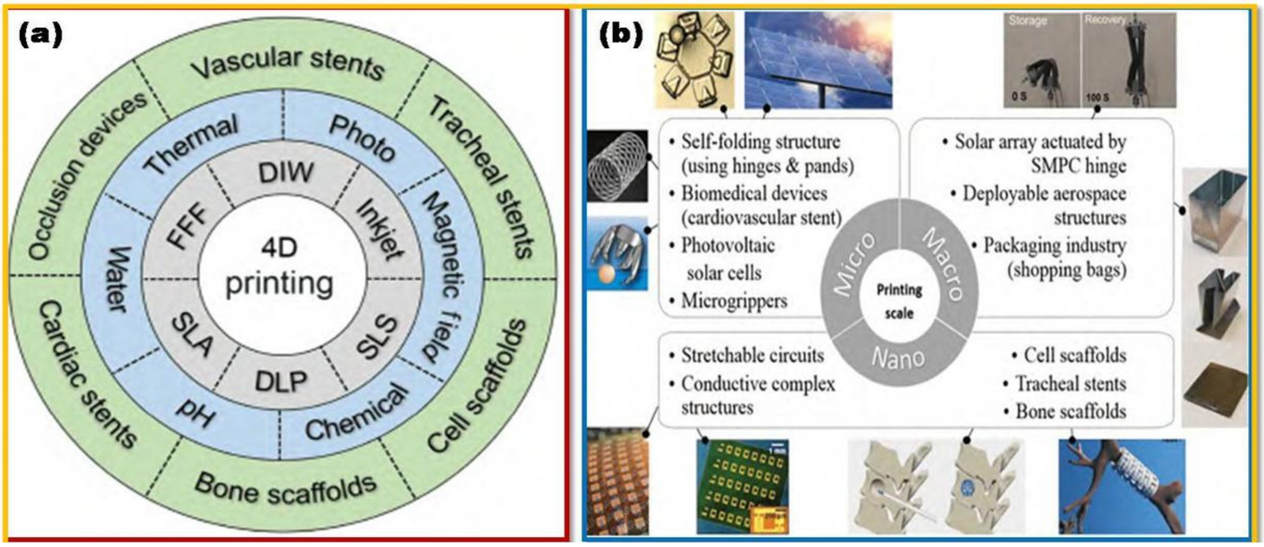

Figure 13 Premised on 4-DPT in stimulation by varying conditions, 3-DPT objects can undergo fabrication into varying biomedical uses via differing 3-DPT techniques. The parameters and the classes involved in 4-DPT are presented. (1) 3-DPT: FFF, DIW, SLS, DLP, SLA, and inkjet; (2) 4-DPT stimulus (thermal, light, chemical, pH, water, and magnetic field); (3) biomedical uses of 4-DPT: vascular stents, tracheal stents, cell scaffolds, bone scaffolds, cardiac stents, occlusion devices and other applications (a). Multi-purpose applications of 4-DPT structures [114].

6.1 Healthcare

4-DPT uses in healthcare applications have garnered great interest globally. As the healthcare segment is a vast area, this section is subdivided into the following six sub-sections: dentistry, orthopedics, pharmaceuticals, drug delivery, biomedical devices, and tissue engineering [104-115].

6.1.1 Dentistry

4-DPT is a potential material for fabricating components that function in an oral environment, with humidity and temperature variation [116]. Certain challenges linked with this technology in improving the dentistry industry include not required dimensional variations, an unstable environment, and behavioral changes [117].

6.1.2 Orthopedics

The quest for artificial bones as well as orthopedic implantations has escalated and 4-DPT offers a dynamic architecture and stimulus responsivity imperative in the orthopedic sector [118]. Advancements in the field of orthopedics using 4-DPT have been reported with the usage of materials including hydrogels, PLA, SMP, and SMA for the construction of knee prostheses, intricate composite springs for fabricating parts such as the ankle, lower leg, and foot prosthetics [119-121].

6.1.3 Pharmaceuticals

Reports have insinuated that 4-DPT is still evolving, requiring more studies before usage as consumable medication [122]. It is perceived that further investigation will be conducted in this regard for materials investigation, manufacturing, and so on [123]. Investigations into polymeric chemical architectures for oral medication have garnered attention for varying SMP research and uses within the pharmaceutical segment [124].

6.1.4 Drug Delivery

In previous years, distinct enhancements in drug-delivery strategies have been achieved [125]. Here, enhancements in drug efficacy are intended to be attained via a drug-delivery approach with minimal aftermath effects. 4-DPT has exhibited potential for accelerating the development of drug-delivery mechanisms. 4-DPT's self-folding and unfolding attributes facilitate carefully manipulated encapsulation and the effective release of medication via a programmable approach [126]. Nevertheless, a school of thought has postulated that innovative drug delivery via 4-DPT is presently constrained and biomedically unsuitable as applications require high external stimuli [127].

6.1.5 Biomedical Gadgets

The biomedical segment has displayed escalated attention to the use of 4-DPT or bioprinting. Investigations in biomedical engineering segments have revealed that materials such as hydrogels, SMPs, and so on are suitable for biomedical applications [128]. The fabrication strategies for construction of biomedical gadgets include DIW, FDM and SLA [129-131].

6.1.6 Tissue Engineering

Deficiencies inherent in 3-DPT can be mitigated using 4-DPT technologies. A vast range of research has been conducted in previous decades on ginger tissue engineering strategies [132, 133]. 3-DPT has facilitated improvement in tissue engineering. Nevertheless, there are varying challenges and hindrances linked with 3-DPT [134]. The emergence of 4-DPT has shown potential for mitigating these challenges, which include the capability of implant placement in hitherto inaccessible positions and minimally invasive surgeries [135].

Various investigators have utilized different techniques for constructing 4-DPT gadgets, including FDM, SLA, and DLP, using stimuli such as temperature, light, and magnetism with materials such as SMP, hydrogel, and SMA [136, 137].

6.2 Aerospace

An issue linked with the aerospace segment is the construction intricacies of components as well as the challenges faced in assembling these components [138]. Another notable issue is the expense of airplane replacement components, as well as intermittent disruption of the global supply network [139]. 4-DPT technology resolves these challenges by creating lower assembly components and saving time [140]. Varying investigations have reported escalated developments in aerospace components such as wings, aircraft spare parts and airplanes [141].

6.3 Electronics

Due to its inherent attributes, 4-DPT has been utilized in a vast range of electronic uses, including sensors, circuits, actuators, magnets, robotics, energy storage gadgets, antennas, and so on. The printing steps include SLS, FDM, DIW, DLP and SLA [142-144]. Commonly prevalent materials linked with electronic uses are shape-memory polymeric matrices, shape-memory hydrogels, and shape-memory alloys [145]. The stimuli propounded for constructing 4-DPT electronic gadgets are heating, light, magnetic, and water [146-150].

6.4 Food

Varying investigations have been reported on food fabrication utilizing 4-DPT strategies [151]. Commonly propounded strategies in the literature linked with the food segment include FDM, SLA, DIW, DLP, and SLM [152, 153].

6.5 Renewable Energy

4-DPT is capable of overcoming renewable energy hindrances of low efficiency and expensiveness [154]. Though prospects of 4-DPT to enhance energy efficiency have been elucidated, 4-DPT usage in the renewable energy segment remains underdeveloped in comparison with other applications.

7. Challenges and Future Outlook

The manufacturing procedure and designing of 4-DPT objects are similar to 3-DPT technology. Thus, it has been opined that a notable restrain in designing and constructing 4-DPT architectures includes limited levels of 3-D printers capable of printing 4-D components and the paucity of bespoke software. Hence, in order to escalate the manufacturing of 4-DPT figurines, the use of advanced and bespoke printers and software has become imperative. 4-DPT technology design and formulation present obstacles to the advancement of this technology [155]. Hence, a quest exists for mathematical modeling capable of predicting 4-DPT components [156]. On the other hand, varying research has been conducted on a vast range of PNCs for multifunctional applications [157-244].

8. Conclusion

Though varying investigations have been conducted to study the fabrication of 4-D components utilizing varying construction strategies, features, stimuli, vast materials, and programmable figurines, a paucity of expanded comprehension of design factors facilitating further studies exists. It was opined that most inverse challenges are based on unsure steps. Here, it is anticipated that a systematic and outlined strategy would enhance the efficiency of the 4-DPT design procedure and architecture. It has been opined that hindrances in 4-DPT involve comprehension of the features of 4-DPT components. Hence, the inclusion of varying parameters as well as their impact on 4-DPT designing would escalate advances in 4-DPT technology.

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Author Contributions

Engr. Dr. Christopher Igwe Idumah conceptualized, wrote and supervised the paper. Ifeanyi Emmanuel Okoye contributed in project development while Chioma Joan Ikebudu supervised the project development.

Competing Interests

The authors have declared that no competing interests exist.

References

1. Bhardwaj H, Jangde RK. Biomedical application of 3D printing. In: 3D printing and microfluidics in dermatology. Boca Raton, FL: CRC Press; 2024. pp. 56-80.
2. Sajjad R, Chauhdary ST, Anwar MT, Zahid A, Khosa AA, Imran M, et al. A review of 4D printing-technologies, shape shifting, smart polymer based materials, and biomedical applications. Adv Ind Eng Polym Res. 2024; 7: 20-36.
3. Mahdavi M, Zolfaghari A. Four-dimensional printing of continuous glass fiber-reinforced thermoplastics. Compos B Eng. 2024; 268: 111091.
4. Van Hoa S, Fereidouni M. Conical shells made by 4D printing of composites. Compos Part A Appl Sci Manuf. 2024; 178: 107971.
5. Saska S, Pilatti L, Blay A, Shibli JA. Bioresorbable polymers: Advanced materials and 4D printing for tissue engineering. Polymers. 2021; 13: 563.
6. Zahid A, Anwar MT, Ahmed A, Raza Y, Gohar GA, Jamshaid M. Synthesis and investigation of mechanical properties of the acrylonitrile butadiene styrene fiber composites using fused deposition modeling. 3D Print Addit Manuf. 2024; 11: e764-e772.
7. Kalogeropoulou M, Díaz-Payno PJ, Mirzaali MJ, van Osch GJ, Fratila-Apachitei LE, Zadpoor AA. 4D printed shape-shifting biomaterials for tissue engineering and regenerative medicine applications. Biofabrication. 2024; 16: 022002.
8. Sajjad R, Butt SU, Saeed HA, Anwar MT, Rasheed T. Impact of multiple infill strategy on the structural strength of single build FDM printed parts. J Manuf Process. 2023; 89: 105-110.
9. Zhan J, Li K, Ma R, Zhu L, Fang J, Cao H, et al. Achieving fine tailoring of elastocaloric properties of laser powder bed-fused NiTi alloy via laser beam manipulation. Int J Mach Tools Manuf. 2024; 202: 104210.
10. Teng X, Zhang M, Adhikari B, Ma Y. 4D printed pH-responsive labels of methacrylic anhydride grafted konjac glucomannan for detecting quality changes in respiring climacteric fruits. Food Hydrocoll. 2024; 149: 109543.
11. Cho SY, Ho DH, Jo SB, Cho JH. Direct 4D printing of functionally graded hydrogel networks for biodegradable, untethered, and multimorphic soft robots. Int J Extrem Manuf. 2024; 6: 025002.
12. Yang H, Huang S, Zhang H, Zhang J, Sheng J, Chen F, et al. 4D printed zero Poisson's ratio metamaterials with vibration isolation properties for magnetic response. Smart Mater Struct. 2024; 33: 025015.

13. Li H, Hao J, Liu X. Research progress and perspective of metallic implant biomaterials for craniomaxillofacial surgeries. Biomater Sci. 2024; 12: 252-269.
14. Li XR, Deng QS, Liu PL, He SH, Gao Y, Wei ZY, et al. Three-dimensional printed biomimetic multilayer scaffolds coordinated with sleep-related small extracellular vesicles: A strategy for extracellular matrix homeostasis and macrophage polarization to enhance osteochondral regeneration. View. 2024; 5: 20230069.
15. Kim JJ, Bae M, Kim J, Cho DW. Application of biomaterial-based three-dimensional bioprinting for organ-on-a-chip fabrication. Int J Bioprint. 2024; 10: 1972.
16. Zhao L, Yu R, He Y, Zhang M, Tian F, Wang L, et al. 3D printed epoxy/acrylate hybrid polymers with excellent mechanical and shape memory properties via UV and thermal cationic dual-curing mechanism. Addit Manuf. 2024; 79: 103904.
17. Bhusnure OG, Gholve SV, Sugave BK, Dongre RC, Gore SA, Giram PS. 3D printing & pharmaceutical manufacturing: Opportunities and challenges. Int J Bioassays. 2016; 5: 4723-4738.
18. Min JK, Mosadegh B, Dunham S, Al'Aref SJ. 3D printing applications in cardiovascular medicine. Cambridge, MA: Academic Press; 2018.
19. Bajpai A, Baigent A, Raghav S, Brádaigh CÓ, Koutsos V, Radacsi N. 4D printing: Materials, technologies, and future applications in the biomedical field. Sustainability. 2020; 12: 10628.
20. Razzaq MY, Gonzalez-Gutierrez J, Mertz G, Ruch D, Schmidt DF, Westermann S. 4D printing of multicomponent shape-memory polymer formulations. Appl Sci. 2022; 12: 7880.
21. Mallakpour S, Tabesh F, Hussain CM. 3D and 4D printing: From innovation to evolution. Adv Colloid Interface Sci. 2021; 294: 102482.
22. Joshi S, Rawat K, Karunakaran C, Rajamohan V, Mathew AT, Koziol K, et al. 4D printing of materials for the future: Opportunities and challenges. Appl Mater Today. 2020; 18: 100490.
23. Kholkhoev BC, Bardakova KN, Nikishina AN, Matveev ZA, Efremov YM, Frolova AA, et al. 4D-printing of mechanically durable high-temperature shape memory polymer with good irradiation resistance. Appl Mater Today. 2024; 36: 102022.
24. Shahbazi M, Jäger H, Ettelaie R, Chen J, Mohammadi A, Kashi PA. 4D printing of poly-Pickering high internal phase emulsions to assembly a thermo-responsive shape-memory hierarchical macroporous scaffold. Addit Manuf. 2024; 81: 103977.
25. Feng P, Zhao R, Yang F, Peng S, Pan H, Shuai C. Co-continuous structure enhanced magnetic responsive shape memory PLLA/TPU blend fabricated by 4D printing. Virtual Phys Prototyp. 2024; 19: e2290186.
26. Yakacki CM, Shandas R, Lanning C, Rech B, Eckstein A, Gall K. Unconstrained recovery characterization of shape-memory polymer networks for cardiovascular applications. Biomaterials. 2007; 28: 2255-2263.
27. Tamay DG, Dursun Usal T, Alagoz AS, Yucel D, Hasirci N, Hasirci V. 3D and 4D printing of polymers for tissue engineering applications. Front Bioeng Biotechnol. 2019; 7: 164.
28. Momeni F, Ni J. Invited article: 4D printing as a new paradigm for manufacturing with minimum energy consumption. arXiv. 2018. doi: 10.48550/arXiv.1811.12609.
29. Mulakkal MC, Trask RS, Ting VP, Seddon AM. Responsive cellulose-hydrogel composite ink for 4D printing. Mater Des. 2018; 160: 108-118.
30. Akbari S, Sakhaei AH, Kowsari K, Yang B, Serjouei A, Yuanfang Z, et al. Enhanced multimaterial 4D printing with active hinges. Smart Mater Struct. 2018; 27: 065027.

31. Ahmed K, Shiblee MN, Khosla A, Nagahara L, Thundat T, Furukawa H. Recent progresses in 4D printing of gel materials. J Electrochem Soc. 2020; 167: 037563.
32. Sossou G, Demoly F, Montavon G, Gomes S. Design for 4D printing: Rapidly exploring the design space around smart materials. Procedia CIRP. 2018; 70: 120-125.
33. Wang W, Caetano G, Ambler WS, Blaker JJ, Frade MA, Mandal P, et al. Enhancing the hydrophilicity and cell attachment of 3D printed PCL/graphene scaffolds for bone tissue engineering. Materials. 2016; 9: 992.
34. Chu H, Yang W, Sun L, Cai S, Yang R, Liang W, et al. 4D printing: A review on recent progresses. Micromachines. 2020; 11: 796.
35. Biswas MC, Chakraborty S, Bhattacharjee A, Mohammed Z. 4D printing of shape memory materials for textiles: Mechanism, mathematical modeling, and challenges. Adv Funct Mater. 2021; 31: 2100257.
36. Sahafnejad-Mohammadi I, Karamimoghadam M, Zolfagharian A, Akrami M, Bodaghi M. 4D printing technology in medical engineering: A narrative review. J Braz Soc Mech Sci Eng. 2022; 44: 233.
37. Shen B, Erol O, Fang L, Kang SH. Programming the time into 3D printing: Current advances and future directions in 4D printing. Multifunct Mater. 2020; 3: 012001.
38. Javaid M, Haleem A, Singh RP, Rab S, Suman R, Kumar L. Significance of 4D printing for dentistry: Materials, process, and potentials. J Oral Biol Craniofac Res. 2022; 12: 388-395.
39. Bodaghi M, Damanpack AR, Liao WH. Self-expanding/shrinking structures by 4D printing. Smart Mater Struct. 2016; 25: 105034.
40. Pugliese R, Regondi S. Artificial intelligence-empowered 3D and 4D printing technologies toward smarter biomedical materials and approaches. Polymers. 2022; 14: 2794.
41. Pinho AC, Buga CS, Piedade AP. The chemistry behind 4D printing. Appl Mater Today. 2020; 19: 100611.
42. Lui YS, Sow WT, Tan LP, Wu Y, Lai Y, Li H. 4D printing and stimuli-responsive materials in biomedical aspects. Acta Biomater. 2019; 92: 19-36.
43. Ashammakhi N, Ahadian S, Zengjie F, Suthiwanich K, Lorestani F, Orive G, et al. Advances and future perspectives in 4D bioprinting. Biotechnol J. 2018; 13: 1800148.
44. Maraveas C, Bayer IS, Bartzanas T. 4D printing: Perspectives for the production of sustainable plastics for agriculture. Biotechnol Adv. 2022; 54: 107785.
45. Ali M, Alam F, Fah YF, Shiryayev O, Vahdati N, Butt H. 4D printed thermochromic Fresnel lenses for sensing applications. Compos B Eng. 2022; 230: 109514.
46. Choi J, Kwon OC, Jo W, Lee HJ, Moon MW. 4D printing technology: A review. 3D Print Addit Manuf. 2015; 2: 159-167.
47. del Barrio J, Sánchez-Somolinos C. Light to shape the future: From photolithography to 4D printing. Adv Opt Mater. 2019; 7: 1900598.
48. Yang Q, Gao B, Xu F. Recent advances in 4D bioprinting. Biotechnol J. 2020; 15: 1900086.
49. Zhao W, Zhang F, Leng J, Liu Y. Personalized 4D printing of bioinspired tracheal scaffold concept based on magnetic stimulated shape memory composites. Compos Sci Technol. 2019; 184: 107866.
50. Wu H, Zhang X, Ma Z, Zhang C, Ai J, Chen P, et al. 4D printing: A material combination concept to realize 4D printed products with newly emerging property/functionality. Adv Sci. 2020; 7: 2070046.

51. Yang D, Mei H, Yao L, Yang W, Yao Y, Cheng L, et al. 3D/4D printed tunable electrical metamaterials with more sophisticated structures. J Mater Chem C. 2021; 9: 12010-12036.
52. Rayate A, Jain PK. A review on 4D printing material composites and their applications. Mater Today Proc. 2018; 5: 20474-20484.
53. Hu Y, Wang Z, Jin D, Zhang C, Sun R, Li Z, et al. Botanical-inspired 4D printing of hydrogel at the microscale. Adv Funct Mater. 2020; 30: 1907377.
54. Falahati M, Ahmadvand P, Safaee S, Chang YC, Lyu Z, Chen R, et al. Smart polymers and nanocomposites for 3D and 4D printing. Mater Today. 2020; 40: 215-245.
55. Mitchell A, Lafont U, Hołyńska M, Semprimoschnig CJ. Additive manufacturing-A review of 4D printing and future applications. Addit Manuf. 2018; 24: 606-626.
56. Chen C, Zhang M, Mujumdar AS, Phuhongsung P. Investigation of 4D printing of lotus root-compound pigment gel: Effect of pH on rapid colour change. Food Res Int. 2021; 148: 110630.
57. Kim K, Guo Y, Bae J, Choi S, Song HY, Park S, et al. 4D printing of hygroscopic liquid crystal elastomer actuators. Small. 2021; 17: 2100910.
58. Yu YJ, Hearon K, Wilson TS, Maitland DJ. The effect of moisture absorption on the physical properties of polyurethane shape memory polymer foams. Smart Mater Struct. 2011; 20: 085010.
59. Caputo MP, Berkowitz AE, Armstrong A, Müllner P, Solomon CV. 4D printing of net shape parts made from Ni-Mn-Ga magnetic shape-memory alloys. Addit Manuf. 2018; 21: 579-588.
60. Bargardi FL, Le Ferrand H, Libanori R, Studart AR. Bio-inspired self-shaping ceramics. Nat Commun. 2016; 7: 13912.
61. Goo B, Hong CH, Park K. 4D printing using anisotropic thermal deformation of 3D-printed thermoplastic parts. Mater Des. 2020; 188: 108485.
62. Ramesh S, Kiran reddy S, Usha C, Naulakha NK, Adithyakumar CR, Lohith Kumar Reddy M. Advancements in the research of 4D printing-a review. IOP Conf Ser Mater Sci Eng. 2018; 376: 012123.
63. Roudbarian N, Baniasadi M, Nayyeri P, Ansari M, Hedayati R, Baghani M. Enhancing shape memory properties of multi-layered and multi-material polymer composites in 4D printing. Smart Mater Struct. 2021; 30: 105006.
64. Melocchi A, Uboldi M, Cerea M, Foppoli A, Maroni A, Moutaharrik S, et al. Shape memory materials and 4D printing in pharmaceutics. Adv Drug Deliv Rev. 2021; 173: 216-237.
65. Lei D, Yang Y, Liu Z, Chen S, Song B, Shen A, et al. A general strategy of 3D printing thermosets for diverse applications. Mater Horiz. 2019; 6: 394-404.
66. Zhang C, Cai D, Liao P, Su JW, Deng H, Vardhanabhuti B, et al. 4D printing of shape-memory polymeric scaffolds for adaptive biomedical implantation. Acta Biomater. 2021; 122: 101-110.
67. Roach DJ, Kuang X, Yuan C, Chen K, Qi HJ. Novel ink for ambient condition printing of liquid crystal elastomers for 4D printing. Smart Mater Struct. 2018; 27: 125011.
68. Hingorani H, Zhang YF, Zhang B, Serjouei A, Ge Q. Modified commercial UV curable elastomers for passive 4D printing. Int J Smart Nano Mater. 2019; 10: 225-236.
69. Khorsandi D, Fahimipour A, Abasian P, Saber SS, Seyedi M, Ghanavati S, et al. 3D and 4D printing in dentistry and maxillofacial surgery: Printing techniques, materials, and applications. Acta Biomater. 2021; 122: 26-49.

70. He Y, Yu R, Li X, Zhang M, Zhang Y, Yang X, et al. Digital light processing 4D printing of transparent, strong, highly conductive hydrogels. ACS Appl Mater Interfaces. 2021; 13: 36286-36294.
71. Dong Y, Wang S, Ke Y, Ding L, Zeng X, Magdassi S, et al. 4D printed hydrogels: Fabrication, materials, and applications. Adv Mater Technol. 2020; 5: 2000034.
72. Ma S, Zhang Y, Wang M, Liang Y, Ren L, Ren L. Recent progress in 4D printing of stimuli-responsive polymeric materials. Sci China Technol Sci. 2020; 63: 532-544.
73. Tran TS, Balu R, Mettu S, Roy Choudhury N, Dutta NK. 4D printing of hydrogels: Innovation in material design and emerging smart systems for drug delivery. Pharmaceuticals. 2022; 15: 1282.
74. Zastrow M. 3D printing gets bigger, faster and stronger. Nature. 2020; 578: 20-23.
75. Rastogi P, Kandasubramanian B. Breakthrough in the printing tactics for stimuli-responsive materials: 4D printing. Chem Eng J. 2019; 366: 264-304.
76. Eckel ZC, Zhou C, Martin JH, Jacobsen AJ, Carter WB, Schaedler TA. Additive manufacturing of polymer-derived ceramics. Science. 2016; 351: 58-62.
77. Huebsch N, Mooney DJ. Inspiration and application in the evolution of biomaterials. Nature. 2009; 462: 426-432.
78. Del Pozo M, Sol JA, Schenning AP, Debije MG. 4D printing of liquid crystals: What's right for me? Adv Mater. 2022; 34: 2104390.
79. Wang Q, Tian X, Huang L, Li D, Malakhov AV, Polilov AN. Programmable morphing composites with embedded continuous fibers by 4D printing. Mater Des. 2018; 155: 404-413.
80. You D, Chen G, Liu C, Ye X, Wang S, Dong M, et al. 4D printing of multi-responsive membrane for accelerated in vivo bone healing via remote regulation of stem cell fate. Adv Funct Mater. 2021; 31: 2103920.
81. Kang M, Pyo Y, young Jang J, Park Y, Son YH, Choi M, et al. Design of a shape memory composite (SMC) using 4D printing technology. Sens Actuators A Phys. 2018; 283: 187-195.
82. Liu K, Zhang Q, Zhou C, Shi Y, Sun C, Sun H, et al. 4D printing of lead zirconate titanate piezoelectric composites transducer based on direct ink writing. Front Mater. 2021; 8: 659441.
83. Choong YY, Maleksaeedi S, Eng H, Wei J, Su PC. 4D printing of high performance shape memory polymer using stereolithography. Mater Des. 2017; 126: 219-225.
84. Zhao T, Yu R, Li X, Cheng B, Zhang Y, Yang X, et al. 4D printing of shape memory polyurethane via stereolithography. Eur Polym J. 2018; 101: 120-126.
85. Zhang B, Li H, Cheng J, Ye H, Sakhaei AH, Yuan C, et al. Mechanically robust and UV-curable shape-memory polymers for digital light processing based 4D printing. Adv Mater. 2021; 33: 2101298.
86. Invernizzi M, Turri S, Levi M, Suriano R. 4D printed thermally activated self-healing and shape memory polycaprolactone-based polymers. Eur Polym J. 2018; 101: 169-176.
87. Choong YY, Maleksaeedi S, Eng H, Yu S, Wei J, Su PC. High speed 4D printing of shape memory polymers with nanosilica. Appl Mater Today. 2020; 18: 100515.
88. Ouyang H, Li X, Lu X, Xia H. Selective laser sintering 4D printing of dynamic cross-linked polyurethane containing Diels-alder bonds. ACS Appl Polym Mater. 2022; 4: 4035-4046.
89. Ding Z, Yuan C, Peng X, Wang T, Qi HJ, Dunn ML. Direct 4D printing via active composite materials. Sci Adv. 2017; 3: e1602890.
90. Abolhasani D, Han SW, VanTyne CJ, Kang N, Moon YH. Powder bed fusion of two-functional Cu-Al-Ni shape memory alloys utilized for 4D printing. J Alloys Compd. 2022; 922: 166228.

91. Nadgorny M, Xiao Z, Chen C, Connal LA. Three-dimensional printing of pH-responsive and functional polymers on an affordable desktop printer. ACS Appl Mater Interfaces. 2016; 8: 28946-28954.
92. Yang H, Leow WR, Wang T, Wang J, Yu J, He K, et al. 3D printed photoresponsive devices based on shape memory composites. Adv Mater. 2017; 29: 1701627.
93. Le Duigou A, Castro M, Bevan R, Martin N. 3D printing of wood fibre biocomposites: From mechanical to actuation functionality. Mater Des. 2016; 96: 106-114.
94. Megdich A, Habibi M, Laperrière L. A review on 4D printing: Material structures, stimuli and additive manufacturing techniques. Mater Lett. 2023; 337: 133977.
95. Nikolova MP, Chavali MS. Recent advances in biomaterials for 3D scaffolds: A review. Bioact Mater. 2019; 4: 271-292.
96. Liu G, Zhang X, Chen X, He Y, Cheng L, Huo M, et al. Additive manufacturing of structural materials. Mater Sci Eng R Rep. 2021; 145: 100596.
97. Wan X, Luo L, Liu Y, Leng J. Direct ink writing based 4D printing of materials and their applications. Adv Sci. 2020; 7: 2001000.
98. Boparai KS, Singh R, Singh H. Development of rapid tooling using fused deposition modeling: A review. Rapid Prototyp J. 2016; 22: 281-299.
99. Senatov FS, Niaza KV, Zadorozhnyy MY, Maksimkin AV, Kaloshkin SD, Estrin YZ. Mechanical properties and shape memory effect of 3D-printed PLA-based porous scaffolds. J Mech Behav Biomed Mater. 2016; 57: 139-148.
100. Tian X, Liu T, Yang C, Wang Q, Li D. Interface and performance of 3D printed continuous carbon fiber reinforced PLA composites. Compos Part A Appl Sci Manuf. 2016; 88: 198-205.
101. Baker AB, Bates SR, Llewellyn-Jones TM, Valori LP, Dicker MP, Trask RS. 4D printing with robust thermoplastic polyurethane hydrogel-elastomer trilayers. Mater Des. 2019; 163: 107544.
102. Boyle BM, French TA, Pearson RM, McCarthy BG, Miyake GM. Structural color for additive manufacturing: 3D-printed photonic crystals from block copolymers. ACS Nano. 2017; 11: 3052-3058.
103. Wang Z, Abdulla R, Parker B, Samanipour R, Ghosh S, Kim K. A simple and high-resolution stereolithography-based 3D bioprinting system using visible light crosslinkable bioinks. Biofabrication. 2015; 7: 045009.
104. Qu H. Additive manufacturing for bone tissue engineering scaffolds. Mater Today Commun. 2020; 24: 101024.
105. Noroozi R, Bodaghi M, Jafari H, Zolfagharian A, Fotouhi M. Shape-adaptive metastructures with variable bandgap regions by 4D printing. Polymers. 2020; 12: 519.
106. Han D, Morde RS, Mariani S, La Mattina AA, Vignali E, Yang C, et al. 4D printing of a bioinspired microneedle array with backward-facing barbs for enhanced tissue adhesion. Adv Funct Mater. 2020; 30: 1909197.
107. Zarek M, Mansour N, Shapira S, Cohn D. 4D printing of shape memory-based personalized endoluminal medical devices. Macromol Rapid Commun. 2017; 38: 1600628.
108. Leong KF, Wiria FE, Chua CK, Li SH. Characterization of a poly-ε-caprolactone polymeric drug delivery device built by selective laser sintering. Biomed Mater Eng. 2007; 17: 147-157.
109. Ahmed A, Arya S, Gupta V, Furukawa H, Khosla A. 4D printing: Fundamentals, materials, applications and challenges. Polymer. 2021; 228: 123926.

110. Melly SK, Liu L, Liu Y, Leng J. On 4D printing as a revolutionary fabrication technique for smart structures. Smart Mater Struct. 2020; 29: 083001.
111. Namathoti S, Vakkalagadda MR. Development of multiwalled carbon nanotubes/halloysite nanotubes reinforced thermal responsive shape memory polymer nanocomposites for enhanced mechanical and shape recovery characteristics in 4D printing applications. Polymers. 2023; 15: 1371.
112. Fang JH, Hsu HH, Hsu RS, Peng CK, Lu YJ, Chen YY, et al. 4D printing of stretchable nanocookie@ conduit material hosting biocues and magnetoelectric stimulation for neurite sprouting. NPG Asia Mater. 2020; 12: 61.
113. Kim SH, Seo YB, Yeon YK, Lee YJ, Park HS, Sultan MT, et al. 4D-bioprinted silk hydrogels for tissue engineering. Biomaterials. 2020; 260: 120281.
114. Li Y, Zhang F, Liu Y, Leng J. 4D printed shape memory polymers and their structures for biomedical applications. Sci China Technol Sci. 2020; 63: 545-560.
115. Zarek M, Layani M, Cooperstein I, Sachyani E, Cohn D, Magdassi S. 3D printing of shape memory polymers for flexible electronic devices. Adv Mater. 2015; 28: 4449-4454.
116. Buj-Corral I, Domínguez-Fernández A, Gómez-Gejo A. Effect of printing parameters on dimensional error and surface roughness obtained in direct ink writing (DIW) processes. Materials. 2020; 13: 2157.
117. Kim Y, Yuk H, Zhao R, Chester SA, Zhao X. Printing ferromagnetic domains for untethered fast-transforming soft materials. Nature. 2018; 558: 274-279.
118. Liu J, Erol O, Pantula A, Liu W, Jiang Z, Kobayashi K, et al. Dual-gel 4D printing of bioinspired tubes. ACS Appl Mater Interfaces. 2019; 11: 8492-8498.
119. Felton SM, Tolley MT, Shin B, Onal CD, Demaine ED, Rus D, et al. Self-folding with shape memory composites. Soft Matter. 2013; 9: 7688-7694.
120. Carcassi OB, Contrada F, Grassi G. A review of bio-reactive envelopes and their future developments for 3D/4D printing technologies. Adv Build Ski. 2018; 139: 139-147.
121. Kim SK, Joo YS, Lee Y. Sensible media simulation in an automobile application and human responses to sensory effects. ETRI J. 2013; 35: 1001-1010.
122. Crețu C, Agop-Forna D, Forna NC. Computerized techniques used for 3d printing in proshodontics. A systematic review. Rom J Oral Rehabil. 2021; 13: 25-36.
123. Elshazly TM, Keilig L, Alkabani Y, Ghoneima A, Abuzayda M, Talaat W, et al. Potential application of 4D technology in fabrication of orthodontic aligners. Front Mater. 2022; 8: 794536.
124. Pradhan SR, Husain M, Singh R, Banwait SS. A case study of 4D-imaging-assisted 4D printing for clinical dentistry for canines. In: 4D imaging to 4D printing. Boca Raton, FL: CRC Press; 2022. pp. 119-136.
125. Haleem A, Javaid M, Vaishya R. 4D printing and its applications in orthopaedics. J Clin Orthop Trauma. 2018; 9: 275-276.
126. Javaid M, Haleem A. Significant advancements of 4D printing in the field of orthopaedics. J Clin Orthop Trauma. 2020; 11: S485-S490.
127. Govindarajan T, Shandas R. Shape memory polymers containing higher acrylate content display increased endothelial cell attachment. Polymers. 2017; 9: 572.
128. Yuan B, Zhu M, Chung CY. Biomedical porous shape memory alloys for hard-tissue replacement materials. Materials. 2018; 11: 1716.

129. Wang J, Wang Z, Song Z, Ren L, Liu Q, Ren L. Programming multistage shape memory and variable recovery force with 4D printing parameters. Adv Mater Technol. 2019; 4: 1900535.
130. Grinberg D, Siddique S, Le MQ, Liang R, Capsal JF, Cottinet PJ. 4D printing based piezoelectric composite for medical applications. J Polym Sci B Polym Phys. 2019; 57: 109-115.
131. Van Hoa S. Development of composite springs using 4D printing method. Compos Struct. 2019; 210: 869-876.
132. Bae YH, Park K. Advanced drug delivery 2020 and beyond: Perspectives on the future. Adv Drug Deliv Rev. 2020; 158: 4-16.
133. Ding H, Zhang X, Liu Y, Ramakrishna S. Review of mechanisms and deformation behaviors in 4D printing. Int J Adv Manuf Technol. 2019; 105: 4633-4649.
134. du Toit LC, Choonara YE, Kumar P, Pillay V. 4D printing and beyond: Where to from here? In: Advanced 3D-printed systems and nanosystems for drug delivery and tissue engineering. Amsterdam, Netherlands: Elsevier; 2020. pp. 139-157.
135. Melocchi A, Uboldi M, Inverardi N, Briatico-Vangosa F, Baldi F, Pandini S, et al. Expandable drug delivery system for gastric retention based on shape memory polymers: Development via 4D printing and extrusion. Int J Pharm. 2019; 571: 118700.
136. Melocchi A, Inverardi N, Uboldi M, Baldi F, Maroni A, Pandini S, et al. Retentive device for intravesical drug delivery based on water-induced shape memory response of poly (vinyl alcohol): Design concept and 4D printing feasibility. Int J Pharm. 2019; 559: 299-311.
137. Su JW, Gao W, Trinh K, Kenderes SM, Pulatsu ET, Zhang C, et al. 4D printing of polyurethane paint-based composites. Int J Smart Nano Mater. 2019; 10: 237-248.
138. Zhou Y, Zhou D, Cao P, Zhang X, Wang Q, Wang T, et al. 4D printing of shape memory vascular stent based on βCD-g-Polycaprolactone. Macromol Rapid Commun. 2021; 42: 2100176.
139. Freitag L, Gördes M, Zarogoulidis P, Darwiche K, Franzen D, Funke F, et al. Towards individualized tracheobronchial stents: Technical, practical and legal considerations. Respiration. 2017; 94: 442-456.
140. Lin C, Liu L, Liu Y, Leng J. 4D printing of bioinspired absorbable left atrial appendage occluders: A proof-of-concept study. ACS Appl Mater Interfaces. 2021; 13: 12668-12678.
141. Kuang X, Chen K, Dunn CK, Wu J, Li VC, Qi HJ. 3D printing of highly stretchable, shape-memory, and self-healing elastomer toward novel 4D printing. ACS Appl Mater Interfaces. 2018; 10: 7381-7388.
142. De Marco C, Alcântara CC, Kim S, Briatico F, Kadioglu A, de Bernardis G, et al. Indirect 3D and 4D printing of soft robotic microstructures. Adv Mater Technol. 2019; 4: 1900332.
143. Lin C, Zhang L, Liu Y, Liu L, Leng J. 4D printing of personalized shape memory polymer vascular stents with negative Poisson's ratio structure: A preliminary study. Sci China Technol Sci. 2020; 63: 578-588.
144. Roato I, Masante B, Putame G, Massai D, Mussano F. Challenges of periodontal tissue engineering: Increasing biomimicry through 3D printing and controlled dynamic environment. Nanomaterials. 2022; 12: 3878.
145. Javaid M, Haleem A. 4D printing applications in medical field: A brief review. Clin Epidemiol Glob Health. 2019; 7: 317-321.
146. Cui C, Kim DO, Pack MY, Han B, Han L, Sun Y, et al. 4D printing of self-folding and cell-encapsulating 3D microstructures as scaffolds for tissue-engineering applications. Biofabrication. 2020; 12: 045018.

147. Lai J, Li J, Wang M. 3D printed porous tissue engineering scaffolds with the self-folding ability and controlled release of growth factor. MRS Commun. 2020; 10: 579-586.
148. Miao S, Cui H, Nowicki M, Lee SJ, Almeida J, Zhou X, et al. Photolithographic-stereolithographic-tandem fabrication of 4D smart scaffolds for improved stem cell cardiomyogenic differentiation. Biofabrication. 2018; 10: 035007.
149. Zhang J, Zhao S, Zhu M, Zhu Y, Zhang Y, Liu Z, et al. 3D-printed magnetic Fe_3O_4/MBG/PCL composite scaffolds with multifunctionality of bone regeneration, local anticancer drug delivery and hyperthermia. J Mater Chem B. 2014; 2: 7583-7595.
150. Miao S, Zhu W, Castro NJ, Leng J, Zhang LG. Four-dimensional printing hierarchy scaffolds with highly biocompatible smart polymers for tissue engineering applications. Tissue Eng Part C Methods. 2016; 22: 952-963.
151. Ntouanoglou K, Stavropoulos P, Mourtzis D. 4D printing prospects for the aerospace industry: A critical review. Procedia Manuf. 2018; 18: 120-129.
152. Sossou G, Demoly F, Belkebir H, Qi HJ, Gomes S, Montavon G. Design for 4D printing: Modeling and computation of smart materials distributions. Mater Des. 2019; 181: 108074.
153. Zhang Y, Wang Q, Yi S, Lin Z, Wang C, Chen Z, et al. 4D printing of magnetoactive soft materials for on-demand magnetic actuation transformation. ACS Appl Mater Interfaces. 2021; 13: 4174-4184.
154. Li X, Yang Y, Zhang Y, Wang T, Yang Z, Wang Q, et al. Dual-method molding of 4D shape memory polyimide ink. Mater Des. 2020; 191: 108606.
155. Mu Q, Dunn CK, Wang L, Dunn ML, Qi HJ, Wang T. Thermal cure effects on electromechanical properties of conductive wires by direct ink write for 4D printing and soft machines. Smart Mater Struct. 2017; 26: 045008.
156. Cesarano F, Maurizi M, Gao C, Berto F, Penta F, Bertolin C. Experimental investigation of thermal passive-reactive sensors using 4D-printing and shape-memory biopolymers. Sustainability. 2022; 14: 14788.
157. Idumah CI, Nwuzor IC, Odera RS. Recent advances in polymer hydrogel nanoarchitectures and applications. Curr Res Green Sustain Chem. 2021; 4: 100143.
158. Idumah CI, Ezika AC, Okpechi VU. Emerging trends in polymer aerogel nanoarchitectures, surfaces, interfaces and applications. Surf Interfaces. 2021; 25: 101258.
159. Idumah CI. Progress in polymer nanocomposites for bone regeneration and engineering. Polym Polym Compos. 2021; 29: 509-527.
160. Idumah CI. Novel trends in self-healable polymer nanocomposites. J Thermoplast Compos Mater. 2021; 34: 834-858.
161. Idumah CI, Ezeani EO, Nwuzor IC. A review: Advancements in conductive polymers nanocomposites. Polym Plast Technol Mater. 2021; 60: 756-783.
162. Idumah CI. Recent advancements in self-healing polymers, polymer blends, and nanocomposites. Polym Polym Compos. 2021; 29: 246-258.
163. Idumah CI. Recent advancements in thermolysis of plastic solid wastes to liquid fuel. J Therm Anal Calorim. 2021; 147: 3495-3508.
164. Idumah CI, Obele CM, Enwerem UE. On interfacial and surface behavior of polymeric MXenes nanoarchitectures and applications. Curr Res Green Sustain Chem. 2021; 4: 100104.
165. El-Sherbiny IM, Yacoub MH. Hydrogel scaffolds for tissue engineering: Progress and challenges. Glob Cardiol Sci Pract. 2013; 2013: 38.

166. Idumah CI. Novel trends in polymer aerogel nanocomposites. Polym Plast Technol Mater. 2021; 60: 1519-1531.
167. Nwuzor IC, Idumah CI, Nwanonenyi SC, Ezeani OE. Emerging trends in self-polishing anti-fouling coatings for marine environment. Saf Extreme Environ. 2021; 3: 9-25.
168. Idumah CI. Novel trends in conductive polymeric nanocomposites, and bionanocomposites. Synth Met. 2021; 273: 116674.
169. Idumah CI, Ogbu JE, Ndem JU, Obiana V. Influence of chemical modification of kenaf fiber on xGNP-PP nano-biocomposites. SN Appl Sci. 2019; 1: 1261.
170. Idumah CI, Hassan A, Affam AC. A review of recent developments in flammability of polymer nanocomposites. Rev Chem Eng. 2015; 31: 149-177.
171. Idumah CI, Hassan A. Characterization and preparation of conductive exfoliated graphene nanoplatelets kenaf fibre hybrid polypropylene composites. Synth Met. 2016; 212: 91-104.
172. Idumah CI, Hassan A. Recently emerging trends in thermal conductivity of polymer nanocomposites. Rev Chem Eng. 2016; 32: 413-457.
173. Idumah CI, Hassan A. Emerging trends in flame retardancy of biofibers, biopolymers, biocomposites, and bionanocomposites. Rev Chem Eng. 2016; 32: 115-148.
174. Idumah CI, Hassan A. Emerging trends in graphene carbon based polymer nanocomposites and applications. Rev Chem Eng. 2016; 32: 223-264.
175. Idumah CI, Hassan A. Effect of exfoliated graphite nanoplatelets on thermal and heat deflection properties of kenaf polypropylene hybrid nanocomposites. J Polym Eng. 2016; 36: 877-889.
176. Idumah CI, Hassan A. Emerging trends in eco-compliant, synergistic, and hybrid assembling of multifunctional polymeric bionanocomposites. Rev Chem Eng. 2016; 32: 305-361.
177. Idumah CI, Hassan A, Bourbigot S. Influence of exfoliated graphene nanoplatelets on flame retardancy of kenaf flour polypropylene hybrid nanocomposites. J Anal Appl Pyrolysis. 2017; 123: 65-72.
178. Idumah CI, Hassan A. Hibiscus cannabinus fiber/PP based nano-biocomposites reinforced with graphene nanoplatelets. J Nat Fibers. 2017; 14: 691-706.
179. Idumah CI, Hassan A, Ogbu J, Ndem JU, Nwuzor IC. Recently emerging advancements in halloysite nanotubes polymer nanocomposites. Compos Interfaces. 2019; 26: 751-824.
180. Idumah CI, Hassan A, Bourbigot S. Synergistic effect of exfoliated graphene nanoplatelets and non-halogen flame retardants on flame retardancy and thermal properties of kenaf flour-PP nanocomposites. J Therm Anal Calorim. 2018; 134: 1681-1703.
181. Idumah CI, Hassan A, Ihuoma DE. Recently emerging trends in polymer nanocomposites packaging materials. Polym Plast Technol Mater. 2019; 58: 1054-1109.
182. Idumah CI, Hassan A, Ogbu JE, Ndem JU, Oti W, Obiana V. Electrical, thermal and flammability properties of conductive filler kenaf-reinforced polymer nanocomposites. J Thermoplast Compos Mater. 2020; 33: 516-540.
183. Idumah CI, Obele CM. Understanding interfacial influence on properties of polymer nanocomposites. Surf Interfaces. 2021; 22: 100879.
184. Idumah CI, Obele CM, Ezeani EO. Understanding interfacial dispersions in ecobenign polymer nano-biocomposites. Polym Plast Technol Mater. 2021; 60: 233-252.
185. Idumah CI, Obele CM, Emmanuel EO, Hassan A. Recently emerging nanotechnological advancements in polymer nanocomposite coatings for anti-corrosion, anti-fouling and self-healing. Surf Interfaces. 2020; 21: 100734.

186. Bandyopadhyay A, Heer B. Additive manufacturing of multi-material structures. Mater Sci Eng R Rep. 2018; 129: 1-16.
187. Idumah CI, Zurina M, Hassan A, Norhayani O, Shuhadah IN. Recently emerging trends in bone replacement polymer nanocomposites. In: Nanostructured polymer composites for biomedical applications. Amsterdam, Netherlands: Elsevier; 2019. pp. 139-166.
188. Idumah CI. Recent advancements in conducting polymer bionanocomposites and hydrogels for biomedical applications. Int J Polym Mater Polym Biomater. 2020; 71: 513-530.
189. Monzón MD, Paz R, Pei E, Ortega F, Suárez LA, Ortega Z, Alemán ME, Plucinski T, Clow N. 4D printing: Processability and measurement of recovery force in shape memory polymers. Int J Adv Manuf Technol. 2017; 89: 1827-1836.
190. Idumah CI. Influence of nanotechnology in polymeric textiles, applications, and fight against COVID-19. J Text Inst. 2021; 112: 2056-2076.
191. Idumah CI, Nwabanne JT, Tanjung FA. Novel trends in poly (lactic) acid hybrid bionanocomposites. Clean Mater. 2021; 2: 100022.
192. Idumah CI, Ezeani OE, Okonkwo UC, Nwuzor IC, Odera SR. Novel trends in MXene/conducting polymeric hybrid nanoclusters. J Clust Sci. 2023; 34: 45-76.
193. Idumah CI. Recently emerging trends in magnetic polymer hydrogel nanoarchitectures. PolymPlast Technol Mater. 2022; 61: 1039-1070.
194. Idumah CI, Okonkwo UC, Obele CM. Recently emerging advancements in montmorillonite polymeric nanoarchitectures and applications. Clean Mater. 2022; 4: 100071.
195. Tanjung FA, Kuswardani RA, Idumah CI, Siregar JP, Karim A. Characterization of mechanical and thermal properties of esterified lignin modified polypropylene composites filled with chitosan fibers. Polym Polym Compos. 2022; 30. doi: 10.1177/09673911221082482.
196. Idumah CI. Recent trends in MXene polymeric hydrogel bionanoarchitectures and applications. Clean Mater. 2022; 5: 100103.
197. Idumah CI. Emerging trends in poly (lactic-co-glycolic) acid bionanoarchitectures and applications. Clean Mater. 2022; 5: 100102.
198. Idumah CI. A review on polyaniline and graphene nanocomposites for supercapacitors. Polym Plast Technol Mater. 2022; 61: 1871-1907.
199. Idumah CI. Recent advancements in electromagnetic interference shielding of polymer and mxene nanocomposites. Polym Plast Technol Mater. 2023; 62: 19-53.
200. Idumah CI. Influence of surfaces and interfaces on MXene and MXene hybrid polymeric nanoarchitectures, properties, and applications. J Mater Sci. 2022; 57: 14579-14619.
201. Okonkwo UC, Idumah CI, Okafor CE, Ohagwu CC, Aronu ME, Okokpujie IP, et al. Development, characterization, and properties of polymeric nanoarchitectures for radiation attenuation. J Inorg Organomet Polym Mater. 2022; 32: 4093-4113.
202. Idumah CI. Characterization and fabrication of xerogel polymeric nanocomposites and multifunctional applications [Internet]. Durham, NC: Research Square; 2022. Available from: https://www.researchsquare.com/article/rs-1961392/v1.
203. Idumah CI. Influence of morphology and architecture on properties and applications of MXene polymeric nanocomposites. J Thermoplast Compos Mater. 2023; 36: 4124-4161.
204. Idumah CI, Nwuzor IC, Odera SR, Timothy UJ, Ngenegbo U, Tanjung FA. Recent advances in polymeric hydrogel nanoarchitectures for drug delivery applications. Int J Polym Mater Polym Biomater. 2024; 73: 1-32.

205. Idumah CI. Recently emerging advancements in thermal conductivity and flame retardancy of MXene polymeric nanoarchitectures. Polym Plast Technol Mater. 2023; 62: 510-546.
206. Idumah CI. Recently emerging advancements in polymeric nanogel nanoarchitectures for drug delivery applications. Int J Polym Mater Polym Biomater. 2024; 73: 104-116.
207. Idumah CI. Design, development, and drug delivery applications of graphene polymeric nanocomposites and bionanocomposites. Emergent Mater. 2023; 6: 777-807.
208. Idumah CI. Recently emerging trends in flame retardancy of phosphorene polymeric nanocomposites and applications. J Anal Appl Pyrolysis. 2023; 169: 105855.
209. Leist SK, Gao D, Chiou R, Zhou J. Investigating the shape memory properties of 4D printed polylactic acid (PLA) and the concept of 4D printing onto nylon fabrics for the creation of smart textiles. Virtual Phys Prototyp. 2017; 12: 290-300.
210. Idumah CI. Phosphorene polymeric nanocomposites for biomedical applications: A review. Int J Polym Mater Polym Biomater. 2024; 73: 292-309.
211. Idumah CI. Emerging advancements in xerogel polymeric bionanoarchitectures and applications. JCIS Open. 2023; 9: 100073.
212. Idumah CI, Low JH, Emmanuel EO. Recently emerging trends in xerogel polymeric nanoarchitectures and multifunctional applications. Polym Bull. 2023; 80: 11557-11587.
213. Idumah CI. Recent advances on graphene polymeric bionanoarchitectures for biomedicals. JCIS Open. 2023; 9: 100070.
214. Idumah CI, Odera RS, Ezeani EO, Low JH, Tanjung FA, Damiri F, et al. Construction, characterization, properties and multifunctional applications of stimuli-responsive shape memory polymeric nanoarchitectures: A review. Polym Plast Technol Mater. 2023; 62: 1247-1272.
215. Idumah CI. Thermal expansivity of polymer nanocomposites and applications. Polym Plast Technol Mater. 2023; 62: 1178-1203.
216. Idumah CI. Novel advancements in xerogel polymeric nanoarchitectures and multifunctional applications. J Porous Mater. 2023; 30: 1597-1615.
217. Wei H, Zhang Q, Yao Y, Liu L, Liu Y, Leng J. Direct-write fabrication of 4D active shape-changing structures based on a shape memory polymer and its nanocomposite. ACS Appl Mater Interfaces. 2017; 9: 876-883.
218. Idumah CI. MXene polymeric nanoarchitectures mechanical, deformation, and failure mechanism: A review. Polym Plast Technol Mater. 2023; 62: 443-466.
219. Idumah CI. Multifunctional properties optimization and stimuli-responsivity of shape memory polymeric nanoarchitectures and applications. Polym Eng Sci. 2023; 63: 1857-1873.
220. Idumah CI, Iwuchukwu FU, Okoye I, Ogbu JE. Flame retardant mechanisms of metal organic frameworks (MOFs) polymeric nanoarchitectures. Polym Plast Technol Mater. 2024; 63: 161-187.
221. Idumah CI, Ogbu JE. Flame retardant mechanisms of montmorillonites, layered double hydroxides and molybdenum disulfide polymeric nanoarchitectures for safety in extreme environments. Polym Plast Technol Mater. 2024; 63: 639-666.
222. Idumah CI. Recent advancements in flame retardancy of polymer nanocomposites. Online encyclopedia of polymers, polymeric materials, and polymer technology. Oxford, UK: Routledge; 2024.

223. Odera RS, Idumah CI, Ezeani EO, Okpechi VU, Madu IO, Oyeoka HC, et al. Novel advancements in flame retardant mechanisms of halloysite nanotubes polymeric nanoarchitectures. Polym Plast Technol Mater. 2024; 63: 312-345.
224. An J, Chua CK, Mironov V. A perspective on 4D bioprinting. Int J Bioprint. 2016; 2: 3-5.
225. Lee AY, An J, Chua CK. Two-way 4D printing: a review on the reversibility of 3D-printed shape memory materials. Engineering. 2017; 3: 663-674.
226. Idumah CI. Recent advancements in fire retardant mechanisms of carbon nanotubes, graphene, and fullerene polymeric nanoarchitectures. J Anal Appl Pyrolysis. 2023; 174: 106113.
227. Hornat CC, Yang Y, Urban MW. Quantitative predictions of shape-memory effects in polymers. Adv Mater. 2017; 29: 1603334.
228. Naficy S, Gately R, Gorkin III R, Xin H, Spinks GM. 4D printing of reversible shape morphing hydrogel structures. Macromol Mater Eng. 2017; 302: 1600212.
229. Idumah CI. Emerging advancements in flame retardancy of polypropylene nanocomposites. J Thermoplast Compos Mater. 2022; 35: 2665-2704.
230. Idumah CI. Design, fabrication, characterization and properties of metallic and conductive smart polymeric textiles for multifunctional applications. Nano Struct Nano Objects. 2023; 35: 100982.
231. Idumah CI. Emerging advancements in hybrid molybdenum disulfide polymeric nanoarchitectures and multifunctional applications. Polym Plast Technol Mater. 2024; 63: 2521-2548.
232. Idumah CI. Recent advancements in hybrid electrochemical biosensors nanoarchitectronics. Hybrid Adv. 2024; 8: 100347.
233. Idumah CI, Odera RS, Ezeani EO. Exploring polymeric nanotextile devices: Progress and outlook. Int J Cloth Sci Technol. 2024; 36: 961-1003.
234. Idumah CI. Poly (α-caprolactone) (PCL) biopolymeric bionanoarchitectures for tissue engineering applications. Int J Polym Mater Polym Biomater. 2024. doi: 10.1080/00914037.2024.2372795.
235. Damiri F, Fatimi A, Musuc AM, Santos AC, Paszkiewicz S, Idumah CI, et al. Nano-hydroxyapatite (nHAp) scaffolds for bone regeneration: Preparation, characterization and biological applications. J Drug Deliv Sci Technol. 2024; 95: 105601.
236. Ogbu JE, Idumah CI. Poly (lactic) acid (PLA) hybrid bionanoarchitectures for tissue engineering. Int J Polym Mater Polym Biomater. 2024. doi: 10.1080/00914037.2024.2343313.
237. Bodaghi M, Damanpack AR, Liao WH. Triple shape memory polymers by 4D printing. Smart Mater Struct. 2018; 27:065010.
238. Idumah CI. Progress in magneto-biopolymeric bionanoarchitectures for biomedical applications. Int J Polym Mater Polym Biomater. 2024. doi: 10.1080/00914037.2024.2374378.
239. Ogbu JE, Idumah CI. Metal organic frameworks (MOFs)@conducting polymeric nanoarchitectures for electrochemical energy storage applications. Polym Plast Technol Mater. 2024; 63: 939-974.
240. Okoye IJ, Idumah CI, Ogbu JE, Obi C, Ezenkwa O, Ogah OA, et al. Development, fabrication, characterization, features and multifarious applications of Cryogel polymeric nanoarchitectures: A review. Polym Plast Technol Mater. 2024; 63: 990-1010.
241. Mandon CA, Blum LJ, Marquette CA. 3D–4D printed objects: New bioactive material opportunities. Micromachines. 2017; 8: 102.

242. Obi CC, Nwabanne JT, Igbokwe PK, Idumah CI, Okpechi VU, Oyeoka HC. Novel advances in synthesis and catalytic applications of metal-organic frameworks-based nanocatalysts for CO_2 capture and transformation. J Environ Chem Eng. 2024; 12: 112835.
243. Momeni F, Liu X, Ni J. A review of 4D printing. Mater Des. 2017; 122: 42-79.
244. Bhushan B, Caspers M. An overview of additive manufacturing (3D printing) for microfabrication. Microsyst Technol. 2017; 23: 1117-1124.