REVIEW PAPER

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Review of 4D Printing Materials and their Properties

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Since its introduction, the 3D printing technology has been widely used in fields such as design, rapid prototyping, and biomedical devices, owing to its advantages of inexpensive, facile embodiment of computer 3D files into physical objects. Later, 4D printing was introduced by adding the temporal dimension to 3D. Stimuli such as heat, humidity, pH, and light trigger the actuation of printed objects without motors or wires. Smart materials that respond to external stimuli are good candidates for 4D printing. In this paper, we review the recent research on 4D printing, and categorize it with respect to the activating stimuli. The mechanical properties of 4D printing materials are mentioned as well. Finally, the future of 4D printing is discussed.

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1. Introduction

Additive manufacturing has been the subject of increasing interest for manufacturing complex three-dimensional (3D) objects by joining or layering materials.[1-3] 3D printing is a well-known additive manufacturing technology that allows researchers, manufacturers, and private users to fabricate custom 3D objects using computer software and computer aided design (CAD). The emergence of 3D printing boosted the field of rapid prototyping due to inexpensive and fast embodiment of CAD data.[4] Owing to facile and customizable characteristics of 3D printing, this approach has become widely adopted in various fields, such as fabrication of fashion and jewelry items,[5,6] polymer printed textiles,[7] supercapacitors,[8] mechanical metamaterials and sensors[9,10], bio-hybrid robotics,[11] and tissue and scaffolds.[1,11-18]

With the introduction of smart materials, the "smartness" of materials, capturing their responses to external stimuli has been utilized for shape recovery, sensors, and actuators.[19-22] In addition, attempts to combine smart materials and 3D printing resulted in 3D objects that are activated by environment and/or external stimuli. These stimuli-responsive 3D printed objects were dubbed "4D printed objects", highlighting time as the fourth dimension.[23] Shape morphing after printing is the main characteristic of 4D printing. Shape variations in 4D printed objects can be induced by different external stimuli, to cause expansion, shrinkage, or folding of the printed objects. For example, self-folding and automatic response of 4D printed objects was obtained using smart materials. In general, the characteristics of such dynamic transformations are defined by different principles for objects composed of one smart material and bilayer structures with different properties and inhomogeneity.[24,25] Stimuli-wise, 4D printing can be categorized as induced by temperature, humidity, or solvents, as well as pH or light.[26] In this paper, we review recent advances in 4D printing, focusing on stimuli. In addition, we discuss some important properties of materials that are used for actuating, such as the glass transition temperature, mechanical properties, recovery rate, and swell ratio.

4D printing is likely to play a key role in future devices, owing to its clear advantages. Printed 2D sheets can reduce the space required for transportation, thus reducing manual labor.[27] 4D printed actuators, without wires, motors, and batteries, can allow researchers to implement micro/nano-actuators and/or smart devices. Applications of 4D printing have been reported in various fields, such as biomedical devices,[28] security,[29] fabrication of precise patterned surfaces for optics, electronic devices,[30] structures with multi-directional properties,[31] and soft actuators.[32] As the 4D printing technology is developed, various additional applications are envisioned to emerge in the future.

2. Shape Memory Effect in 4D Printing

Smart materials are materials that respond to external stimuli by transforming their shape and/or volume and changing the physical properties, such as Young's modulus, stiffness, and resistance. Especially, smart materials that exhibit the shape memory effect (SME) are able to recover their original shape following environmental

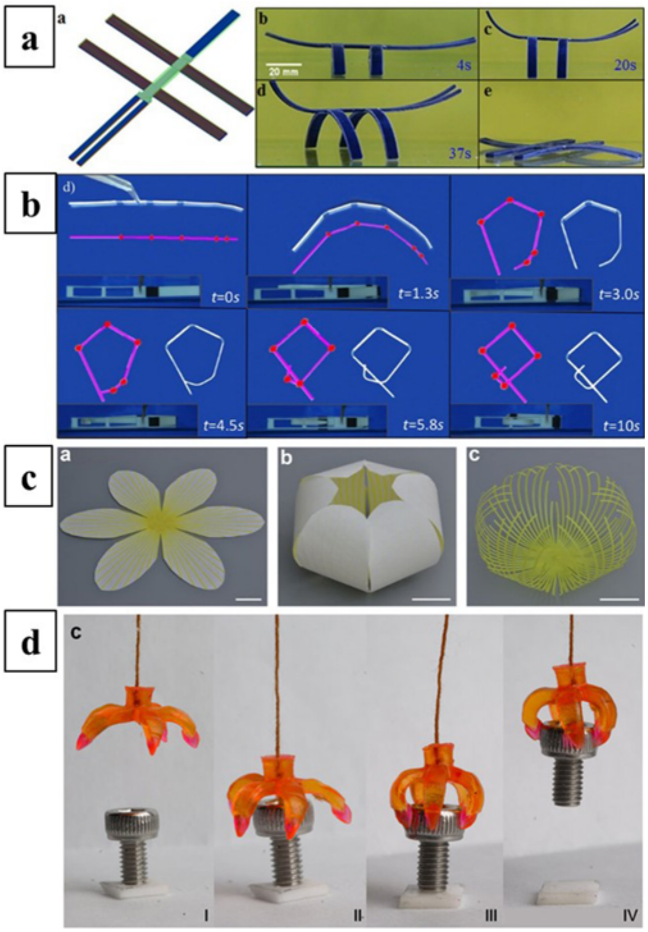

Fig. 1 4D printings responsive to thermal stimuli. (a) Sequential folding of a structure mimicking an insect composed of a fiber.[38] Reused with permission of the Nature publishing group. (b) A 1D strand with a smart hinge section with different transition temperatures.[40] Reused with permission of the Nature publishing group. (c) Formation of a flower-like 3D shape from a planar sheet with uniform internal strain.[44] Reused with permission of the Nature publishing group. (d) A multi-material gripper.[45] Reused with permission of the Nature publishing group

changes such as changes in humidity, pH, irradiation, and temperature.[20,33-35]

These transformable characteristics of materials that exhibit the SME have attracted the attention of researchers, because these properties allow to design objects that can be activated after printing. Polymers that exhibit the SME, known as shape memory polymers (SMPs), are proper candidate materials for 4D printing technology.

2.1 Transformations Using Thermal Stimuli

Thermal response SMPs react to thermal stimuli by transforming or reverting their memorized shapes. Once a permanent shape has been memorized, a thermal response SMP can revert its shape from a temporary shape to the permanent shape by absorbing thermal energy. In general, thermal response SMPs possess a characteristic transition temperature point, such as the glass-transition temperature. This transformation entails the recovery force. This recovery force has been harnessed for material activation in 4D printing.

Ge et al. (2013) introduced the concept of printed active composite materials (PAC) fabricated by directly imprinting fibers of SMPs into an elastomeric matrix. They suggested that the orientation of fibers affected the thermal response behavior of the SMPs. The glass transition temperatures of the elastomeric matrix and the SMP fibers were ~-5 and ~35ºC, respectively.[36] A PAC was applied in a hinge section as an active part of a 3D printed rod. Ge et al. (2014) fabricated PAC hinges with SMP fibers consisting of the material termed "Gray 60" with the glass transition temperature of ~47ºC. The deformation angle of the hinge was measured with respect to the strain and hinge's length, and the maximal deformation angle was ~-20˚ and was obtained for a 10-mm-long hinge.[37] Utilizing thermal response SMPs to achieve two or more shape changes with increasing temperature, Wu et al. (2016) had fabricated composite materials using more than one type of SMP fibers. Because SMPs have unique transition temperatures, multi-shape active composites should be fabricated with multi-materials. These authors used two fibers with the glass transition temperatures of ~57 and ~38ºC, respectively. The matrix was prepared with TangoBlack+, which has the lowest glass transition temperature (~2ºC) among the materials that were used by the researchers. Fibers were printed inside of the matrix of a two-layer composite. Owing to the different glass transition temperatures of the matrix and the two fibers, the composites exhibited three types of temporary shapes, and the permanent shape was recovered for temperatures above the glass transition temperatures of the both fibers. Fig. 1(a) shows the active motion of printed objects consisting of SMP fibers that have different glass transition temperatures.[38]

For achieving more complex motion of printed objects, Kai et al. (2015) used seven thermal response SMPs, each with a different glass transition temperature. An inhomogeneous strand was fabricated with hinges composed of SMPs for sequential shape recovery process. Fig. 1(b) shows the sequential folding of the one-dimensional (1D) strand with the hinge section. The seven epoxy polymers had glass transition temperatures ranging from ~32 to ~65ºC. When the strand with a graded hinge section was immersed in hot water at 100ºC, which is higher than the glass transition temperatures of all hinge section's SMPs, sequential shape recovery motion was generated by the graded hinge section.[39,40]

The concept of PAC was utilized in biomedical scaffolds fabricated using a stereolithography (SLA) printer that was assembled by Miao et al. (2016). Considering the biocompatibility for biomedical scaffolds, polymerized epoxidized soybean oil acrylate was used as a repeated unit for thermal response SMPs. The polymerization process was triggered by an ultraviolet laser and the frequency of the laser affected the extent of polymerization. The researchers synthesized biocompatible SMPs with thermal response properties and glass transition temperature of ~20ºC. The printed object consisted of a soy bean oil base polymer that could revert its original shape at ~37ºC.[16] Miao et al. (2016) reported scaffolds that exhibited the SME with graded porosity. Polycaprolactone (PCL), which is a well-known biocompatible polymer, crosslinked with two monomer groups, PCL triol and castor oil, was expected to achieve the SME. Gradient-distributed scaffold channels were obtained using

3D printing.[17]

Bakarich et al. (2015) designed a smart temperature-responsive valve that was composed of hydrogels. Hydrogels were utilized in 4D printing due to their high toughness and volume reversibility in response to environmental changes. Alginate/poly (N-isopropylacrylamide) (PNIPAAm) inks were prepared to obtain a smart valve with the actuating temperature ranging from 20 to 60°C. The smart valve closed to reduce the flow rate with length changes of 41-49% at 60°C owing to the transition temperature of the smart valve, which was in the 32-35°C range.[41]

For morphing printed flat two-dimensional (2D) sheets to 3D objects, Kwok et al. (2015) proposed a shape optimization technique by inserting cuts in a printed 2D sheet to avoid intersection of 2D patterns and deflection of a 3D shape surface with shape change. Interior and boundary cuts were designed by considering mathematical and simulation results. A 2D sheet that was printed based on the SLA process with interior and boundary cuts transformed into a 3D shape more clearly than that fabricated without cuts. Polystyrene films were located in the hinge section due to shrinkable characteristics under heating.[24]

Bodaghi et al. (2016) demonstrated the possibility of fabricating actuating units with different SMP fibers in a flexible beam. They achieved self-expansion and self-shrinkage based on the anisotropy during the printing process. Self-expansion/shrinkage characteristics were validated both experimentally and numerically. The researchers fabricated planar and tubular shapes composed of periodically arranged actuating units. The actuating units were made from commercialized SMPs in the 3D printer library of Stratasys.[42]

Zhang et al. (2015) proposed to use 3D printing for achieving uniform internal strains in thermal response SMPs. To obtain permanently shaped thermal response SMPs, an external force should be applied to form the shape and it may induce uneven strain on the SMPs. The researchers argued that 3D printing can be used to achieve uniform internal strains by using a platform as a constraint during the shape-programming process. The stored internal strains have to be considered for more accurate motion and for avoiding unexpected shape changes.[43]

Uniform distribution of internal strains enables symmetric deformations of 3D printed objects. Zhang et al. (2016) used the advantages of the above-explained method of 3D printing to fabricate inexpensive and lightweight 3D objects with thermal response characteristics. A planar sheet printed with uniform internal strain was shown in Fig. 1(c). The researchers printed polylactic acid (PLA) strips as a thermal response layer on a fixed sheet with the structure similar to the leaf vein structure, and cut the printed sheet into a six-petal shape. The cut bilayer sheet was rolled into a flow-like shape in response to a thermal stimulus. Such lightweight smart structures could be used for adaptive metamaterials whose band gap can be changed due to the transformation of the underlying lattice structure in response to a proper thermal stimulus.[44]

The efforts to obtain SMPs with different transition temperatures are ongoing. To design thermal response SMPs without commercial materials, Ge et al. (2016) synthesized SMPs from monomers with various mass fractions of crosslinker polymers and utilized projection microstereolithography (PμSL) to create high-resolution multi-materials in 4D printing. They fabricated a multi-material gripper that was shown in Fig. 1(d). The resolution obtained using the PμSL process reached a few microns. Owing to photo-curable polymers with various crosslinkers, the researchers were able to fabricate devices with a wide range of glass transition temperatures.[45]

Simulations and theoretical analyses of SMPs were conducted for predicting their active motion response. Because the PACs in response to thermal stimuli were based on the thermally active SMPs, the governing equations for numerical simulations were derived from the equations for SMPs. Analytical solutions were based on the lamina composite materials theory. As the SMPs consisted of glassy and rubbery phases, the strain function was defined by inelastic strain that occurred in glassy or rubbery phases and strain determined by thermal phase transformation.[42,46] Simulation results were compared with experimental results regarding the strain, force and recovery behavior with respect to deformation and stimuli.[38,44,45,47]

2.2 Transformations in Solvents

Water or solvents drive the SME in SMPs. Hydrophilic (water-soluble) polymers usually exhibit the SME in response to water. Penetration of water into hydrophilic SMPs may reduce the glass transition temperature below room temperature.[48] Lower glass transition temperature enables the printed objects to exhibit the SME at room temperature. As the driving force for obtaining active 3D printed objects, water-induced SME was characterized by a slower recovery of shape compared with the SME induced by heat. Despite the disadvantage of slow reaction time, water response SMPs have been utilized for objects that are used in aquatic environments or at room temperature.

Tibbits (2014) harnessed the volume reversibility effect of a hydrophilic polymer that expanded to 150% of its original volume, to develop a multi-material 1D strand that was used to form the abbreviation 'MIT' in water.[23]

The possibility of obtaining water response SMPs was investigated by Raviv et al. (2014). Linear objects were composed of alternating series of rigid objects and SMPs, and ring-shaped objects were printed. In addition, the researchers fabricated 3D printed objects for folding motion, which had a hinge section consisting of SMPs. These printed models were activated in water with water response SMPs that exhibited a maximal volume expansion of 200% of the original volume. The SMPs used by the researchers were composed of hydrophilic acrylated monomers with a small amount of difunctional molecules.[49]

By controlling the orientation of particles in materials during printing using an external magnetic force, different mechanical or swelling properties were reported by Kokkinis et al. (2015), who managed to align fused silica particles in anisotropic reinforced materials. Combining stiff materials with a soft swelling material in 3D printed objects, shape morphing was triggered owing to the different alignments of these particles.[50] The inhomogeneous printed 3D shape was used as a key-locker, shown in Fig. 2(a).

Duigou et al. (2016) used natural phenomena, such as the dispersion of pinecone seeds and hygroscopicity of wood fiber, to design moisture-actuated 3D printed objects. They incorporated commercially available wood and coconut fibers at different orientation into

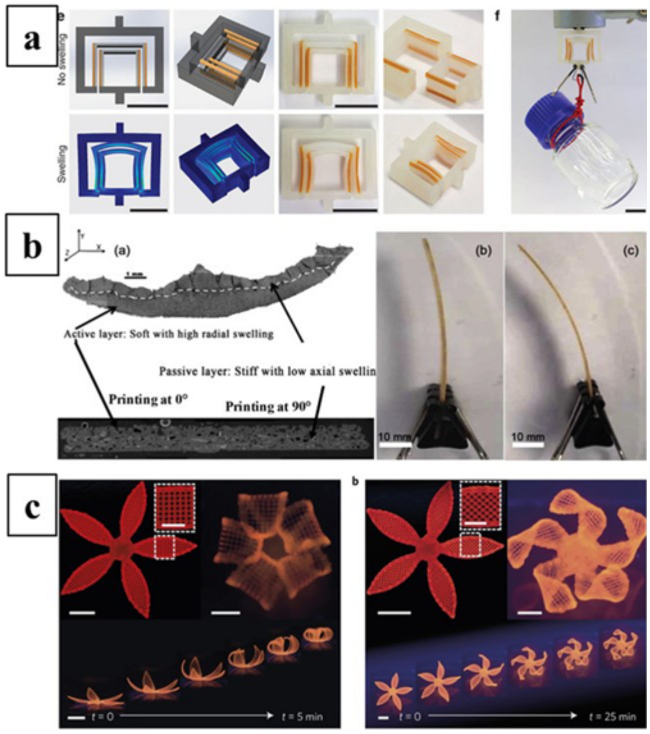

Fig. 2 4D printings activated by water. (a) A key-lock structure composed of particles that reinforce the composite.[50] Reused with permission of the Nature publishing group. (b) A hygromorph composite with wood fibers.[51] Reused with permission of Elsevier. (c) Formation of a flower-like 3D shape of a bilayer structure composed of a cellulose fiber composite.[55] Reused with permission of the Nature publishing group

elastomeric polymers. The highest tensile stress was shown for a matrix with a 0° orientation fiber; the magnitude of this stress was ~30 MPa and it was shown that water uptake ratio increases with reducing tensile strength.[51] The researchers fabricated composites with different orientations of fibers, as shown in Fig. 2(b).

Hydrogels, which are widely used in bio-applications due to their biocompatibility and superior water absorption characteristics, expand when immersed in water.[52] Hydrogels were used in 3D printing to fabricate functional or strength-enhanced printed objects.[53,54] Gladman et al. (2016) were inspired by botanical hydration systems and mixed fibrils with a hydrogel to achieve water response SME. The fibrils acted as smart materials in the composite and were aligned owing to the shear that was induced during the printing process. This anisotropic alignment of fibrils caused differences in longitudinal and transverse strains in terms of swelling. The transverse deformation was larger than the longitudinal one, because the fibrils expanded more in the transverse direction. Likewise, the differences, for the longitudinal and transverse elastic moduli, were ~40 and ~20 kPa, respectively. The anisotropic swelling property was harnessed to perform folding with various curvatures. Fig. 2(c) shows the formation of a flower-like 3D shape of a bilayer structure. The bilayer structure composed of an anisotropic composite with fibrils was used for obtaining complex shapes, such as a flower with ruffling.[55]

The water swell ratio is likely to change with temperature and Naficy et al. (2016) fabricated a bilayer composed of two different hydrogels whose swell ratio varied with temperature. Polyether-based polyurethane with different base monomers and composition ratio exhibited significantly different water swelling ratios at 20 and 60°C. The different swell ratios for this bilayer structure induced opposite signs of curvature at 20 and 60°C.[56]

Au et al. (2015) used the pressure of a liquid flow to design an automatically controlled valve using polydimethylsiloxane (PDMS). The flow rate was controlled by a 3D printed valve that changed its status according to the pressure induced by the flow. This automatic valve was composed of the soft PDMS whose Young's modulus was ~2 MPa, instead of smart materials such as hydrogels or water response SMPs. Without using smart materials or SMPs, Au et al. fabricated smart 3D printed objects.[57]

pH-sensitive polymers have been considered for drug delivery systems, to distinguish between healthy cells and diseased cells. Because healthy cells and cancerous cells cannot be distinguished by conventional anticancer drugs, SMPs response to temperature or pH was utilized for drug delivery devices.[12,35] Nadgorny et al. (2016) fabricated a macro-porous poly 2-vinylpyridine (P2VP) membrane by adding acrylonitrile-butadiene-styrene (ABS), to enhance the mechanical stability of P2VP, to stabilize injection during 3D printing. ABS with P2VP had the glass transition temperature of 120°C and enabled a reversible flow control owing to its swelling and shrinking response to pH variations.[58]

3. The Future of 4D Printing

4D printing is a relatively new and interesting research field and has significant potential for expansion. As 4D technology originated from the 3D printing technology, there are inherent challenges such as resolution, material limitations, mechanical properties and feasibility of achieving complex geometries.[59-62] 4D printing was based on the 3D printing technology such as fused deposition modeling (FDM), SLA, selective laser melting and selective laser sintering (SLS).[63,64] Commercialized 3D poly-jet printers typically has a resolution of few tens of micrometers.[61] For precise 3D shape fabrication and accurate moving, the high resolution is required for development of tissue or scaffolds or micro/nano actuator.[13,65] Improvement of resolution also led to a higher surface quality because the roughness of printed object was determined by the nozzle size. Polymeric materials of 4D printing were injected through the nozzle of 3D printer. Due to the layer by layer manufacturing, printed objects had anisotropic mechanical properties which were affected by adhesion between the polymer strands.[60,66] As most of the PACs are multi-material systems, adhesion and interlayer behavior would be a limitation to adopt functional polymeric materials.[67] Furthermore, durability of active motion of 4D printed objects was one of the obstacles for commercialization. Mechanical degradation that occurred in printed multi-material systems during thermo-mechanical cycling was identified as a fundamental issue[68]. There was also chemical degradation during the curing process. Ultra violet lights for curing photopolymers were found to cause damage of polymer and degradation of properties.[51] The thermal energy also affected the network structure significantly.[60] This

Table 1 Summary of recent research results on 4D printing materials and their properties

Year	Researcher	Materials	Printing process	Properties
2013	Ge et al.[36]	A composite of SMP fibers in an elastomeric matrix	Polyjet (Object Connex 260, Stratasys)	· Glass transition temperature Elastomeric matrix: ~-5ºC Fibers: ~35ºC · Young's modulus Elastomeric matrix: ~0.7 MPa at 15ºC Fibers: 3.3 MPa at 60ºC 13.3 MPa at 15ºC
2014	Ge et al.[37]	A composite of SMP fibers in an elastomeric matrix · TangoBlack as the elastomeric matrix · Gray 60 as the SMP fiber	Polyjet (Object Connex 260, Stratasys)	· Glass transition temperature TangoBlack: ~-5ºC Gray 60: ~47ºC · Young's modulus TangoBlack: ~0.7 MPa Gray 60: ~6 MPa (from paper)
2016	Wu et al. [38]	A composite of two SMP fibers for multiple transition temperatures · TangoBlack+ as the elastomeric matrix · DM 8530 (Gray 60), DM 9895 as the SMP fibers	Polyjet (Object Connex 260, Stratasys)	· Glass transition temperature TangoBlack+: ~2ºC DM 8530, DM 9895: ~57ºC, ~38ºC respectively · Tensile strength DM 8530 : 29-38 MPa DM 9895 : 8.5-10 MPa (from the data sheet of production company)
2015, 2016	Kai and Mao et al.[39,40]	Inhomogeneous with a hinge section · Epoxy polymers as the hinge	Polyjet (Object Connex 260, Stratasys)	· Glass transition temperature Epoxys: ~32, ~35, ~55, ~60, ~65ºC
2016	Miao et al.[16]	· Soybean oil acrylate · Ciba Irgacure 819	Customized 3D printer using SLA	· Glass transition temperature Soybean sample: ~20ºC
2016	Miao et al.[17]	A PCL-based composite · PCL · PCL triol · Caster oil	Rhinoceros 3D (McNeel)	· Glass transition temperature Sample based PCL: -8, 9, 21, 35, 0ºC Recovery speed (º/s): 69.5, 30.0, 23.1, 3.9, 75.5
2015	Bakarich et al.[41]	A composite of hydrogels · Alginate/PNIPAAm	3D-Bioplotter	· Young's modulus 10 % of NiPAAm: ~0.29 MPa at 20ºC ~1.4 MPa at 60ºC 15 % of NiPAAm: ~0.26 MPa at 20ºC ~1.8 MPa at 60ºC 20 % of NiPAAm: ~0.17 MPa at 20ºC ~1.9 MPa at 60ºC
2015, 2016	Zhang et al.[44]	· PLA	3D polymer printer (MakerBot Replicator 2, MakerBot)	· Glass transition temperature PLA: 60~65ºC
2016	Ge et al.[45]	· Phenylbis (2, 4, 6-trimethylbenzoyl) phosphine oxide as a photo-initiator · Methacrylate based polymer · Sudan I and Rhodamine B as photo -absorber	Customized SLA 3D printer	· Glass transition temperature TangoBlack: ~-5ºC Gray 60: ~47ºC · Young's modulus Sample A: 16.5 MPa with 5% failure strain Sample B: 0.92 MPa with 99% failure strain
2014	Raviv et al.[49]	Hydrophilic polymer · Vinyl Caprolactam · Polyethylene · Epoxy diacrylate oligomer · Iragcure 819 · Wetting agent	PolyJet (Object Connex 500, Stratsys)	· Young's modulus Rigid material: 2 GPa with Poisson's ratio of 0.4 Expanding material: 40 MPa in the dry state 5 MPa when fully swollen
2015	Kokkinis et al.[50]	A composite with particles · Polyurethane acrylate · Fumed silica particles · Iragcure 819 as photo-initiator	Customized magnetically assisted 3D printer (3D Discovery, regenHU)	· Young's modulus Matrix polymer: ~5 MPa Particle composite polymer: ~5 MPa, ~8.5 MPa (with respect to the orientation of particles)
2016	Duigou et al.[51]	A composite of wood fibers PLA and poly (Hydroxyalkanoate) · 40 wt% wood fiber · 40 wt% coconut fiber	3D printer (i3 Rework, Prusa)	· Young's modulus 0º compressed composite: ~4000 MPa with ~0.15% of swelling 90º compressed composite: ~ 3500MPa with ~0.43% of swelling 90º with high speed printing: ~ 900 MPa with ~0.5% of swelling

Table 1 Continued

Year	Researcher	Materials	Printing process	Properties
2016	Gladman et al.[55]	A composite of wood-derived fibrils · Cellulose micro-fibrils · Hydrogels (poly (N,N-dimethylacrylamide) matrix with PNIPAAm)	Inkjet printing method	· Young's modulus Stiff filler : > 100 GPa Printed composite: ~40 kPa, ~10% swelling strain (Longitudinal) ~20 kPa, ~40% swelling strain (Transverse)
2016	Naficy et al.[56]	A composite of fibers · Hydrogels (Alginate (Alg) / poly (Acrylamide) (PAAm))	3D-Bioplotter	· Young's modulus Hydrogels (Alg/PAAm): 26 kPa (Cast) ~66 kPa (Printed)
2015	Au et al.[57]	· PDMS · Rigid part	3D SLA printer (XC 11122, WaterShed)	· Young's modulus Rigid part : 2700 MPa (Poisson's ratio of 0.3) PDMS : ~2 MPa
2016	Nadgorny et al.[58]	· P2VP · ABS	3D printer (Replicator 2X, Makerbot)	

degradation of material caused the limitation on polymer or materials for 4D printing. This degradation of materials is a limitation on the use of polymers or materials in 4D printing. In the biomedical field, advances in biocompatible materials would be an issue, because the SLA process that can reach high resolution cannot utilize biocompatible materials that were approved by the Food and Drug Administration (such as PCL, PLA, and poly-L-lactic acid). FDM, SLS and inkjet processing, can be used to print these biocompatible materials without chemical modifications.[15,69] Likewise, various printable materials can widen the scope of 4D printing applications with respect to a variety of external stimuli. Besides, glass transition temperature of 4D printed objects was too high for human body. Because permanent shape is recovered above the glass transition temperature, glass transition temperature of 4D printed objects is a factor that affects active motion. In order to tailor the glass transition temperature, copolymerizing for changing the length of crosslink polymers could be adopted.[70]

Materials for 4D printing should be printable with properties of low glass transition temperature and suitable viscosity. Instead of SMPs, wood fibers and botanical cellulose, with the smart behavior as described above, are good candidate materials for 4D printing. On the other hand, developing the fundamental understanding of the mechanical properties of materials suitable for 4D printing can trigger the smart effects of 3D structures. In the case of Au et al. (2015), as explained above, the researchers achieved a pressure response valve using soft characteristics of PDMS. Therefore, understanding the mechanical properties and structure is important for 4D printing.[71]

Simulations have been conducted with simulation tools such as ABAQUS and COMSOL.[38,39] Most of the reported simulation results were concerned with the behavior of stress-strain curve with respect to temperature, deformation and bending behavior in 1D or 2D. Based on the classic lamina theory or SMPs behavior model, parameters such as thermo-mechanical properties were defined through experimental results. Numerous simulations were carried out using simpler models with rigid and actuating parts modeled in 1D or 2D because of complexity of 3D models. Even though actuation of 4D printed object could be predicted through a 2D model, self-collision and optimal design needs a 3D model.[24] Active motion induced by SME was analyzed using deformation behavior model of SMPs. However, the active motion of 4D printed objects was due to the deformation mismatching, swelling effect or optimized structure. Development of theoretical model for PAC would be a task for future work.

4D printing, a novel technology of additive manufacturing, has a strong potential for biomedical applications as well. Patient oriented products such as vascular, dental, artificial organs may be fabricated using 4D printing.[59,68,72] Also, micro-gripper or medical staple with self-tightening function which induces defined stress with stimulus was introduced.[20] Overcoming the low mechanical strength and durability of PAC will broaden 4D printing into artificial muscles which are subject to peak stress in range of 40-80 MPa.[73] Besides, 4D printing technology may also be utilized in fields of sensors and electrical devices.[74]

4. Summary

In this paper, we reviewed the recent research on 4D printing, categorizing the research efforts by activation stimuli. Table 1 summarizes the up-to-date research efforts on 4D printing. Based on the compilation of the recent works in this area, efforts to develop 4D printing technology as a viable tool in advanced manufacturing and prototyping are expected to expand rapidly in the near future.

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