

Additive Manufacturing of Soft Materials

Subjects: Others

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The growing demand for wearable devices, soft robotics, and tissue engineering in recent years has led to an increased effort in the field of soft materials. With the advent of personalized devices, the one-shape-fits-all manufacturing methods may soon no longer be the standard for the rapidly increasing market of soft devices. Recent findings have pushed technology and materials in the area of additive manufacturing (AM) as an alternative fabrication method for soft functional devices, taking geometrical designs and functionality to greater heights.

Keywords: additive manufacturing ; soft materials ; smart materials ; stretchable devices

1. Introduction

Soft materials have developed as the key materials to address challenges in engineering fields where flexibility, large motions, and lightweight are desired. These types of materials can be easily deformed by thermal and mechanical stresses owing to their low Young's modulus at room temperature (<100 MPa) ^[1] and high elongation without breaking. Additionally, soft materials can be found in various states such as colloids, liquids, gels, and polymers. Many soft materials display inherent structures or properties that can be significantly altered through external stimuli in a controlled manner and can be regarded as functional materials. Examples of these intrinsic functional properties include shape memory, dielectric, self-healing, and color-changing properties. Some soft materials may display more than one of these properties or can respond to multiple stimuli and are considered to be multifunctional. Additionally, soft material can be given magnetic, piezoelectric, or piezoresistive properties by incorporating functional filler.

Additive manufacturing (AM) of soft materials has been gaining popularity in recent years due to the growing interest in wearable electronics, tailored biomedical implants, and soft robotics. In the rapidly increasing market for soft devices, the one-shape-fits-all approach may soon no longer be the standard. Because of the limitations and cost associated with creating new geometries through traditional manufacturing methods, AM has been considered the future for soft material processing. In AM, a computer designed structure is sliced into individual layers and then these layers are physically realized through a variety of methods such as deposition of build material through a nozzle, jetting of binder onto a build material substrate, photopolymerization of a material vat, or thermal coalescence of powder particles. AM techniques enable freedom of geometrical design, customization with no added cost, and fabrication of complex geometries.

Materials that are otherwise rigid can be engineered to achieve softness and stretchability through advanced geometries and then be considered engineering soft materials ^[2]. Advanced geometries such as lattice and auxetic structures have previously been used to tune the mechanical properties of polymer and polymer composites which has allowed for some rigid polymers to have larger deformations without rupture. Examples of these are seen in many biomedical applications where material compliance to the geometry of the human body is necessary. The geometric freedom granted through AM has led to progress in these advanced designs; for this reason, engineering soft materials will be considered in this review.

The many AM technologies that have been developed have aided in the development of functional materials through intelligent design of structures, the development of stimuli-responsive 3D geometries, and functionality gradients through multi-material use in each individual layer. Next, different AM technologies and their application in soft functional materials manufacturing will be discussed. Then, the recent advancements, future trends and governing mechanism for AM processed functional materials will be detailed. Lastly, advances and challenges in applying these functional materials will be discussed.

1.1. Material Extrusion

Material Extrusion (ME) is an AM method that selectively deposits material through a nozzle onto a movable substrate in a layer-by-layer fashion to produce a three-dimensional part. ME is the most commonly used methodology, especially for rapid prototyping due to low cost, ease of use, and market availability. The most two common techniques for ME are fused deposition modeling (FDM) and direct ink write (DIW) also known as robocasting, paste extrusion (PE) or bio-extrusion (when applied for biomedical purposes).

FDM and DIW differ in the materials they use, and the way solidification is achieved. FDM uses thermoplastic filaments and has a fast solidification process through the cooling of the printed material below its glass transition temperature ^[3].

DIW does not require the temperature to achieve solidification and instead works with feed materials that flow due to a shear-thinning effect and retain their shape after deposition thanks to a high storage modulus (G').

FDM has been used to successfully fabricate soft functional devices using thermoplastic polyurethanes (TPU), and shape memory polymers (SMP). In contrast, since DIW only has the requirement of appropriate rheological properties for its print materials, it has expanded to include a large soft material selection including polymers with a wide range of molecular weights, liquid crystal elastomers hydrogels, and SMPs [4].

ME techniques are also of interest since they can incorporate multi-head nozzles to realize devices with elaborate designs with the use of selectively deposited support material or can produce devices with structural and functional regions by carefully placing different materials together using the different nozzles [5]. Common applications for these AM technologies have been sensors, soft robotics, biomedical, and wearable devices [6][7].

1.2. Vat Photopolymerization

Vat photopolymerization (VP) is an AM method in which a vat of liquid photopolymer resin is selectively cured by a light source in a layer-by-layer manner to construct a three-dimensional object. VP includes various techniques that differ in the way that the light source, typically ultraviolet (UV) light, is projected onto the liquid photopolymer reservoir [8]. In processes such as stereolithography (SLA), micro-stereolithography (u-SL), and two-photon polymerization (TPP), light is projected from a single-point source that traces the part's shape until a full layer is built. Processes such as digital light processing (DLP) and continuous liquid interphase production (CLIP) operate with a specialized projector that cures an entire layer at once.

VP is one of the more promising AM methods for soft material printing due to the ability to fabricate delicate objects with high resolution, close tolerances, and smooth surface finishes. Additionally, the ability to incorporate filler material into the resin allows for tunability of physical and mechanical properties leading to better control over the functionality of the final part. Despite the numerous advantages, there is a lack of available soft materials compatible with the technology. Moreover, end-use parts manufactured through VP often require more extensive post-processing steps than other AM methods and have limited production size and strength, narrowing the use of the technology for many practical applications.

VP has been previously used to print soft materials through free radical polymerization (FRP) by attaching acrylate and methacrylate functional groups to elastomer monomer, allowing for the formation of covalent crosslinks upon UV exposure. In recent years, however, research on soft material printing through VP has been moving towards click chemistries, especially thiol-ene reactions, due to the mild reaction conditions, insensitivity to oxygen or water, rapid polymerization rate, high efficiency, and low cytotoxicity. Thiol-ene click chemistries have become an efficient tool to covalently crosslink polysiloxanes into silicone elastomers, gels, and encapsulants, and have received great attention in 3D printing technologies since it exhibits high resolution and accuracy through instantaneous formations of crosslinked networks only at the local and temporal exposure to UV-radiation [9].

1.3. Material Jetting

Material jetting (MJ) is an AM method in which droplets of liquid photopolymer are selectively deposited and cured successively layer by layer. MJ offers fewer manufacturing difficulties than other AM methods such as vat polymerization, which ensures similar resolution between prints and a higher rate of production. MJ also provides a more efficient method of deposition, line-wise deposition, compared to the other AM methods previously discussed in which deposition is point-wise. Thus, the technology can achieve high accuracy and smooth surface finishes often without the need for post-processing.

MJ consists of several techniques, including drop-on-demand (DOD), PolyJet printing, and nanoparticle jetting (NPJ). DOD printers operate by accurately depositing photopolymer resins on a substrate and subsequently curing through UV-radiation layer by layer until the full structure is created. In PolyJet printing, an ultra-thin layer of photopolymer resin is sprayed on the build platform and cured through UV light. Gel-like support materials that can easily be removed by hand or dissolved are used in this technique to support complex geometries. Lastly, NPJ nanoparticles or support nanoparticles are incorporated in a resin that is sprayed onto a build platform in the form of tiny droplets. Solvents used for flow in the nanoparticle resin are then evaporated by the high temperatures inside of the machine, leaving behind structures made from nanoparticle materials.

MJ systems have become popular in recent years due to their capability for multi-material printing through DOD [10]. Although used for more advanced purposes, the MJ printing methods share many similarities to traditional 2D document printing systems making it possible for 3D printers to easily be used in an ordinary office rather than a laboratory environment. Advances in MJ technology have led to the fabrication of technology such as heat-responsive active composite structures [11] and functionally graded actuators for soft robots [12].

Although MJ is a promising AM method for soft materials, the technology, just like other AM methods, suffers from limited availability of materials that are printable. Additionally, wax-like materials, which are widely used due to their compatibility

with MJ tend to be rather fragile, limiting the application for the structure produced through this method.

1.4. Other Additive Manufacturing Methods

Table 1 summarizes the AM methods previously discussed. The remaining AM methods (binder jetting, directed energy deposition, and sheet lamination) will not be discussed in further detail since these methods are typically reserved for processing metals, ceramics, or hard polymers and are not used for the development of soft structures (inherent and engineered) as previously described.

Table 1. Summary of advantages and disadvantages of additive manufacturing methods and techniques used for the fabrication of soft functional materials.

Printing Technology	Specific Methodology	Deposition	Feature Size	Materials	Features	Drawbacks
Material Extrusion	Fuse Deposition Modeling	Line	$\approx 200 \mu\text{m}$ ^[13]	Thermoplastics	<ul style="list-style-type: none"> Low maintenance Low cost Simplicity Potential for multi-material printing 	<ul style="list-style-type: none"> Voids Limited to complex geometric prints
	Direct Ink Write	Line	$\approx 120 \mu\text{m}$ ^[14]	Thermoplastics Thermosets Elastomers Hydrogels Nanoparticles	<ul style="list-style-type: none"> Large availability of materials Rapid prototyping Potential for multi-material printing 	<ul style="list-style-type: none"> Warping Cracks Post-processing
	Stereolithography	Light single point	$\approx 50 \mu\text{m}$ ^[15]	Thermoset Elastomers Acrylate resins Nanoparticles	<ul style="list-style-type: none"> High resolution Close tolerances 	<ul style="list-style-type: none"> Low material availability
	Micro-Stereolithography	Light single point	$\approx 10 \mu\text{m}$ ^[16]		<ul style="list-style-type: none"> Smooth surface finishes 	<ul style="list-style-type: none"> Long printing times
Vat Photopolymerization	Two-Photon Polymerization	Light single point	$\approx 0.3 \mu\text{m}$ ^[17]		<ul style="list-style-type: none"> Complex geometric prints 	<ul style="list-style-type: none"> Extensive post-processing
	Continuous Liquid Interface Production	Light entire layer	$\approx 0.4 \mu\text{m}$ ^[18]	Thermoplastic Acrylate resins Nanoparticles	<ul style="list-style-type: none"> High resolution 	<ul style="list-style-type: none"> Low material availability
	Digital Light Processing	Light entire layer	$\approx 200 \mu\text{m}$ ^[19]		<ul style="list-style-type: none"> Wavelength multiplexing 	<ul style="list-style-type: none"> Post-processing

Printing Technology	Specific Methodology	Deposition	Feature Size	Materials	Features	Drawbacks
Material Jetting					<ul style="list-style-type: none"> High accuracy 	
	Drop on Demand	Drop	$\approx 32 \mu\text{m}$ ^[20]	Polymers Thermoplastic Acrylate resins Elastomers Nanoparticles	<ul style="list-style-type: none"> Little to no post-processing 	<ul style="list-style-type: none"> Inconsistent material droplet spread
	Nanoparticle Jetting	Drop	$\approx 10 \mu\text{m}$ ^[21]		<ul style="list-style-type: none"> Capability to fabricate functionally graded materials Potential for multi-material printing 	

2. Materials and Methods

2.1. Shape Memory Polymers

Shape memory polymers (SPs) are stimulus-responsive materials that can store different geometries in memory as a “temporary shape” and then return to their permanent shape by applying an external stimulus. SMPs have a high entropy state at their permanent shape, however, when stress is applied and reaches plastic deformation at their transition temperature (T_{trans}), this allows them to reach a low entropy state. When cooling to temperatures below their T_{trans} without removing the stress, the entropy is frozen at a low state, which allows a temporary shape to be fixed by trapping the kinetic energy^{[22][23]}. Lastly, when a stimulus is applied at T_{trans} , the chain mobility of the material is reactivated and returned to its high entropy state^{[22][23]}. SMPs must have a soft and a hard component, forming an interlinked polymer chain to activate functionalization of the material with a reversible shape memory effect (SME). The soft component allows elastic deformations or the shape morphing at T_{trans} , while the hard component, usually a crosslinker, determines the permanent shape of the material. The performance of the SME for shape-memory materials is typically characterized by measuring their shape fixity ratio (R_s), which measures the material's capability to be deformed into a temporary shape, and their shape recovery ratio (R_r). **Table 2** further summarizes AM processed SMPs, the AM method used for their fabrication, glass transition temperature, elastic modulus, elongation at break, durability, shape fixity and shape recovery.

Table 2. Summary of recent studies in the fabrication of SMPs using AM technologies and their impact on mechanical properties including shape fixity and shape recovery.

Materials	Technique	Glass Transition Temperature (°C)	Elastic Modulus (MPa)	Elongation at Break (%)	Durability (Cycles)	Shape Fixity (%)	Shape Recovery (%)	Elastic Modulus (MPa)	Elongation at Break (%)	Ref.
tBA, DEGDA with nanosilica fillers	DLP	56.23	-	85.2	10	100	90-97	-	85.2	[24]
filaflex embedded with polycaprolactone	FDM	70	48	700	10	76	97	48	700	[25]
N-butyl Acrylate	UV-assisted DIW	95.2	610	25.4 (Ultimate strain)	3	97.1	98.5	610	25.4 (Ultimate strain)	[26]
Polycyclooctene with boron nitrate and MWCNT	FDM	70	3.85 (Storage modulus)	-	-	98.9	99.2	3.85 (Storage modulus)	-	[27]
Poly(lactic acid (PLA)/Fe ₃ O ₄ composites	FDM	66.6	1600 (Storage modulus)	-	-	96.8	96.3	1600 (Storage modulus)	-	[28]
poly(dimethyl acrylamide-co-stearyl acrylate and/or lauryl acrylate) (PDMAAm-co-SA)	SLA	-	-	-	3	99.8	87.6	-	-	[29]

Materials	Technique	Glass Transition Temperature (°C)	Elastic Modulus (MPa)	Elongation at Break (%)	Durability (Cycles)	Shape Fixity (%)	Shape Recovery (%)	Elastic Modulus (MPa)	Elongation at Break (%)	Ref.
2-Methacryloyloxy 4-formylbenzoate	DLP	57	57 ± 4.0	39.30 ± 1.0	3	97.5 ± 0.30	91.4 ± 0.20	57 ± 4.0	39.30 ± 1.0	[30]
Poly(ethylene terephthalate) (PET)	FDM	85–100	-	45	7	100	90–98	-	45	[31]
poly(ethylene glycol) dimethacrylate (PEGDMA), isobornyl acrylate and 2-ethylhexyl acrylate	DLP	125	-	-	10	92.6	95.3	-	-	[32]

SMPs have recently gained significant attention due to diverse advantages such as their light weight, flexibility of programming mechanisms, high shape deformability, biocompatibility, and biodegradability for actuator applications. SMPs are also attractive materials to fabricate diverse types of sensors for soft robotics and aerospace applications and for minimally invasive surgery devices for biomedical purposes. 3D printing offers an effortless way to fabricate more elaborate designs, AM has the flexibility to control some of the factors that have been found to affect SME's performance including geometry, print path direction, and thickness of the sample [33]. VP has been of interest for processing SMPs due to its in-situ polymerization process that allows the fabrication of elaborate geometries for very specific applications. SLA and DLP have been reported in the fabrication of origami structures, biomimetic, and soft robotic devices. Choong et al. evaluated the use of nanosilica dispersed in tBA-co-DEGDA photocurable resin using DLP to enhance nucleation and accelerate the polymerization rate, which significantly reduced fabrication time with Rs of 100% and Rr of 87% [24]. For ME, FDM and UV-assisted DIW have been reported in the fabrication of SMPs with biomedical purposes and soft robotics application [25]. Villacres et al. used the FDM technique to print a semi-crystalline TPU where they evaluated the effect of printing orientation and infill on the SME. It was found that a print angle orientation of 60° and 100% infill resulted in an increment of failure strain and strength where the infill content had a higher influence on mechanical properties [34]. Chen et al. fabricated tough epoxy and N-butyl Acrylate SMPs composites by UV-assisted DIW with Rs of 97.1% and Rr of 98.5% [26]. Lastly, Jeon et al. fabricated multicolored photo responsive SMP structures through Polyjet printing that showed different geometries when triggered by assorted color lights of different wavelengths [35].

There are two main classifications by stimuli response known as thermal-responsive and chemo-responsive. Thermal-responsive SMPs are triggered by applying heat to the material and raising their temperature up to their T_{trans}. However, using a direct heating method could restrict their applications, which has led to the use of functional fillers to fabricate SMPs composites that trigger SME by alternative methods, such as electricity, magnetism, light, and ultrasound. Liu et al. fabricated multi-responsive SMPs using Polycyclooctene with boron nitride and multi-wall carbon nanotubes (MWCNTs) by the FDM technique. By using 20 wt.% MWCNTs in the composite, the SME could be triggered by heat (under water at 70 °C), light (100 mW·cm²), and electricity (5 V) with outstanding properties, Rs of 98.9% and Rr of 99.2% [27]. Zhang et al. fabricated PLA-Fe₃O₄ composites by FDM using magnetism (27.5 kHz) as an alternative stimulus for SME. It was found that a higher content of Fe₃O₄ led to a higher Rr, where PLA-Fe₃O₄-20% mass fraction gave the best results with Rs of 96.8% and Rr of 96.3% [28].

In chemo-responsive SMPs, the SME is triggered by altering the ionic strength to promote plasticizing and lower T_{trans} below room temperature [36]. The most common method consists of submerging the SMP in a medium, such as an organic solvent or water, that triggers the plasticizing. Recovery time can be decreased by reducing the dimensions of the polymers to micro-fibers [37]. Solvent-responsive SMPs commonly report the use of organic solvents such as ethanol, dimethyl sulfoxide methanol, and N-N dimethylformamide (DMF) [3, 12]. Some water responsive SMPs includes hydrogels (Polyvinyl alcohol, polyethylene glycol) [38] and TPUs [37]. Shiblee et al. fabricated water-responsive shape memory gels by SLA process using poly (dimethyl acrylamide-co-stearyl acrylate and/or lauryl acrylate) (PDMAAm-co-SA) by incorporating hydrophilic and hydrophobic monomers in the formulation. This shape-memory gel showed an Rs of 99.8% and Rr of 87.6% after the first cycle and Rr of 99.8% after the second cycle, the authors attributed the change of Rr to the training phenomenon [29].

Thermal-responsive SMPs are mainly activated by hot programming, which consists of heating the material to its T_{trans}. The main advantage of hot programming is a high R_s, a minimal springback and it usually requires a small amount of applied stress to produce a plastic deformation [39]. Li et al. fabricated Bisphenol-A glycerolate diacrylate (BPAGA) SMPs by DLP technique using hot programming method at glass transition temperature obtaining R_r of about 97% and R_s of 100% [40]. On the other hand, chemo responsive SMPs are activated by either hot or cold programming. Cold programming is possible below T_{trans} and usually occurs at room temperature. However, cold programming is usually more challenging since some thermosets are brittle at their rubbery point leading to possible fractures [39]. Keshavarzan et

al. evaluated hot programming and cold programming methods for BCC and rhombic structures using 3DM-LED.W, which is a commercial SMP resin for DLP. It was found that cold programming is beneficial for higher energy absorption while hot programming obtained a higher shape fixity ratio, it was also noticed that rhombic structures have a better energy absorption and recovery due to higher strength and stiffness [32].

SMPs show different behaviors according to the number of geometries that can be stored in memory, which depends on the network elasticity of the material [39]. Lastly, multi-SMPs are materials that can learn more than three geometries additionally to their permanent shape. Peng et al. synthesized triple SMPs by using poly(ethylene glycol) dimethacrylate (PEGDMA), isobornyl acrylate and 2-ethylhexyl acrylate through DLP. The SMPs were able to store two different geometries in memory with an Rs of 92.6% and Rr of 95.3% without a significant degradation after 10 cycles, proving the effectiveness of SMPs [41].

SMPs with chemical crosslinking are usually thermosets and have stronger bonds than physically crosslinked polymers and higher shape recovery. However, SMPs with chemical crosslinks cannot be reprocessed unless they have dynamic bonds. Some SMPs with chemical crosslinking take advantage of dynamic chemistries such as transesterification, transcarbamoylation, Diels–Alder bonds, disulfide bonds, diselenide bonds, and imine bonds [38]. Thermadapts are a type of SMPs with dynamic covalent bonds that have recently gained attention due to their capability to change the temporary shape after curing. Some of the dynamic covalent bonds used to fabricate SMPs are hindered urea bonds and triazolinedione. Miao et al. developed thermadapt SMPs (2-Methacryloyloxy and 4-formylbenzoate) with dynamic imine covalent bonds using DLP that allowed changing the temporary shape after printing for different actuation purposes that can be useful for soft robotics applications [30]. Davidson et al. used LCEs to develop thermadapt SMPs by radical-mediated dynamic covalent bonds using the hot DIW technique. When exposed to UV light during actuation, the exchangeable bonds that allow the change of the permanent shape of LCE are activated [42]. Some SMPs that reported the use of physical crosslinking include hydrogen bonds, ionic bonds, π -stacking, charge transfer interactions [38]. Chen et al. synthesized PET copolyester using π -stacking synergistic crosslinking to induce enhance shape memory properties by the FDM technique. The optimal copolyester was P(ET-co-PN) 20 with an Rs of 100% and Rr of 98%, it was also found to have some levels of self-healing due to π -stacking crosslinking and flame retardant properties due to the nature of PET [31].

SMPs have a diverse range of applications due to their unique mechanism, where 3D printing contributes to the evolution of elaborate designs. Many efforts to control the responsiveness by alternative methods besides direct heating have been made. An interesting research direction could be the development of SMPs with dual responsive mechanisms for different purposes that expand their fields of application. Furthermore, multi-material printing may allow the fabrication of SMPs that can store multiple geometries in memory. The evaluation of 3D printing structures to fabricate reprocessable SMPs with dynamic covalent bonds is another interesting research direction that can redefine SMPs' functionality.

2.2. Self-Healing Materials

Self-healing polymers are a branch of functional materials designed to take advantage of intricate physical or chemical processes to reform broken bonds caused by mechanical damage. The ability of self-healing polymers to respond to damage that may be difficult to detect, helps prevent the propagation of cracks or ruptures that result from the polymer's exposure to fatigue, abrasion, and other deteriorating forces during regular operation. Recent advances in AM have led to an increase in the development of self-healing materials that overcome the design limitations of traditional casting methods, resulting in self-healable structures with increased complexity and tunable properties. For this reason, the application of self-healing polymers has extended beyond protective coatings to wearable devices, implantable biomedical devices, health monitors, and electronic skins.

The healing efficiency of AM processed self-healing polymers is often measured through the restoration percentage of physical properties such as fracture strain and corresponding tensile or compressive stress. Additionally, the recovery time can also be an indicator of performance and in the case of non-autonomic processes, the activation energy required to trigger the self-healing process, which can be calculated through the Arrhenius equation. **Table 3** further summarizes AM processed self-healing polymers, the AM method used for their fabrication, their functional chemistry, recovery performance, recovery conditions, and applications.

Table 3. Summary of recent studies on AM processable self-healing polymers highlighting mechanical robustness and healing efficiency.

Materials	Tensile Strength	Max Strain	Technique	Application	Self-Healing	Stimulus	Healing Time	Efficiency	Ref.
Semi-interpenetrating polymer network elastomer	5 MPa	600%	UV-assisted DIW	Biomedical Devices	Embedded semicrystalline thermoplastic	Heat at 80 °C	20 min	<30%	[43]

Materials	Tensile Strength	Max Strain	Technique	Application	Self-Healing	Stimulus	Healing Time	Efficiency	Ref.
Ferrogel	-	288%	DIW Bioprinting	Drug Delivery and Tissue Engineering	Reversible Imine Bond Formation	No Stimulus	10 min	~95%	[44]
Dynamic Covalent Polymer Networks	3.3 MPa	140%	FDM	-	Diels–Alder Reaction	Heat at 80 °C Deionized Water at RT	12 h	96% ~70%	[45]
Photoelastomer Ink	16 kPa	130%	SLA	Soft Actuators, Structural Composites, Architected Electronics	Disulfide Exchange	Heat at 60 °C	2 h	100%	[46]
Fluid Elastic Actuators	13–129 kPa	45–400%	SLA	Soft Robotics	Unreacted Prepolymer Resin	Sunlight ~15,000 cd m ²	30 s	-	[47]
Physically Crosslinked Hydrogels	95 kPa	1300%	SLA	Flexible Devices, Soft Robotics, Tissue Engineering	Hydrophobic Association	Contact	6 h	~100%	[48]
Silicone Elastomer	~225 kPa	~330%	SLA	Endurable Wearables, Flexible Electronics	Ionic Bonding	Heat at 100 °C	12 h	>90%	[49]
Host–Guest Supramolecular Hydrogel	0.3–0.5 MPa	70%	DIW	Biomedical	Host–Guest Interactions	Mechanical Stress	1 h	Up to 80%	[50]
PEDOT:PSS with Polymeric Surfactant	3 MPa	35%	DIW	Energy Harvesting	Surfactant	Electrical Current 10–3 A	1 s	85% electrical output	[51]
Polyurethane Elastomer	3.39 ± 0.09 MPa	400.38%	DLP	-	Disulfide Exchange	Heat at 80 °C	12 h	95% First healing	[52]

In the past two years, there has been a surge in the AM of crosslinked gels with reversible imine Schiff bonding. For example, Kim et al. demonstrated the design and preparation of biocompatible, polysaccharides-based, self-healing hydrogels [53]. These hydrogels were processed through extrusion-based bioprinting to form stable geometries such as donuts, disks, and filamentous structures. The hydrogels displayed autonomic healing ability in ambient conditions (room temperature in air). The healing was based on reversible crosslinks comprising of imine bonds and hydrazine bonds, that were capable of completely restoring functionality within 10 min. The same research group took the concept one step further by incorporating iron oxide nanoparticles. This ferrogel was capable of fully recovering autonomously after gel breakage in a lapse of 10 min in three different conditions (in air at room temperature, in a buffer solution, and under a magnetic field). Additionally, this ferrogel also demonstrated shape memory capabilities that were triggered by the presence of a magnetic field [44]. In another example, Lei et al. synthesized a gelatin-based self-healing hydrogel from dialdehyde carboxymethyl cellulose and amino-modified gelatin. The hydrogel showed good fatigue resistance by recovering its original strength during 10 cyclic compressive loading and unloading tests and by having a healing efficiency of up to 90% after being heated for 1 h at 37 °C. Additionally, the hydrogel possessed ideal hemocompatibility and cytocompatibility, making it a prospective candidate for injectable tissue engineering scaffolds [54].

While self-healing gels are mainly processed through material extrusion AM techniques, most self-healing elastomers are processed through UV-based methods such as VP and MJ. Due to the nature of the technology and the rigidity of elastomers compared to gels, AM processed self-healing elastomers can obtain more complex designs, higher resolutions, better surface quality, and overall faster printing speeds, especially through the use of click chemistries such as thiol-ene photopolymerization.

Pertaining to VP, Liu et al. demonstrated the fabrication of hydrolysis-resistant silicone elastomers through photopolymerization conversion of vinyl in thiol-ene photoreactions in a stereolithography process [49]. This self-healing silicone elastomer demonstrated a healing efficiency higher than 90% when heated at 100 °C for 12 h. The silicone elastomers could be healed multiple times through reversible ionic crosslinks without losing significant strength. Furthermore, the silicone elastomers were shown to be reprocessable, retaining 85% of their original strength when pulverized and re-casted. Similarly, Yu et al. developed a photocurable PDMS-based elastomer through the same photopolymerization and AM technique but with dynamic covalent crosslinks [46]. Through disulfide exchange, this

photoelastomer was able to completely regain 100% of its original strength in significantly less time (2 h) and under milder conditions (60 °C) than the silicone elastomer Liu et al. prepared, however, with less translucency.

In regard to UV-light-assisted methods, Kuang et al. developed a novel semi-interpenetrating polymer (semi-IPN) composite for UV-light-assisted DIW that displayed self-healing properties ^[43]. Photocurable resin composed of urethane diacrylate, and n-butyl acrylate was incorporated to assist in the shape retention of the printed beads of the material when post-cured after extrusion of every layer. This allowed the group to fabricate complex structures with high stretchability like an Archimedean spiral capable of stretching over 300% strain with negligible in-plane anisotropy. The healing in the semi-IPN elastomer is based mainly on the diffusion of a semicrystalline polymer, polycaprolactone, and partially from hydrogen bonding between urethanes. As such, the elastomer demonstrated the ability to heal micro-cracks (3 mm long and 30 µm wide) after heat treatment at 80 °C for 20 min leaving only slight scarring. The elastomer was also able to heal larger cracks such as a notched gap, however, the healing efficiency was relatively low (<30%) in comparison to the self-healing materials previously discussed. Additionally, the elastomer possessed shape memory capabilities associated to the crystalline component of the elastomer. While self-healing elastomers still have a long way to go to be ready for consumer-based applications, in terms of mechanical robustness, significant progress has been made over the past few years to achieve faster healing under mild conditions (low temperatures/pressure) and better printability.

Despite self-healing materials being some of the most varied, AM processable self-healing polymers are still relatively limited due to the novelty of AM technology. One of the shortcomings of self-healing polymers is their fragility, especially for gels. Through free-standing AM techniques such as DIW and MJ, the hydrogels are susceptible to collapsing under their own weight. Although the use of support particulate gel beds is not uncommon, the manufacturing process of the particle can significantly affect the quality of the gel. For this reason, Senios et al. developed a fluid-gel bed that provides support to 3D extruded structures and prevents them from collapsing under their own weight prior to being crosslinked ^[55]. This process, known as suspended layer additive manufacturing (SLAM), was shown to be able to overcome limitations associated with printing low viscosity inks such as spread when depositing and sagging in multilayered structures, thus allowing for the fabrication of hydrogels with even more intricate designs than previously achievable. The development of AM assisting techniques such as SLAM, will help broaden the material catalog and allow for their use in a wider range of applications and push for commercial goods such as wearable electronics.

2.3. Electronic Polymers

Electronic soft polymers are those that exhibit changes to their electronic properties, such as polarization, capacitance, or resistance when exposed to mechanical, thermal, light, or pH stimulus. These characteristics have made electroactive polymers useful for actuating ^[56], sensing ^[57], and energy harvesting ^[58] applications, and to develop as a very important research area.

There exist various families of electronic polymers defined by the governing physical mechanism of their functionality. Examples of electronic polymers include dielectric elastomers, piezoresistive polymers, and piezoelectric polymers. These polymer families have been explored for AM to produce conformable, smart structures with programmed sensing and actuating behaviors.

Dielectric elastomers (DEs) are electroded elastomers that respond with large actuation to applied electric fields due to their high compliances. The Coulombic forces that result from the applied electric field cause a reduction in the thickness and anisotropic expansion of the electrode area of the elastomer. DEs are quite useful as actuators for biomedical ^[59] and soft robotics ^[60] because of their large strains, low noise, and quick response times. However, DEs have inherent disadvantages such as requiring large electric fields upwards of 100 kV/mm ^[60] and having isotropic non-directed deformations.

AM processes have been used in recent years to obtain three-dimensional dielectric elastomer actuators (DEAs). AM provides advantages to DEs such as the ability to build different elements such as the DE films, the electrodes, or the rigid frames together using a wide variety of deposition methods. ME and MJ technologies have been mainly used for the manufacturing of DEs ^[61]. Progress in MJ of DEAs has been driven by the development of rubbers suitable for jetting into films with controlled distribution and thickness. For example, AM patterned films were obtained through MJ using commercial silicone rubber by diluting them in a solvent to obtain suitable jetting properties prior to printing ^[61]. Careful design of the printing inks resulted in prints with comparable properties to traditionally casted films. Another approach to building DEAs using MJ that has been explored is the aerosol jetting of graphene oxide electrodes onto DE films ^[62]. The capability to pattern electrodes onto dielectric elastomer films allowed for electrode patterns that were unaffected by substrate stretching and it was proposed that stacked DEAs could be produced by alternating layers of silicone and graphene oxide jetting.

Multi-material manufacturing approaches enabled by AM have been used to fabricate fully functional DE actuators. In one example, a unimorph cantilever was built by selective deposition of an active barium titanate/silicon DE layer, a passive stiff silicon layer, and ionogel electrodes ^[63]. All different elements were built using a single AM process and the resulting cantilever bent upon the application of an electric field. In a similar multi-material approach, 3D actuators were manufactured by printing rigid thermoplastic frames on a prestretched acrylic DE substrate using FDM ^[64]. Stretched DEs

were used as a substrate so that once the print was finished and the substrate was released, the contraction of the substrate would transform into bending due to the mismatch of modulus across the thickness. The resulting curled-up structures followed predictions using minimization of energy approach and showcased how three-dimensional complex actuators could be built using intelligent design of printed patterns onto a DE substrate. Similarly, honeycombs of TPU were patterned using FDM into both sides of acrylic DE substrates to obtain anisotropic unidirectional actuators [65]. Higher degrees of anisotropy were obtained by varying the rib angle of the honeycombs and increasing the pre-stretch ratios of the DEs during print. Under optimal conditions, an axial strain of 15.8% with only -0.97% transverse strain was achieved by loading with 7.5 kV.

Overall, the necessity to pre-stretch DEs to obtain useful actuation behaviors limits the incorporation of these materials into all AM processes. DEs will see further development only in multi-material approaches where complete actuators can be built in one AM process. Still, smart design for AM will continue to develop and result in actuators with efficient electromechanical energy transfer.

Piezoresistive materials respond with a change in electrical resistance when strained. In the case of piezoresistive polymer composites, a network of electrically conductive fillers embedded in a thermoplastic or thermoset elastomer matrix is disturbed by strain causing a variation in the electrical conductivity of the composites [66]. This variation in electrical resistance as a function of strain if large, can be used to accurately measure strain. For piezoresistive polymer composites, sensitivity is maximum when the concentration of the filler approaches what is known as the percolation threshold. At this concentration, it is possible for agglomerations to form and impact the sensitivity. Thus, manufacturing methods for piezoresistive composites must ensure that agglomerations do not occur. Among the suitable manufacturing processes for piezoresistive composites, AM has emerged as one of the most important prospects because of the freedom in design, and because of the control of filler alignment possible in processes such as ME.

Piezoresistive soft polymer composites have been manufactured through ME using different matrix and filler systems [67][68][69][70][71]. For example, sensors of TPU with CNT fillers were manufactured using FDM [68]. The use of AM enabled new or enhanced properties in some cases. For example, biaxial strain sensors made of TPU with CNT fillers were manufactured using FDM [68]. The different patterns of CNT electrode deposition allowed for different designs, each with its own sensitivities to axial and transverse deformations, with largely unaffected mechanical properties (all materials exhibited ~50% axial strain at 4 MPa loading). In another work, a hierarchically porous lattice of TPU was printed and bonded to a stretchable matrix of the same TPU and used as a conformable sensor [70]. The macroscale porosity was controlled by the spacing of the struts, while intermediate and small-scale porosities were achieved through sacrificial fillers burned out after printing. The hierarchical porosity achieved anisotropy in response allowing the sensor to be bonded to curved substrates without affecting its pressure sensitivity. This was not previously possible for conventionally casted sensors. Other approaches used in AM of piezoresistive polymer composites to enhance their performance have consisted of using particle-matrix interface modifiers [67] and embedding CNTs to a printed elastomer lattice using partial melting [69].

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Piezoresistive polymers have been widely developed for AM using ME. Further control of the porosity, and design of metamaterial structures will enable enhanced sensitivity and a broader range of operation. However, other AM processes with higher resolutions such as VP will be needed to develop smaller piezoresistive polymer sensors for use in MEMS.

Piezoelectric materials possess a permanent polarization that when disturbed through mechanical loading produces a voltage across the material. These materials are electromechanically coupled so mechanical loads produce voltages and applied voltages cause strains. Because of this characteristic, piezoelectric materials can function as both electrically driven actuators [74] and as mechanical sensors [75].

Flexible piezoelectric materials have been developed with the help of AM by printing polymers as well as nanocomposites with piezoelectric ceramic fillers. Optimization of concentration, along with intelligent structure design, has allowed materials to exhibit larger coupling coefficients as well as increased elongations. Strategies for AM of soft piezoelectrics have focused on intelligent structure design to overcome the inherent stiffness of common piezoelectric materials such as PVDF and ceramics. For example, Li et al. used electrical field-assisted FDM to produce piezoelectric sheets with designed deformations made with nanocomposites of sodium niobate ceramics and PVDF [76]. Chiral patterns were built into the sheets to allow large deformations. Thus, once the sheets were rolled onto artery-like structures they could expand to sense radial pressures such as those found in blood flow inside the human body. Similarly, Yao et al. developed flexible and wearable piezoelectric sensors using lattice patterns through DLP [77]. Highly sensitive but soft piezoelectric lattices were possible thanks to surface functionalization of the piezoelectric ceramic fillers, which enhanced mechanical energy transfer at lower solid loadings. Three-dimensional honeycomb structures were printed using the high-resolution photopolymerization printing method and the performance of the sensors surpassed piezoelectric polymers in sensitivity and compliance. Another approach towards building compliant piezoelectric structures through AM consisted of infiltration of a ceramic lattice with PDMS elastomer [78]. This strategy allowed for complex structures to be built using only a ceramic-filled resin using SLA while still being able to obtain complaint structures afterwards.

Soft piezoelectric materials have been developed for AM despite the limited selection of polymer systems that exhibit piezoelectric polymers and the high stiffness of bulk nanocomposites of piezoelectric ceramics and elastomers. Continued development of metamaterial structures and identification of unique piezoelectric behaviors will continue to drive AM of soft piezoelectric structures composed of polymers and ceramic fillers.

Table 4 below summarizes the different efforts to print electronic polymers for sensing and actuation applications, highlights the specific elements fabricated using AM, their softness, and their individual performance.

Table 4. Summary of various soft electronic polymers recently manufactured through AM for use as sensors and actuators and their performances achieved.

Material	Application	Role of Printed Material	Young's Modulus or Elasticity	Max Strain	Printing Technique	Performance	Ref.
Silicone elastomer	Dielectric actuator	Actuating layer	≈700 kPa	600%	DOD	A maximum areal strain of 6.1% at an electric field of 84.0 V/μm	[61]
Reduced graphene oxide-elastomer nanocomposites	Dielectric actuator	Flexible electrode layer	-	104%	Aerosol Jet Printing	Electrodes with a maximum stretchability of 100% could be bonded to dielectric layers without losing conductivity	[62]
Thermoplastic polyurethane/carbon nanotubes/silver nanoparticles composites	Dielectric actuator	Actuating material	3.44 MPa in print direction	Up to 800% in print direction	FDM	Dielectric constant of 6.32 and a radial extension of 4.69% at an applied 4.67 kV	[79]
Barium titanate filled silicone elastomer	Dielectric actuator	Actuating layer	39.82 kPa	>100%	DIW	Maximum tip displacement of 6 times its thickness at 5.44 kV Blocking force of 17.27 mN and deflection of 0.85 mm under a 0.12 g mass with a 5 kV applied	[63]
Thermoplastic elastomer	Dielectric actuator	Elastic frame	-	-	FDM	A tilt angle of 128° and a blocked force of 24 mN were measured when driven by 6 kV	[64]
Thermoplastic polyurethane	Dielectric actuator	Elastic frame	-	-	FDM	Honeycomb structures could achieve a longitudinal strain of 15.8% and transverse strain of -0.97% at a driving voltage of 7.5 kV	[65]

Material	Application	Role of Printed Material	Young's Modulus or Elasticity	Max Strain	Printing Technique	Performance	Ref.
Thermoplastic polyurethane and multiwalled carbon nanotubes	Piezoresistive sensors	Sensor and electrodes	-	>100%	FDM	Anisotropic electrical resistance responses to strain with gauge factors between 1.5 and 3	[68]
Thermoplastic polyurethane and carbon nanotubes	Piezoresistive sensor	Sensor	≈ 1 MPa at a strain of 30%	-	FDM	Consistent 50% change in developed current during 1500 cycles of 5% strain	[67]
Thermoplastic elastomer	Piezoresistive sensor	Sensor body	-	800%	FDM	Pressure sensitivity as high as 136.8 kPa^{-1} at pressures $< 200 \text{ Pa}$ and GF of 6.85 at stretching	[69]
Thermoplastic polyurethane, carbon black, and silver composites	Piezoresistive sensor	Substrate, sensor, and electrode layers	-	600% for TPU, 120% for electrode layer	DIW	Low sensitivity to in-plane stretching of ($R/R_0 < 7\%$) and pressure sensitivity of 5.54 kPa^{-1} at low pressures ($< 10 \text{ kPa}$)	[70]
PDMS and multi-walled CNT	Piezoresistive sensor	Conductive pattern	-	>70%	DIW	GF of 13.01 with linear responses up to 70% tensile strain	[71]
Ionogels	Piezoresistive sensor	Sensor	Tensile strength of 0.81 MPa at 242% strain	242%	DIW	$\approx 40\%$ change in electrical current under a 29% elongation	[72]
Cellulose nanocrystals and deep eutectic solvent ionogel	Piezoresistive sensor	Sensor	0.20 MPa	At least 790%	DIW	Up to a 3.3 GF in the strain range up to 300% strain	[73]
Barium titanate	Piezoelectric sensor	Sensing lattice	-	-	Ceramic slurry DLP	Compressibility up to at least 10% and direct relationship between recorded voltage and applied strain	[78]
Polyvinylidene fluoride and sodium potassium niobate	Piezoelectric sensor	Sensor	< 1.0 MPa for designed structure	40%	FDM	Pressure sensitivity of $2.295 \text{ mV kPa}^{-1}$ and ability to self-power	[76]
Lead Zirconate Titanate	Piezoelectric sensor	Sensor	Compliance up to $3 \times 10^{-8} \text{ Pa}$	-	Ceramic slurry DLP	Variable piezoelectric charge constant up to 110 pC/N and sensitivity to pressure and extension with high conformability to surfaces	[77]

2.4. Chromic Materials

Chromic materials have the ability to change in appearance in their refractive index (e.g., color, fluorescence, brightness, transparency) when applying different stimuli such as temperature, mechanical stress, electricity, pH concentration, among others. Chromic materials are of interest due to their reversible optical mechanism that can be incorporated into wearable devices for sensing, and for soft robotics. **Table 5** further summarizes AM processed SMPs, the AM method used for their fabrication, applied stimuli, color change, absorbance wavelength and reversibility.

Table 5. Summary of chromic materials and their properties that have been recently processed through AM techniques.

Materials	Matrix	Response Type	Technique	Applied Stimuli	Color-Change	Absorbance Wavelength (nm)	Revers
Spiropyran	Polydimethylsiloxane	Mechanochromic	DIW		Off-white to Purple		Ye
Poly(butyl acrylate)	Polyacrylamide	Mechanochromic and Hydrochromic	DIW	Compression: 5.7 kPa	Entire Wavelength Spectrum Colors	500–900	Ye
Polyethyleneimine-co-poly(acrylic acid)	Polyethylene glycol diacrylate	Hydrochromic	DIW		Blue-Green, and Red	400–650	Ye
Polyurethane acrylate	Isobornyl acrylate	Thermochromic	Projection Micro Stereolithography	74.2–81.7 °C	Black, Red, Blue, Yellow, White	400–800	Ye
Poly(N-isopropylacrylamide)	Silica-alumina based gel	Thermochromic and Electrochromic	DIW	>60 °C and 0.6–1.8 Amp (2–6 V)	Transparent to Opaque State	1400–1900	Ye
Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS)/silver (Ag)	Grid/polyethylene terephthalate	Electrochromic	IJ	–0.6–0 V	Transparent, Black	633	Ye

The use of AM for soft chromic materials provides an effortless method to explore different geometrical designs and obtain tunable, mechanically activated chromic (also known as mechanochromic) responses with reversible optical properties. For example, Rohde et al. used the DIW technique to explore different geometries for mechanochromic composite elastomers, using PDMS microbeads as a matrix with spiropyran aggregates as a functional filler [80]. Activation of the chromic mechanism was possible by applying either a low mechanical strain under uniaxial tension or compression. The soft elastomer composite showed reversible mechanochromic properties displaying a purple color in the area of applied mechanical force and returning to white after releasing such force. Chen et al. fabricated highly stretchable photonic crystal hydrogels with reversible mechanochromic properties by DIW technique [81]. The physically crosslinked poly(butylacrylate) (PBA) composites provided a high elongation at break of 2800% and reversible color change from blue to grey under tension and compression.

Additionally, AM has contributed to the fabrication of complex inks with moisture-activated chromic properties (often referred to as hydrochromism) that allow the obtainment of multiple color changes. For example, Yao et al. developed a 3D printable hydrogel ink for the DIW technique to develop soft actuators with shape memory and appearance tuning properties [85]. By using polyethyleneimine-co-poly (acrylic acid) (PEI-co-PAA), hydrochromism was produced, showing tunable luminescence from blue to green, which can be controlled by water absorption of the actuators in the range of 20% to 90% relative humidity. Moreover, by the incorporation of fluorophore-lanthanide an additional red color was also tunable by water absorption in the sample. The hydrochromic soft actuators also showed a reversible change in opacity from opaque to transparent produced by phase separation caused by dehydration.

Thermally activated chromic (often referred to as thermochromic) are the most reported chromic materials due to the simplicity of their chromism mechanism tuning. One example is Chen et al. who developed a 3D printable resin with polyurethane acrylate (PUAs) oligomer and isobornyl acrylate (IBOA) monomer with shape memory properties for the μ SL process [82]. By the addition of thermochromic microcapsules, it was possible to fabricate self-actuating devices with reversible change colors from red to white with tunable glass transition temperature from 74.2 to 81.7 °C.

Electrically activated chromic materials (also known as electrochromic) have been of interest for soft functional devices as an alternative method to used temperature to trigger a color change. For example, Zhou et al. used DIW technique to fabricate a device using poly(N-isopropylacrylamide) (PNIPAm) as functional particles dispersed in an Si/Al sol-gel, producing a hybrid hydrogel (PSAHH) with reversible appearance properties from opaque to translucent that could be triggered by heat or electricity [83]. These reversible thermochromic and electrochromic properties could be triggered by heating the samples above 60 °C or by increasing current from 0.6 to 1.8 Amp (2–6 V). The change in the sample's appearance was due to the temperature-induced dehydration of PNIPAm particles, which acted as light scattering fillers. Cai et al. used ink-jet printing to fabricate electrochromic WO₃-PEDOT:PSS composites printed on flexible substrates with electrochromic properties [84]. The flexible device showed a fast electrochromic response even under bending conditions in the range of –0.6 to 0 V transitioning from transparent to black and with good electrochemical stability up to 10,000 cycles.

Chromic materials are an emerging research area that has recently found its way into AM techniques for the fabrication of soft functional devices. Due to the high potential of chromic to fabricate wearable devices, it is expected to see future research trends taking advantage of AM to develop multi-responsive devices with reversible chromic properties.

2.5. Multifunctional Soft Materials

Multifunctional materials are those that present two or more functionalities due to their inherent properties or when combined with other functional materials as composites. The functionalities that make up multifunctional materials can be a combination of shape memory, self-healing, actuation, sensing, optical, biological, elastic, etc. In engineered multifunctional material systems, properties are carefully selected to achieve the desired multifunctionalities based on the field of applications. For example, multifunctional biomaterials must first present a therapeutic functionality and then may present added functionality including sensing of body temperature and pressure, or actuation [86]. Other engineered multifunctional materials can provide structural support in demanding environments while providing additional functionality to address very strict requirements [87]. The applications of such materials include energy [88], medicine [87], nanoelectronics, aerospace, defense, semiconductor, and other industries.

Multifunctional materials reduce system complexity by having one material perform functions that would be otherwise performed by multiple different materials. This is beneficial in applications such as soft robotics where weight reduction and simplicity are some of the key characteristics and the use of the least number of materials ensures the best performance possible [89]. The integration of multifunctional materials into structures requires material compatibility and adhesion between different components. AM allows a seamless transition from structural to functional sections through material gradients [90]. Thus, the combined development of materials with multiple functionalities together with the development of AM techniques that easily transition between materials allows for the simplest, most size effective structures. **Table 6** below summarizes the different multifunctional materials and composites that have recently been developed using a variety of AM processes.

Table 6. Different multifunctional soft materials recently manufactured using AM techniques and their applications.

Materials	Modulus	Max Strain (%)	Technique	Application	Functionalities	Ref.
Polyacrylamide	17 KPa	574	DIW	Biocompatible Soft Robotics	Magnetic response	[91]
Polyacrylamide with Carbomer	40 KPa	260	DIW	Biocompatible Soft Robotics	Magnetic response	[91]
PLA-PEA	125 MPa	2.5	DIW	Actuation and Sensing	Shape memory effect and piezoelectric effect	[92]
Polypyrrole (PPy)	498 kPa	1500	DIW	Sensor	Self-healing	[93]
Polydimethylsiloxane (PDMS)	160 kPa	210	DIW	Sensor	Superhydrophobicity	[94]

One of the families of advanced soft materials with the greatest potential for multifunctionality enabled through AM is hydrogels. These materials possess molecular networks swollen in water that, when subject to stimuli such as temperature or strain, may undergo gelling. Gelling constitutes a physical change where the stiffness of the hydrogel, as well as other relevant properties such as the swelling behavior, are altered. Thus, these materials possess sensing and shape change capabilities. Additionally, due to their high inherent compliance, they offer the potential to form functional composites with metallic or carbon fillers without sacrificing their softness. Functional hydrogel composites with electrically [93] or magnetically [31][71][72] responsive fillers have been enabled through AM. For example, hydrogels with self-healing molecular networks have been combined with conductive carbon fillers and used to fabricate complex sensing and healing structures through DIW [93]. Similarly, self-healing hydrogels with magnetic iron particle fillers were printed using DIW [44]. The structures could heal damage over time through reversible imine-bond formations, and the printed structures also exhibited macroscopic shape change in the presence of a magnetic field. Additionally, hydrogels were printed simply through DIW with the use of carbomer as a rheological modifier and their multifunctional properties were showcased [91]. The printed hydrogels showed time-dependent actuation in a hot (50 °C) water environment due to a phase transition and deswelling of one of the printed layers at the water bath temperature. The showcased hydrogels were also mixed with magnetic particle fillers and printed to form a biologically inspired octopus structure. This structure could locomote in the presence of a moving magnetic field and demonstrated the potential to obtain soft robotic nature mimicking structures through DIW [91]. Though magnetic hydrogel composites are capable of motion when a magnetic field is applied, their magnetic response is still considered weak. Thus, Tang et al. instead obtained 3D printed actuating structures that worked through the magnetothermal effect by introducing an alternating magnetic field causing heat and degradation of the hydrogel networks [95]. The printed parts were able to both encase and kill cancer cells after an oscillating magnetic field was applied due to the actuation of the heated hydrogel-filled elastomeric arms.

Composites with SMPs enabled through multi-material AM have shown potential to develop into multifunctional actuators. Bodkhe and Ermanni designed a piezoelectric SMP that changed its shape with temperature and could simultaneously measure the extent of its deformation through the development of a proportional voltage signal [92]. The multifunctional composite was enabled through the deposition of rigid and soft sections with multi-material DIW. The possibilities to tune actuation temperatures from 100 °C down to body temperatures were explored, and a robust sensor capable of withstanding temperatures ranging from 23 °C to 100 °C was presented, and to over 5000 operation cycles. This shape-

memory composite had a shape recovery rate of ~98% and the sensor had a linear voltage response in the force range of 0.1–1 N [92]. Ge et al. combined hydrogels and SMPs through a multi-material DLP print method. UV curable hydrogels were developed by the creation of a water-soluble photoinitiator [96]. To obtain heterogeneous structures of elastomer and hydrogel, a moving stage with “puddles” of the different precursor solutions was placed under the UV light at different times per layer and air-jetted off in-between material exchanges. The multi-material structures were able to perform multiple functions owing to the combination of advanced materials. For example, stents were built that could be cold programmed to a small diameter size and inserted into blood vessels and later would expand through the body temperature induced shape recovery process.

AM has the potential to provide additional functionality through careful geometrical design. As an example, multifunctional silicone structures with hierarchical porosities were built using a combination of micrometer sized sacrificial pore forming fillers and macroscopic infill gaps through DIW [94]. The 3D printed structures that had millimeter sized gaps on their infill attained super hydrophobicity and super olephicity due to their capacity to entrap air at the pores inside and around the printed struts. Moreover, the silicone inks used to print the porous structures were able to be mixed with CNTs, showcasing their capabilities as resistive sensors. The additional functionality of these structures as sensors was demonstrated by wetting them in a CNT bath, subjecting them to cyclic compressions, and measuring the linear electrical resistance response. A linear response was observed up to 10% strain although the highly porous structures could easily be compressed cyclically without loss of elasticity.

3D printed multifunctional materials and structures will continue to develop through the development of AM compatible chemistries, as well as the incorporation of multi-material printing to the different AM technologies. Careful design of new materials will aim to achieve multifunctionality without compromising AM compatibility. The incorporation of heterogeneous materials into AM feed has been highly developed, and thus, the blueprints for a future of yet unrealized multifunctional composites are in place. Multifunctional materials may begin to outpace single function materials due to the benefits they provide including system simplicity and reduction of mass. However, careful design must ensure that coexisting functionalities are not compromised by the presence of one another. AM provides pathways to seamlessly transition from structural to functional elements, and the high resolution of various printing technologies will enable careful control of material deposition to ensure functionalities are not compromised. Together, the fields of AM and advanced materials will continue to develop hand in hand to realize a future with efficient, responsive, and intelligent structures for various industries.

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