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Sustainable Robots 4D Printing

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Nature frequently serves as an inspiration for modern robotics innovations that emphasize secure human–machine interaction. However, the advantages of increased automation and digital technology integration conflict with the global environmental objectives. Accordingly, biodegradable soft robots have been proposed for a range of intelligent applications. Biodegradability provides soft robotics with an extraordinary functional advantage for operations involving intelligent shape transformation in response to external stimuli such as heat, pH, and light. Soft robot fabrication using conventional manufacturing techniques is inflexible, time-consuming, and labor-intensive. Recent advances in 3D and 4D printing of soft materials and multi-materials have become the key to enabling the direct manufacture of soft robotics with complex designs and functions. This review comprises a detailed survey of 3D and 4D printing advances in biodegradable soft sensors and actuators (BSSA), which serve as the most prominent parts of each robotic system. In addition, a concise overview of biodegradable materials for the fabrication of 3D-printed flexible devices with medical along with industrial applications is provided. A complete summary of current additive manufacturing techniques for BSSA is discussed in depth. Moreover, the concept of biodegradable 4D-printed soft actuators and sensors and biohybrid soft robots is reviewed.

1. Introduction

With the advancement of technology, electronic and robotic devices have become increasingly integrated into our daily lives. This link between the digital and biological domains is currently stronger than ever. However, the benefits of increased integration with robots and digital technology are at odds with our global environmental goals.[1] Notably, robots have a significant effect on the environment, which will have a big impact on our lives because, in addition to nonbiodegradable polymers, robotics waste includes hard and toxic components. Also, in environments deemed too hazardous or remote for humans to inhabit, such as the marine environment, robots are often needed to function independently. Hence, if the robot cannot be collected in the event of a failure in the field, it will become a contaminant.[2] The octopus, with its capacity for surviving in chaotic environments, and skeletal muscles, which produce active force and intricate motions, are two excellent examples of how mankind can use nature as a source of inspiration to imitate the biological sustainability and vital functions of various living organisms when designing its appliances.[3] Once more, it is possible to learn from nature and sustainably create our things, minimizing the environmental issues with present technology. The complexity of nature has compelled scientists from a variety of disciplines to duplicate or imitate the fluid motion of animals or their efficient energy management. All these observations have led to the development of soft, lightweight robots. Traditional rigid-bodied robots are often designed to effectively execute certain tasks within well-defined environments. Nevertheless, their capacity to respond and adapt to unforeseen circumstances is generally constrained by the inflexibility of its structural components. Soft robots possess a notable advantage due to its composition mostly consisting of materials that exhibit elastic properties similar to those seen in soft biological systems. This characteristic enables soft robots to exhibit a wide range of motion, interact with their environment in a flexible and secure way, and swiftly adapt to unforeseen circumstances.[4]

The future integration of such soft robots into everyday life may increasingly alleviate environmental issues associated with their use.[5] It should be noted that soft robotics technology can assist in attaining the sustainable development goals of the United Nations and the Paris Climate Agreement through the creation of autonomous, environmentally conscious devices propelled by renewable energy. The exponential development of technology has now impacted every aspect of contemporary

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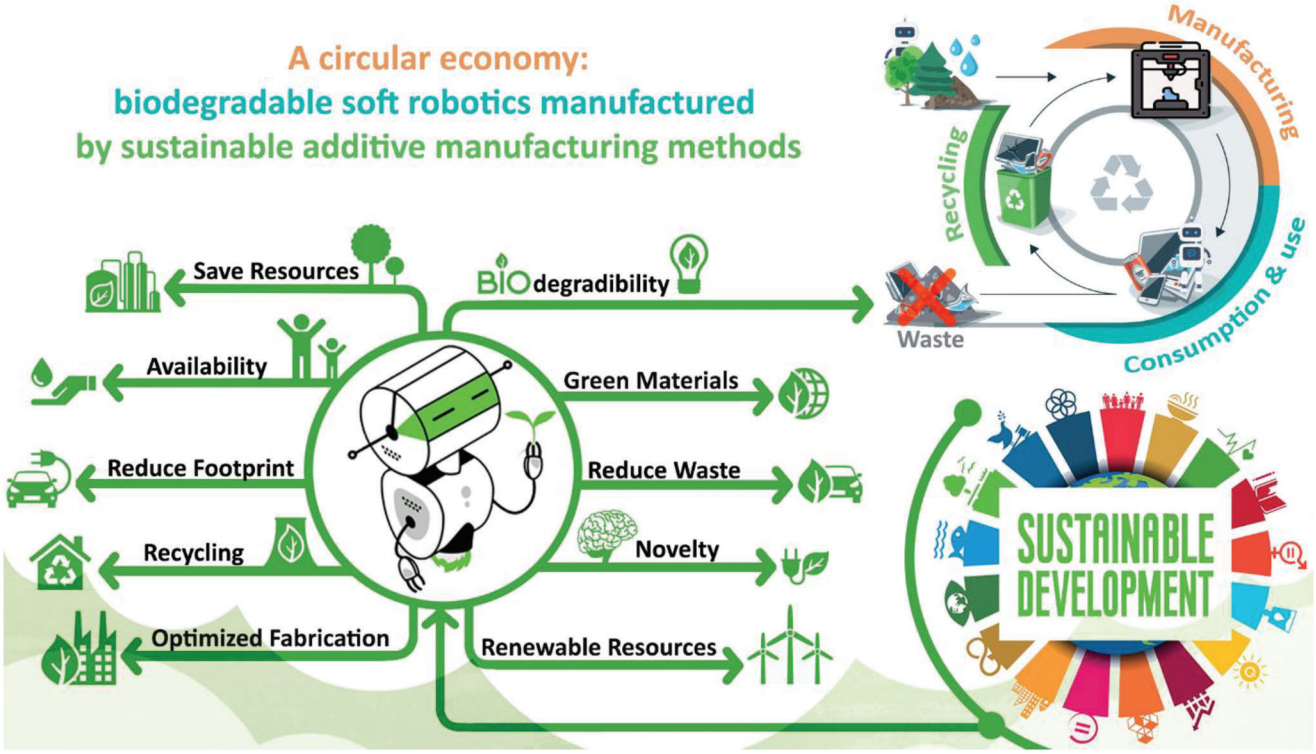


Figure 1. Sustainable robotics development: A circular economy in the fabrication of biodegradable soft robotics by sustainable manufacturing methods in accordance with the UN's sustainable development goals.

life.[6] The negative effects of this development include increasing energy demand, greenhouse gas emissions, deforestation, and environmental pollution. Researchers have a significant motivation to advance research on sustainable materials and robotics in order to meet some of the environmental objectives put forth by the United Nations. Due to climate change, over 3.5 billion people are now in high danger. In terrestrial ecosystems, there is a very high risk of extinction for 3 to 14 percent of species at 1.5 degrees Celsius of global warming and up to 48% at 5 °C of warming, according to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change from 2022.[7] **Figure 1** illustrates how the fabrication of biodegradable soft robotics using sustainable manufacturing techniques like 3D printing technologies is in line with the UN's sustainable development goals and will result in a circular economy that will minimize energy use, waste, and human impact. In addition, the biodegradability of these soft robots is a significant factor that contributes to the eco-friendliness of the devices. Sustainability in robotics encompasses several aspects, such as the availability of renewable resources, recyclability, and biodegradability.

Because of its safety, sustainability, considerable flexibility, and high maneuverability, soft robotics has received a lot of attention from the scientific community in recent years.[8,9] Soft robots provide superior mechanical robustness, human safety, and environmental adaptability owing to their innate compliance and very basic architecture.[10] Traditional robots have joints and are inflexible, while soft robots are flexible and possess several degrees of freedom.[11] Recent advancements in functional materials, manufacturing, modeling, and performance evaluation are all components of soft robotics' rapidly expanding field of research.[12] As soft robots become increasingly ubiquitous in our society and the numerous facets of our everyday lives, their influence on the environment will become a significant source of concern in the near future. It should be noted that a modern generation of materials and manufacturing technologies emerged in the 1940s with the widespread industrial use of synthetic polymers. For more than five decades, synthetic polymers have been a commonly used material in all facets of our lives, including housing, building, packaging, healthcare, automobiles, etc., and it should be mentioned that soft robotics is no exception either.[13] Soft robots are often made of flexible resins or polymers.

The majority of these materials are created by irreversible chemical processes and are made of nonbiodegradable polymers.[14] For the time being, our planet is facing an ever-increasing growth in population and urbanization. Since being primarily petroleum-derived and made of non-biodegradable materials, synthetic polymers generate a significant amount of toxic waste that endangers the ecosystem and all living creatures. A World Bank group report claims that synthetic polymers make up roughly 5–12% of the world's total waste disposal and that over 60% of synthetic polymers wind up in nature as plastic waste. That is to say that this amount of plastic waste constitutes almost 20–30% of the world's total waste disposal by weight.[15] In addition, the decay of man-made materials does not always result in benign outcomes. Each year, 100 billion plastic bag units are consumed in Europe alone, and a large portion of these are accidentally or intentionally discharged into the environment.

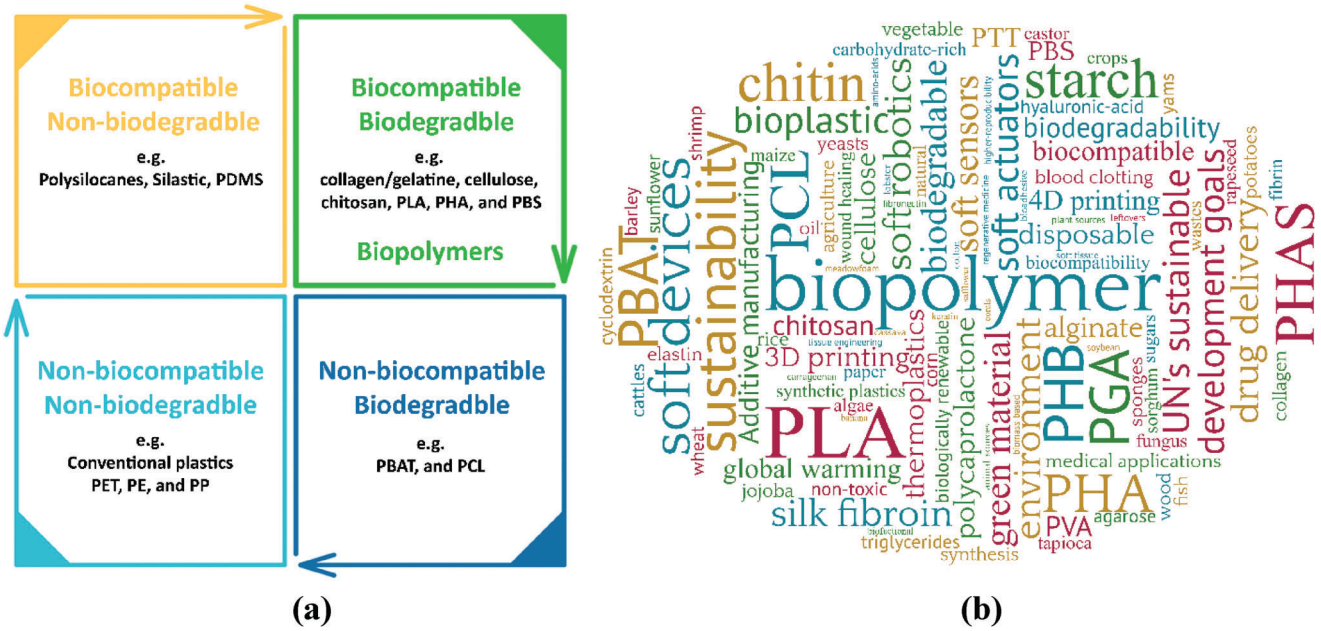


Figure 2. Different types of polymers and biopolymers sources: a) In terms of biocompatibility and biodegradability, materials are classified into four principal categories; b) A word cloud presenting diverse natural and synthetic types of biopolymers as well as its application in diverse fields.

Accordingly, managing plastic waste is a significant environmental challenge that calls for appropriate plastic breakdown techniques and materials. The major synthetic polymers in demand include polyvinyl chloride (PVC), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polyurethane (PU), and polystyrene (PS), which must be mentioned to properly address plastic waste management strategies.[16] To date, many strategies have been created and employed in the management of nonbiodegradable plastic waste. Conventional and advanced plastic waste management are two categories into which these technologies may be divided.[17] Incineration and landfilling are the traditional approaches to disposing of plastic trash.[18] Not only does the incineration of plastic waste use a lot of energy, but it also generates hazardous byproducts. All of these very dangerous byproducts, including CO_2, particulate matter, acidic gases, and heavy metals, contribute to global warming and provoke a host of health concerns.[19,20] Hence, the bulk of plastic garbage is still disposed of in landfills today. However, nonbiodegradable plastic trash decomposes slowly in landfill sites, necessitating the provision of a larger area of land due to the surge in the amount of plastic garbage being disposed of.[21,22] Although recycling synthetic plastics helps the environment, recyclable polymers have poorer-quality mechanical properties and cannot be used for high-end applications.[23–25] According to European union waste management guidelines, landfilling these items should be assigned the lowest priority.[26] Mankind has no option but to seek a sustainable, permanent, ecofriendly solution. Using biodegradable materials that may return to the earth is one approach. Given that the majority of biodegradable materials are derived from natural sources, robotic systems comprised of these materials are predicted to be sustainable.[14]

Due to their ability to break down into smaller pieces over time, naturally available polymers have lately received increased attention.[27,28] Using biodegradable polymers, or biopolymers is an important alternative to synthetic plastic.[29] Since most biodegradable materials come from natural sources, robotic systems made from these materials are likely to be long-lasting, reliable, and environmentally friendly. Furthermore, depending on their composition, they may be recyclable as well.[14,30] By combining research from many different fields, it is expected that soft robots will be made with all sustainable and environmentally friendly parts, such as actuators, sensors, controllers, and batteries, soon. Biodegradability gives soft robotics a huge advantage when it comes to tasks that require the robot to change its shape in response to things like heat, pH, and light.[31] The majority of biodegradable materials are produced in the form of polymers, which are classified as both natural and manufactured soft matter. Among the many naturally made biodegradable materials, protein-based polymers, chitosan, cellulose, and gelatin are the natural polymers that are most often used to make biodegradable soft robots.[32–34] In terms of biodegradability and biocompatibility, the varieties of polymers can be classified into four distinct classes as depicted in **Figure 2**a. In addition, Figure 2b contains a word cloud pertaining to biopolymer sources and the most useful natural and synthetic biopolymers.

One should ideally avoid polymers from non-biocompatible and non-biodegradable areas and give preference to biopolymers from the green region. Note that certain polymers, such as polysiloxanes, are very biocompatible, like the silastic used in medical implants,[13] but they are not biodegradable.[35] Figure 2a illustrates three material selection choices for biodegradable soft robots: 1) biopolymers such as cellulose and gelatin or existing biodegradable plastics such as polylactic acid (PLA)

Table 1. Classification of biopolymeric materials. Reproduced with permission.[26]

Classification	Source	Biopolymers
Polypeptides/ proteins	Animals	Fish protein, collagen, silk, gelatin, casein, whey
	Plants	Soy protein, zein, wheat gluten
Polysaccharides	Animals	Hyaluronic acid, chitosan/chitin
	Plants	Starch, agar, cellulose, carrageenan, pectin, alginate
	Lipids	Fatty acid, carnauba wax, beeswax, oil
Biopolymers produced through microorganisms	Bio-derived monomers	PLA, polyglycolic acid (PGA)
	Microbial polyesters	Polyhydroxyalkanoate (PHA), PCL, polyhydroxybutyrate (PHB), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)
	Bacterial	Cellulose, gelian, dextran, xanthan, polygalactosamine
Synthetic	–	Poly(vinyl alcohol) (PVA), polyvinyl acetate (PVAc)
	Aliphatic polyesters	PLA, PGA, PCL, polybutylene succinate (PBS), polytrimethylene terephthalate (PTT), poly(butylene adipate-co-terephthalate) (PBAT)

and polycaprolactone (PCL) can be used; 2) researchers can select a non-biodegradable biocompatible polymer, such as polydimethylsiloxane (PDMS), and attempt to make it biodegradable; or 3) toxic but degradable polymers can be selected, and efforts should be made to make them non-toxic. The first alternative is the most applicable option to utilize in soft robots, whereas the latter two require study in polymer chemistry.[32] It is noteworthy that bio-based polymeric materials are often put into four different groups based on where they come from and how they are made, as shown in **Table 1**. By replacing nonbiodegradable polymers with bio-based polymers, the world is moving towards a more sustainable, cleaner, and greener environment. These polymers have unique characteristics like renewability, nontoxicity, sustainability, and biodegradability.[36]

Despite significant development, the majority of stimuli-responsive, biodegradable soft robots are still conceptual. Therefore, this gap should be filled with additional research, as it will be necessary to expand biodegradable fabrication industries in the near future to prevent environmental impacts resulting from human activity. Despite these encouraging developments, soft robots have not yet fully demonstrated their anticipated capacity to revolutionize our daily lives. Future research should focus on three areas: a) developing new materials that effectively connect soft and rigid robotic parts and allow the development of multifunctional soft robots with lifelike properties like self-healing, sensing, and growing; b) using computational tools to better understand the dynamics of soft robots; and c) improving the performance of current soft robots by using new control and learning architectures that are more appropriate.[4] Furthermore, to achieve our urgent environmental goals, due to their applicability, there are examples of soft robots that should be prioritized. Healthcare devices, robots that harvest crops and then break them down into compost for the next season's plants, mobile robots that perform tasks in the remote and in-vivo environment, wound patching millibots that work in vivo, drug delivery robot swarms, and small grippers controlled by engineered muscle tissues are all soft robotics advances that should be prioritized to demonstrate how significant it is for our devices to be made biodegradable.

Still, biodegradable soft robot fabrication is presently difficult, time-consuming, and highly labor-intensive. Although conventional fabrication methods, which involve molding and casting, are employed at the moment, recent improvements in the 3D printing of soft materials and multiple materials have made it possible to directly make biodegradable soft robots with complicated designs and functions.[37–39] In addition, customizable and 3D-printable molds and castings are used in several traditional biodegradable soft robot production methods. In general, 3D printing processes like fused filament fabrication (FFF), direct ink writing (DIW), inkjet, and poly jet provide excellent resolution and precision for pattern structures with autonomously programmed geometry and repeatability.[31] Nevertheless, FFF is the most extensively utilized of several 3D printing processes.[40] Due to material limitations, direct 3D printing of biodegradable soft robots has not yet become a widespread manufacturing approach. Despite this, as additional biopolymer materials become compatible with current 3D printing technology, this method is displacing the typical method of biodegradable soft robot production. Researchers have held additive manufacturing (AM) techniques in high regard in recent years, and this regard has grown as a result of the emergence of new technologies, which have led to the creation and development of various methods for using a broader variety of materials and applications.[41] At the moment, PLA is the most popular and widely used biopolymer for 3D printing biodegradable soft robots. This is because PLA has good tensile strength and modulus, a high barrier property, and is an ecofriendly material. Also, it is an entirely biodegradable substance that can be derived from renewable resources like maize, sugarcane, and tapioca starch.[42] 3D printing can build accurate spatial structures from a variety of materials and has been used in many applications. Nevertheless, one shortcoming of 3D printing is that it only analyzes the initial, static condition of the created structures. 4D printing technology has recently evolved to circumvent this constraint.[43]

4D printing is an intriguing area of AM that makes use of time-responsive, programmable materials. When stimulus-responsive polymers are exposed to various environmental stimuli such as heat, light, electricity, humidity, or magnetism, they are programmed to take on a temporary shape and can also change back to their original shapes afterward.[44,45] By combining 4D printing and shape-memory polymer composites, rapid scientific advancements have been made in the field of smart and multifunctional materials in recent years. In this regard, there is a wide range of technical applications in this field, such as wearable electronics, soft robotics, food, smart fabrics, and biomedical devices.[46,47] The current smart materials used in 4D printing exhibit some constraints when applied to the construction of soft robots. For example, the deformation capability of shape memory polymers necessitates post-printing mechanical processing, hence exacerbating manufacturing instability. The deformation of hydrogels is mostly restricted to use in aqueous environments. The liquid crystal elastomer is a polymer that exhibits

stimulus-responsive properties, making it a promising material for enhancing the intelligence and driving behavior variability of soft robotics.[48] However, stimuli-responsive materials in combination with 3D/4D printing have cleared the way for the creation of shape-changing intelligent biodegradable soft robots.[49]

There have been a lot of ongoing efforts in the development of 3D- and 4D-printed biodegradable soft robots at various scales. Very few in-depth articles have addressed 3D/4D printing technologies and materials for fully biodegradable soft robotics, and each of these papers has presented several research potentials, such as the optimization of both material and printer for printing soft materials and the integration of soft actuators and sensors through multi-material printing. Emerging forms of soft, biologically-inspired electronics and robotics have the potential to emulate their natural counterparts not only in terms of performance and capabilities but also in terms of their environmental impact. Microbots operating in vivo, biohybrid machines, soft pneumatic actuators,[50,51] and entirely biodegradable yet resilient actuators and sensors are examples of the cutting-edge in 3D/4D printed biodegradable robotics. These primary measures initiate the evolution of robotics and steer them toward a sustainable future. While attempts have been made to develop biodegradable soft robotics using a variety of eco-friendly actuators, sensors, materials, and even power supplies,[52] it is notable that soft actuators and sensors are the most essential components of a soft robotic system[53]

Actuators are the synthetic muscles that enable soft robotics to perform designed tasks. The designated actuation modality has a significant impact on the design, fabrication, modeling, and efficacy of soft robotics. Soft actuators may be categorized into five distinct categories depending on their actuation mechanism. These include tendon-driven actuation, electroactive polymers such as dielectric elastomer actuators and ionic polymer-metal composite actuators, shape-memory materials including shape-memory alloys and shape-memory polymers, soft fluidic actuators, and hybrid actuators.[54] In this context, researchers have recently devoted significant effort to the development of soft robotic actuation strategies with integrated biomimetic intelligence based on various responsive soft materials such as hydrogels, liquid crystal networks, and shape memory polymers (SMPs).[55]

Hydrogels consist of water and networks of hydrophilic polymer molecules. Hydrogels are three-dimensionally elastic solids due to cross-linked polymer chains. The configuration of the polymer network can be altered to withstand up to 1000% mechanical strain. Due to the high-volume fraction of water, the elastic modulus of hydrogels is in the range of 1–100 kPa, which is gentler than that of other compliant materials. The polymer network of a biocompatible hydrogel consists of non-toxic polymers. Thus, hydrogels can be incorporated into the field of soft robotics in order to increase the variety of biological applications.[56] Liquid crystal elastomers are particularly appealing due to their massive linear form variations (up to 400%) and 3D printability. Liquid crystal elastomers may also be programmed with precise liquid crystal monomer orientations to produce sophisticated reversible modes of deformation, such as Gaussian curvature. Despite its potential, liquid crystal elastomers often need external heating sources, stimuli-responsive inclusions, or chemical changes to assist the liquid crystal phase transition and subsequent shape change, limiting their uses in soft robotics greatly.[57] It is worth mentioning that asymmetric laminated soft actuators and symmetric cylindrical soft actuators based on liquid crystal elastomer have been recently developed for sensing and actuation components in artificial phototropic and light-tracking systems.[58] In contrast to the aforementioned smart composite materials, SMPs, specifically two-way SMPs capable of reversible shape deformation, offer several advantages. These include a substantial output stress, a low driven voltage requirement, a simple construction, and a low cost. Consequently, they have emerged as a prominent area of research within the realm of SMP-based soft actuators. The crucial factor in achieving the shape memory effect is in the development of internal tension inside shape memory polymers or composites. Various strategies have been implemented to achieve reversibility in materials. These include the utilization of two-layer structures or crosslinked networks to induce internal stress disparities, the construction of 3D structures incorporating dynamic reversible covalent bonds, and the synthesis of materials with dual crystal components. Although SMP-based actuators have shown many advantages, there is still potential for further enhancement. This includes the development of a more stable multilayer structure, a simpler design for the multi-molecular network, and the ability to achieve more flexible reversible deformation, among other areas of improvement.[59]

Regarding their applicability, biodegradable 3D/4D printed soft actuators are utilized in many fields, such as agriculture,[60] biomedicine,[61–93] micro positioning,[67,79,94–97] smart surgical instruments,[64,98–101] soft rehabilitation devices,[98,102,103] drug delivery microswimmers,[64,67,68,70,72,73,77,84,85,88,94,34,104–108] sustainable electronics devices,[109–111] soft smart fabrics,[64] muscle tissue membranes,[65,76,89,94,96,112,113] in-vivo robotics,[67,74,83,86,89–91,93,99–101] wearable devices,[95,103,111,114–118] soft smart prosthetics,[114] bionic devices,[69,72,73,114] aeronautics,[119,120] health monitoring equipment,[111,118] edible robots,[121] biomimetic scaffolds,[30,62,76,97,115,122,123] environmental monitoring equipment,[60,79] lightweight smart structures,[116] wireless implants,[69,75,78,83] grippers,[67,98,102,109,113,120,124–130] biohybrid robotics,[89–93] micro-locomotive robots,[89,90,113] microsystem actuators,[92,131] humanoid soft robots,[132] self-morphing structures,[81,116,124,125,127–130,133,134] and food smart packaging.[111]

To complete soft robotics autonomous tasks, the sensorization of soft robotics is a long-standing obstacle that must be surmounted. Since the majority of conventional sensors were designed for rigid structures, it is challenging to incorporate them into the compliant, pliable bodies of soft robotics. Theoretically, soft robots have an infinite number of degrees of freedom; therefore, sensors used to measure their continuous posture changes must have sufficient motion range, accuracy, and resolution. Proprioception and tactile sensing are two sensing strategies in soft robotics that can be applied to soft robots to improve their modeling, control, and safety.[4]

Similarly, biodegradability in flexible sensors offers numerous applications in diverse areas, such as E-tongues for soil quality sensing in agriculture,[135–138] biomedicine,[62,66,77,139,140] liquid sensing,[137,141] humidity sensing,[136,142] strain sensing,[140,143–151] force sensing,[77,139,152–154] magnetic field sensing,[62] gas sensing,[138,155] pH sensing,[66] temperature sensing,[156] ion sensing,[66] wearable soft sensors,[95,111,114,118,143–146,149,151,157] waveguide sensors,[98] soft

sustainable electronics,[95,109,111,118,139,140,144–149,151–153] human motion sensing for healthcare monitoring,[118,145,146,157,158] environment monitoring,[136] bioelectrodes,[145,146] touch sensors,[109] food quality sensing for smart packaging,[138,155] antennas,[156,159] and structures health monitoring.[142] **Figure 3** depicts a brief evolution of additively manufactured BSSA, as well as the ecofriendly material used in their construction.

Herein, this review generally focuses on designs for sustainable technologies, safe and inexpensive manufacturing methods, and biodegradable or renewable materials that do not harm people or the environment. This paper will begin by examining recent advancements in the fabrication of soft robots using AM techniques. According to the available literature, not all AM techniques are utilized in the fabrication of soft robotic systems. Furthermore, due to the compatibility of biodegradable materials, there are obstacles to employing biopolymers in all existing AM techniques used to build soft robotic sensors and actuators. Hence, current AM techniques for building soft, biodegradable robotic systems are examined in this review. An in-depth discussion of biodegradable and eco-friendly 3D printable materials will follow. Since soft actuators and sensors are the most essential components of a soft robotic system, recent advancements and research in biodegradable, 3D-printable soft actuators and sensors will be discussed separately in each AM section.

2. 3D/4D Printing of the Biodegradable Soft Sensors and Actuators

More than 50 years ago, the basic ideas of AM were first studied.[160] AM is a new method of production in which material is added layer by layer to create 3D objects. Based on ISO/ASTM 52900:2015, seven groups of AM processes are specified.[161] The seven processes include binder jetting (BJT), an AM process in which a liquid bonding agent is selectively deposited to join powder materials; directed energy deposition (DED), an AM process in which focused thermal energy is used to fuse materials by melting as they are being deposited; material extrusion (MEX), an AM process in which material is selectively dispensed through a nozzle or orifice; material jetting (MJT), an AM process in which droplets of build material are selectively deposited; powder bed fusion (PBF), an AM process in which thermal energy selectively fuses regions of a powder bed; sheet lamination (SHL), an AM process in which sheets of material are bonded to form a part; and vat photopolymerization (VPP), an AM process in which liquid photopolymer in a vat is selectively cured by light-activated polymerization.[162,163]

There are typically three ways to promote AM in the construction of biodegradable soft robots: quick mold fabrication (in which AM plays a passive function), hybrid (in which AM plays an active role but other manufacturing methods are still utilized), and complete additive manufacturing. Only the third strategy fully exploits AM, while the first two also have advantages. Understanding the basics of the AM process is vital for fostering the appropriate technology for the development of 3D printable, biodegradable soft robots. The objective of this section is to provide an overview of AM techniques employed in the fabrication of full BSSA and discuss their fundamental principles of operation. **Figure 4** provides an overview of different AM techniques used in 3D printing biodegradable soft robotics components.

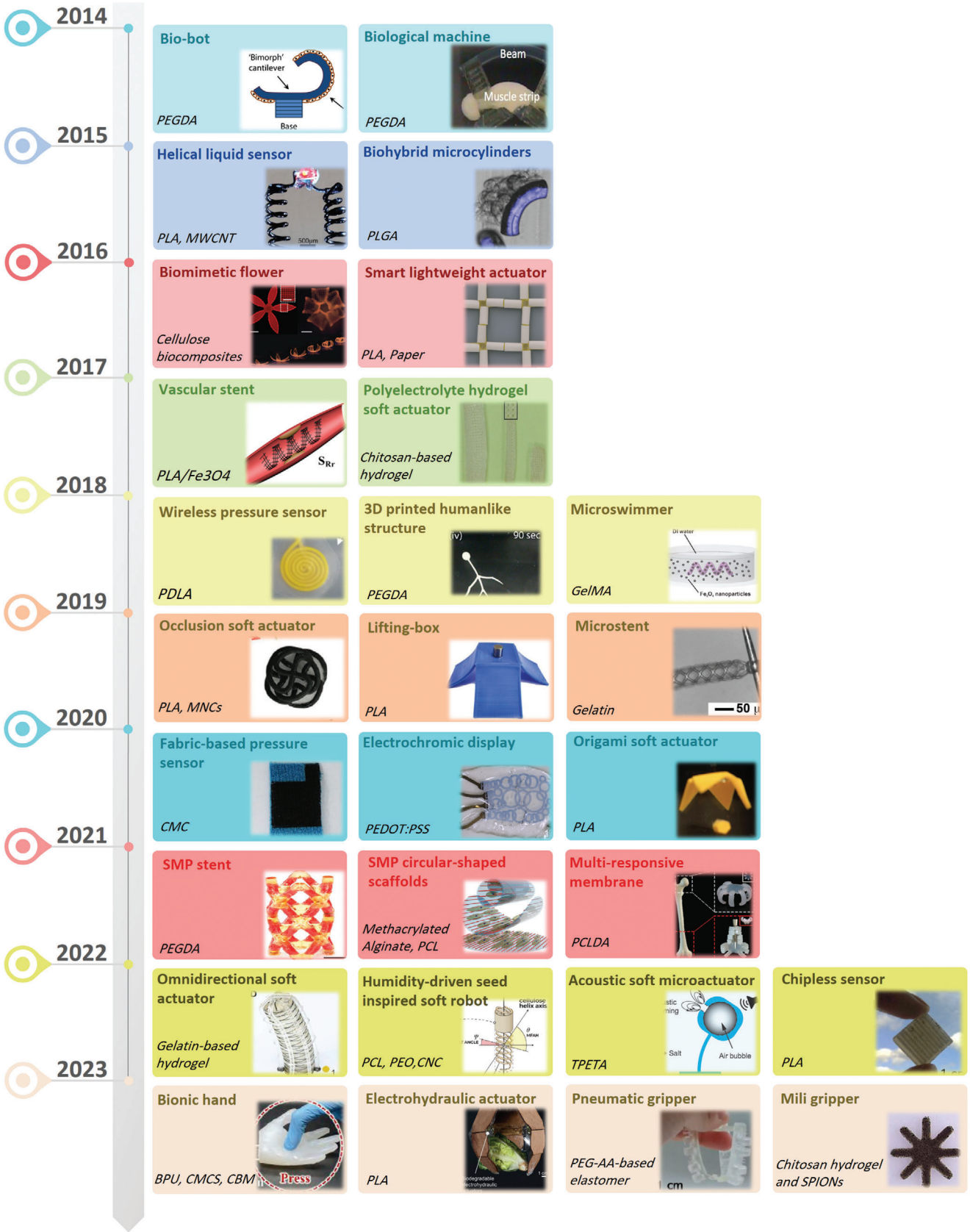
2.1. Material Extrusion (MEX)

MEX technologies include a wide range of different systems, but most of them have to do with the extrusion of thermoplastics or materials that are biologically active. MEX offers a unique potential for the development of AM systems capable of processing biologically active materials. These systems produce bioactive, cell-filled extrudate that can be used to make high-value, therapeutically useful materials.[164] The MEX process starts with the layering of a 3D CAD model. Then, MEX selectively distributes material via a nozzle and deposits it layer by layer to construct a 3D object.[165] Furthermore, by employing various nozzles, MEX systems may concurrently print a wide range of materials, such as multicolored objects or sophisticated sculptures.[166] The challenges and current focus of research in the fabrication of soft robotics regarding MEX additive manufacturing processes revolve primarily around several key areas. First, there is a strong emphasis on enhancing the process's ability to achieve superior performance of the printed components. Second, efforts are being made to expand the range of available materials, thereby enabling greater system integration in extrusion-based AM processes. Thirdly, numerical analysis is being employed to analyze and predict the physical properties of AM MEX-based materials. Last but not least, there is a growing interest in creating models and simulations to comprehend how design and printing strategies affect material performance.[167]

The benefits associated with the use of MEX include the inherent simplicity of the process, the comparatively modest expenses involved, and the extensive range of available feedstock materials. In addition to conventional plastics, fiber-reinforced polymers may also undergo processing. Moreover, it is feasible to manufacture components using concrete, metals, ceramics, and several other materials in this technique. Special MEX systems are capable of facilitating large-format additive manufacturing, characterized by build quantities exceeding 1 m^3, because of their ability to achieve high material deposition rates. The cost per unit for small and medium batch sizes may be comparable between MEX and traditional production procedures. One instance of an application within this particular spectrum of batch sizes pertains to polymer components designed for use in the aerospace sector.[168]

There are many factors that have an impact on the mechanical and geometric qualities, as well as the surface features, of the components manufactured using MEX. These factors include process parameters and material properties. The requirements for the components vary depending on the specific application. Hence, the focus of process monitoring is only on certain quality attributes that are associated with the corresponding criteria. The quality criteria included are the geometric dimensions and density of the pieces. Due to the intricate interplay of several contributing factors, a range of process errors may arise, potentially leading to a decline in the quality of manufactured components.[169]

A number of notable limitations have been observed in the present condition of AM using extrusion-based techniques. These constraints include low deposition rates, inadequate resolution, heat deterioration, and unsatisfactory mechanical qualities shown by the printed components.[164] The phenomenon of nozzle clogging and the existence of substandard 3D printed



components as a consequence of internal voids, as well as the construction of supporting overhangs and interior walls, present some challenges. The fabrication of components with low complexity may be attributed to the presence of overhangs and bridges, which in turn may also result in substantial surface roughness.[170] Additionally, post-processing approaches have the ability to mitigate the generation of waste resulting from the use of support structures. The nondestructive evaluation of interior faults presents several obstacles, which need attention. As previously stated, post-processing is often necessary in MEX-based additive manufacturing. This aspect should be seen as a challenge to both the cost-effectiveness and the quality of the printed components. The presence of interlaminar structural features in this technique has the potential to adversely affect the mechanical characteristics of the components, leading to reduced performance.

ISO/ASTM 52900 articulates that MEX is "a technique for additive manufacturing in which material is distributed in a controlled way through a nozzle or orifice."[171] Accordingly, MEX can be classified into two main sub-groups based on the ISO/ASTM description and the temperature required for the extrusion: FFF or fused deposition modeling (FDM) for the extrusion of melted thermoplastic polymers, and DIW for extrusion without melting.[172,173] The characteristics of different types of MEX systems and the material used in this technique are listed in **Table 2**.

2.1.1. FFF

FFF technology was created by Stratasys Inc., USA, in the 1990s under the name FDM and is one of the most prominent technologies for additive manufacturing.[174] Layer-by-layer, thermoplastic polymer filaments are melted and extruded via a nozzle onto the chosen substrate in the FFF method. Material extrusion systems often use printing heads with two or more extruders to print parts made of different materials at the same time. Also, a common method is to use one extruder to print supports that are dissolvable and can be easily removed from the main part after the printing process is finished. Members of the RepRap project proposed FFF as an alternate moniker.[175] Various other names have been offered, such as fused layer modeling/manufacturing (FLM)[176] and layer plastic deposition (LPD),[177] but they are not popular within the literature. Several research groups have recently improved the strength of 3D-printed polymers by adding continuous fibers to them.[178] Carbon,[179,180] glass,[181,182] wood,[183] and Kevlar[184,185] fibers have been employed as reinforcements, while mostly PLA,[186–188] acrylonitrile butadiene styrene (ABS),[187] nylon,[189] and epoxy resin[190] have been used as the matrix for printing with continuous fibers. The reinforcement of the biodegradable matrix with recyclable material will expand the spectrum of materials used in soft robotic fabrication techniques using AM technologies in terms of their mechanical properties.

There have been established two primary configurations for printing continuous fiber-reinforced composites: 1) in situ fusing of fibers with thermoplastic in the nozzle and 2) extrusion of pre-impregnated fibers.[178] The most popular filaments used in FFF are thermoplastic polymers, such as ABS and biodegradable PLA. In order to limit the use of petroleum-based plastics and environmental damage, several researchers have concentrated their efforts in recent years on creating sustainable materials for use in FFF, such as bioplastic and recycled-based filaments.[191] Furthermore, modern scientific research has produced and evaluated sustainable, biodegradable, eco-friendly, and recyclable materials, such as wood, cellulose, sugars, and lignin.[192,193] Most of this research has been focused on making composite filaments, such as PLA composites. In their research, scientists have proposed several composite materials consisting of a PLA matrix and natural fibers, such as scrap wood flour, since PLA is a renewable

Figure 3. Development of additively manufactured BSSA and the eco-friendly material used in their fabrication. (2014) Schematic of the bio-bot design, a biological bimorph cantilever with a sheet of seeded cardiac cells. Reproduced under the term of CC-BY license.[89] Copyright 2012, The Authors, published by Springer Nature. 3D-printed biological machines. Reproduced with permission.[91] Copyright 2014, National Academy of Science. Two helical sensors supporting and electrically supplying a bright LED light in this optical picture. Reproduced with permission.[141] Copyright 2015, Royal Society of Chemistry. Cardiomyocytes specifically patterned on bicompartmental PLGA/PLCL microcylinders. Reproduced with permission.[93] Copyright 2015, Wiley-VCH GmbH. Biomimetic 4D-printed shape-morphing flower. Reproduced with permission.[115] Copyright 2016, Springer Nature. 3D lightweight actuators from printed composite sheet. Reproduced under the term of CC-BY license.[116] Copyright 2016, The Authors, published by Springer Nature. Application of the 4D scaffold as an intravascular stent. Reproduced with permission.[80] Copyright 2017, American Chemical Society. 3D-printed chitosan-based polyelectrolyte hydrogel soft actuator. Reproduced with permission.[79] Copyright 2017, Elsevier. 3D-printed PDLA wireless pressure sensor. Reproduced with permission.[77] Copyright 2019, Elsevier. 3D printed human-like electroactive hydrogel structure. Reproduced with permission.[113] Copyright 2018, American Chemical Society. Schematic of the biodegradable GelMA helical microswimmer. Reproduced with persmission.[84] Copyright 2018, Wiley-VCH GmbH. Schematic illustration of the biodegradable and remotely controllable shape memory occlusion soft actuator. Reproduced with permission.[75] Copyright 2019, Wiley-VCH GmbH. 3D-printed biodegradable lifting box. Reproduced with permission.[128] Copyright 2019, Wiley-VCH GmbH. Gelatin-based micro stent. Reproduced with permission.[99] Copyright 2019, Wiley-VCH GmbH. Schematic illustrating the of a soft pressure sensor. Reproduced with permission.[154] Copyright 2020, American Chemical Society. Biodegradable inkjet-printed electrochromic display. Reproduced with permission.[111] Copyright 2020, Royal Society of Chemistry. Origami-inspired soft gripper. Reproduced with permission.[126] Copyright 2020, Wiley-VCH GmbH. 3D-printed SMP stent with drug releasing function. Reproduced with permission.[140] Copyright 2021, American Association for the Advancement of Science. 4D-printed Self-folding circular-shaped scaffolds. Reproduced with permission.[96] Copyright 2021, American Chemical Society. 4D-printed of smart membrane. Reproduced with permission.[86] Copyright 2021, Wiley-VCH GmbH. Biodegradable 3D-printed multidirectional self-sensing actuators. Reproduced with permission.[98] Copyright 2022, American Association for the Advancement of Science. 4D printed of humidity-driven seed inspired soft robot. Reproduced with permission.[60] Copyright 2023, Wiley-VCH GmbH. Schematic of 3D printed acoustically programmable soft microactuator. Reproduced with permission.[83] Copyright 2023, Mary Ann Liebert, Inc. 3D-printed biodegradable chipless sensor for wireless subsoil health monitoring. Reproduced under the term of CC-BY license[137] Copyright 2022, The Authors, published by Springer Nature. 4D printed biodegradable bionic hand. Reproduced with permission.[114] Copyright 2023, Elsevier. Biodegradable electrohydraulic soft actuator. Reproduced with permission[102] Copyright 2023, American Association for the Advancement of Science 3D-printed multi-material pneumatic actuator. Reproduced under the term of CC-BY license[131] Copyright 2023, The Authors, published by MDPI. 4D printed untethered mili-gripper. Reproduced with permission.[67] Copyright 2023, Elsevier.

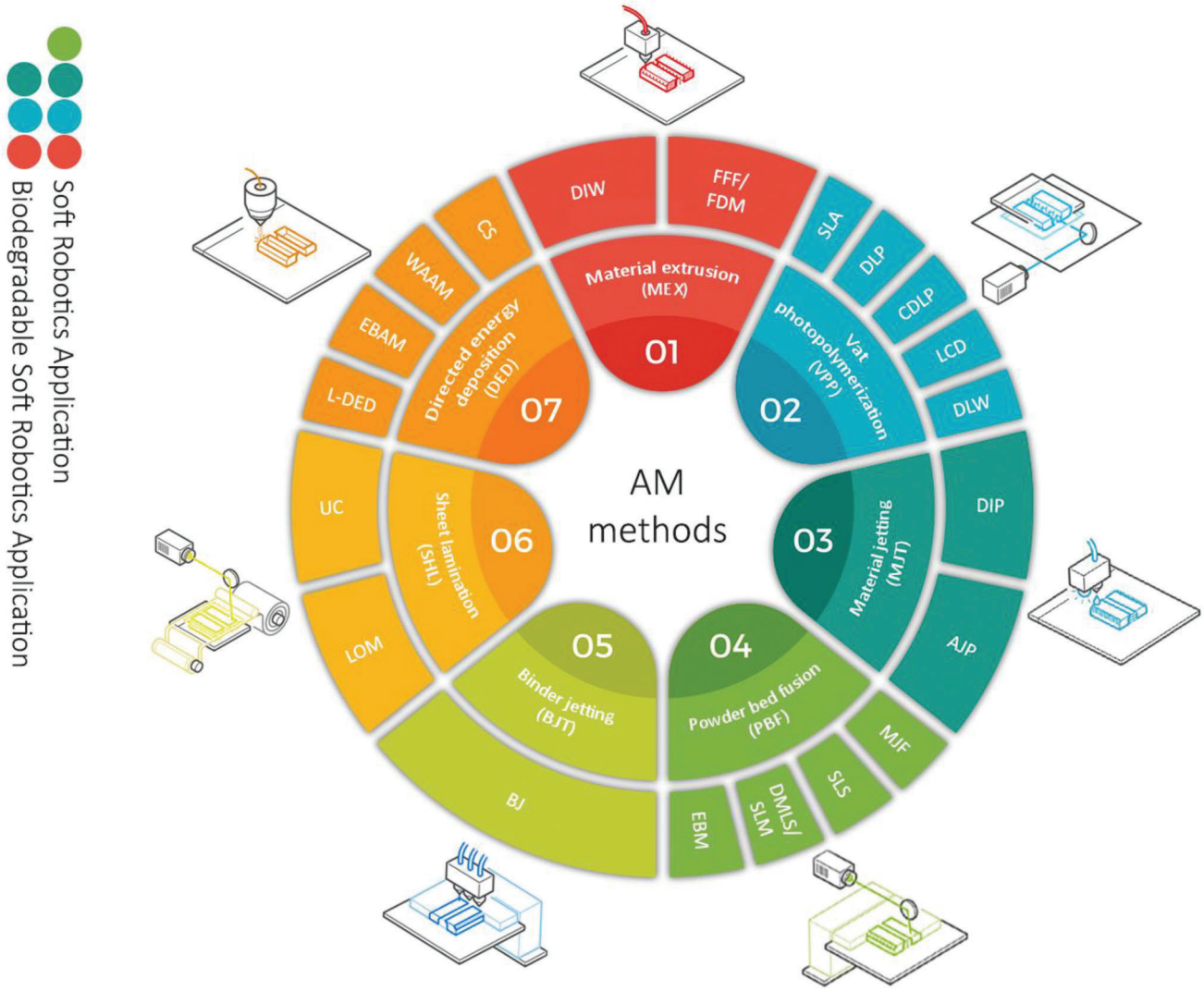


Figure 4. Classification of AM technologies: MEX: direct ink writing (DIW), fused filament fabrication (FFF)—fused deposition modeling (FDM); VPP: stereolithography (SLA), digital light processing (DLP), continuous digital light process (CDLP), liquid crystal display (LCD), direct laser writing (DLW); MJT: direct inject printing (DIP), aerosol jet printing (AJP); PBF: multi-jet fusion (MJF), selective laser sintering (SLS), direct metal laser sintering (DMLS)—selective laser melting (SLM), electron beam melting (EBM); BJT: binder jetting; SHL: laminate object manufacturing (LOM), ultrasonic consolidation (UC); DED: laser directed energy deposition (L-DED), electron beam additive manufacturing (EBAM), wire arc additive manufacturing (WAAM), cold spray (CS).

resource and wood waste can be found abundantly in the environment. Many of these distinct filaments are composed of wood from various plant species, particle sizes, and binders.[194,195]

FFF is the predominant additive manufacturing (AM) technique utilized in this process. The benefits of FFF over conventional manufacturing methods are extremely apparent: it enables the production of molds for the complicated geometries of soft robots while saving time and money.[162] Also, FFF technology is heavily employed in the hybrid construction of biodegradable soft robots; in this method, one or more of several AM technologies are employed to produce some elements of the soft robot, such as actuators and sensors. Moreover, FFF is the most utilized in the construction of soft sensors and actuators, both in the single printing cycle and in the printing of diverse 3D parts in the assembly process of soft robots. Notably, from a material point of view, PLA has been employed the most in the fabrication of biodegradable soft actuators. Many authors have reported the applicability of this material as a SMP in thermal,[61,71,73,81,82,116,119,120,123–128,132,133,197] electrothermal,[109] electrochemical,[135] magnetic,[69,75,78,82,197] and electrohydraulic-based[102,121] actuating soft systems.

In addition to producing soft materials with customized mechanical properties, 4D printing has the potential to be applied to the fabrication of biomedical devices and programmable soft electronics and actuators. Lin et al.[69] made a patient-specific, absorbable left atrial appendage (LAA) occluder with a bioinspired network that mimics the stress-strain curve of LAA tissue and can match the way LAA tissue deforms to reduce complications (**Figure 5**a). The LAA occluder is biocompatible, biodegradable, durable, and can undergo a rapid, complete, and remote-

Table 2. The characteristics of AM technologies used in the fabrication of biodegradable soft robots.

Printing process	Printing principle	Feedstock and bonding	Materials	Advantages/disadvantages	Refs.
Material extrusion (MEX)	Fused filament fabrication (FFF), fused deposition modeling (FDM), fused layer modeling/manufacturing (FLM), layer plastic deposition (LPD)	Solid filament/wire, pellets, paste—fused with heat	Thermoplastics, such as polycarbonate (PC), PP, ABS, PLA, flexible PLA, thermoplastic polyurethane (TPU), polyamide (PA), PVA, thermoplastic elastomers (TPE), polyethylenimine (PEI), polyether ether ketone (PEEK), acrylonitrile styrene acrylate (ASA), HIPS, PET, and nylon; particle filled polymers; fiber filled polymers; metal powder filled polymers; concrete; clay; low melting point metal composites, wood composites, and carbon fiber composites; ...	☑ Wide selection of print materials; Simplicity of implementation; Ability to construct completely functioning components from standard plastics; Simple, low initial and running costs, and fast; Small equipment size; potential for scalability; compatibility with easily accessible and customized input materials ☒ Surfaces of printed items exhibit anisotropy in the z-direction (vertical direction) and a stepped structure; nozzle clogging and low quality; difficulties in the fabrication of supporting overhangs and interior voids; limited complexity (overhangs, bridges); possibility of quite a high surface roughness; waste due to supports; difficulties in the nondestructive characterization of interior flaws; interlaminar structural weakness potential; materials that are extremely soft or have an excessively high transition temperature are difficult to print successfully; postprocessing requirements; limited wall thickness.	[37, 164, 173–178, 180, 186–190]
	Direct ink writing (DIW), robocasting (RC), direct-write assembly (DWA), micro robotic deposition (μRD), 3D dispensing, filament-based direct writing (FBDW), low-temperature deposition manufacturing (LDM); Tip-based direct writing (TBDW); MEX-based bioprinting, MEX-based bioplotting	Granules, paste, or gel materials; liquid polymer—solidification either through liquid evaporation, gelation, or a temperature- or solvent-induced phase change.	Liquid polymer, such as thermoplastic, thermoset, elastomer, biopolymer, polymer matrix composite; colloidal suspension; ceramics, such as oxides, non-oxides, bio-ceramics, ceramic matrix composites; hydrogel; glass, such as bio-glass, silica glass; cement; graphene; metal, such as single metal, alloy, liquid metal; ...	☑ Reduction in post-processing; reduction in material waste; economical and sustainable manufacturing process; material flexibility and highest resolution for an extrusion system; suitable for laboratory and medicinal (bone) uses; capacity to fabricate intricate functional structures; capacity to fabricate high porosity ratio compared to standard production techniques (especially in bioengineering applications) ☒ Low throughput; printed components frequently lack enough mechanical strength; limited component geometry; high cost of the system; little construction volume; more curing after each layer may be necessary, which can impede printing speed	[37, 160, 164, 178, 202–204, 209–212, 213, 214, 223]

(*Continued*)

Table 2. (Continued)

Printing process	Printing principle	Feedstock and bonding	Materials	Advantages/disadvantages	Refs.
Photopolymerization (VPP)	Stereolithography (SLA); microstereolithography (μSLA); low force stereolithography (LFS)	Photopolymer liquid— cured with a laser beam; hybrid photocuring	Photocurable resin (epoxy, vinyl ether or acrylate-based resin); poly (ethylene glycol) diacrylate (PEGDA); hexanediol diacrylate (HDDA); watershed XC 11122 acrylates; polylactic acid-polyurethane (PLA-PUA); urethane dimethacrylate (UDMA); methacrylate resin; formlabs clear methacrylate resin; methacrylic anhydride resin; liquid crystalline polymers (LCPs); trimethylolpropane triacrylate (TMPTA), polyethylene glycol (PEG)-hydrogel; poly (propylene fumarate) (PPF); ...	☑ Excellent surface quality and precision; high spatial resolution; requires post-processing; strong pattern-like structures; no wasted materials; rapid polymerization; ability to print large-size models ☒ Limited mechanical properties; works with photopolymers which are not stable over time and do not have well-defined mechanical properties; costly resin and machines; parts are affected by moisture, heat, and chemicals; unused material is toxic; support required; low printing rate	[178, 230, 237, 238, 239, 243, 245, 255, 279]
	Digital light processing (DLP), mask projection stereolithography (MPSL), maskless projection slurry stereolithography (MPSS), 3D slurry printing (3DSP); microstereolithography (PμSL); volumetric 3D printing, holographic printing, multi-beam AM; lithography-based metal manufacturing (LMM); digital composite manufacturing (DCM)	Photopolymer liquid—cured with a projector; radical photocuring		☑ Higher print speed compared with SLA; excellent accuracy of laying; low-cost printers; high throughput with quick production rate and wide printing area; transparent or clear printing; reducing post-processing workflow steps ☒ Unable to print large-size objects; very expensive resin and machines; commercially, low applicability	[178, 230, 237, 255, 263–266, 267, 279]
	Continuous digital light process (CDLP), continuous liquid interface production (CLIP), digital light synthesis (DLS); high-area rapid printing (HARP)	Photopolymer liquid— cured with LEDs and usually oxygen; radical photopolymerization and thermal polymerization		☑ High build speed; excellent accuracy of laying; low-cost printers ☒ 'Low-viscosity resins required; costly oxygen permeation membrane; uncertainty over the consumable material; expensive materials; unable to print large-size objects	[178, 230, 233, 237, 255, 271–276, 279]

(*Continued*)

Table 2. (Continued)

Printing process	Printing principle	Feedstock and bonding	Materials	Advantages/disadvantages	Refs.
Liquid crystal display (LCD), daylight polymer printing (DPP), masked stereolithography (MSLA)	Photopolymer liquid—cured with an LCD; radical photocuring	☑ High build speed; excellent accuracy; very cheap and affordable printers ☒ Short service life; weak light intensity; relatively high maintenance cost; unable to print large-size objects	[230, 255, 267, 277–279]		
Direct laser writing (DLW): multi-photon polymerization (MPP); two-photon polymerization (2PP/TPP), two-photon lithography (2PL/TPL), two-photon absorption (2PA/TPA)	Photopolymer liquid—cured with a laser or multi-laser beam	Transparent 2PP resin; customized acrylic-based resin; optimized 2PP polymer; polyethylene glycol; bovine serum albumin (BSA); SU-8; ...	☑ Very high resolution; biomedical molding application; no necessity of recoating or layer-by-layer production ☒ Slower and requires expensive and specific equipment; low build speed; limited materials; Inability to print greater volumes	[230, 235, 237, 246–254, 255, 279]	
Material Jetting (MJ)	Direct inkjet printing (DIP): continuous direct inkjet printing (CDIP); drop-on-demand direct inject printing (DoDDIP), piezoelectric inkjet printer, thermal inkjet printer, electrohydrodynamic (EHD), solution electrospinning (SES), melt electrospinning (MES), melt electro-writing (MEW)	Photopolymer and polymer liquid—cured with UV light or heat	Elastomer-like resins; acrylic-like resins; epoxy and PUR; hydrogel; low-viscosity material (cotton fabrics, pectin nanocellulose, alginate); alumina (aluminum oxide); zirconia; stainless steel; waxes; UV-cured resins; polymers such as PP, high-density polyethylene (HDPE), PS, polymethyl methacrylate (PMMA), PC, ABS, HIPS; ...	☑ High resolution due to nanoscale jetting; safer and easier to handle with no loose powder; very nice surface finish; multiple materials can be printed; fast printing speed; widely commercialized; high accuracy; low waste ☒ Slow process; most applications limited to small parts; parts are very expensive; poor fatigue properties; costly; the material tends to have a low ultimate strain; prone to nozzle clogging; postprocessing usually required; poor mechanical properties	[289–292]
	Aerosol jet printing (AJP)			☑ Very high resolution; fast printing speed; high throughput; multiple materials; smooth surface finish ☒ Limited material selection; low part strength compared to bulk materials; substrate requirements; post-processing usually required	[297, 216]

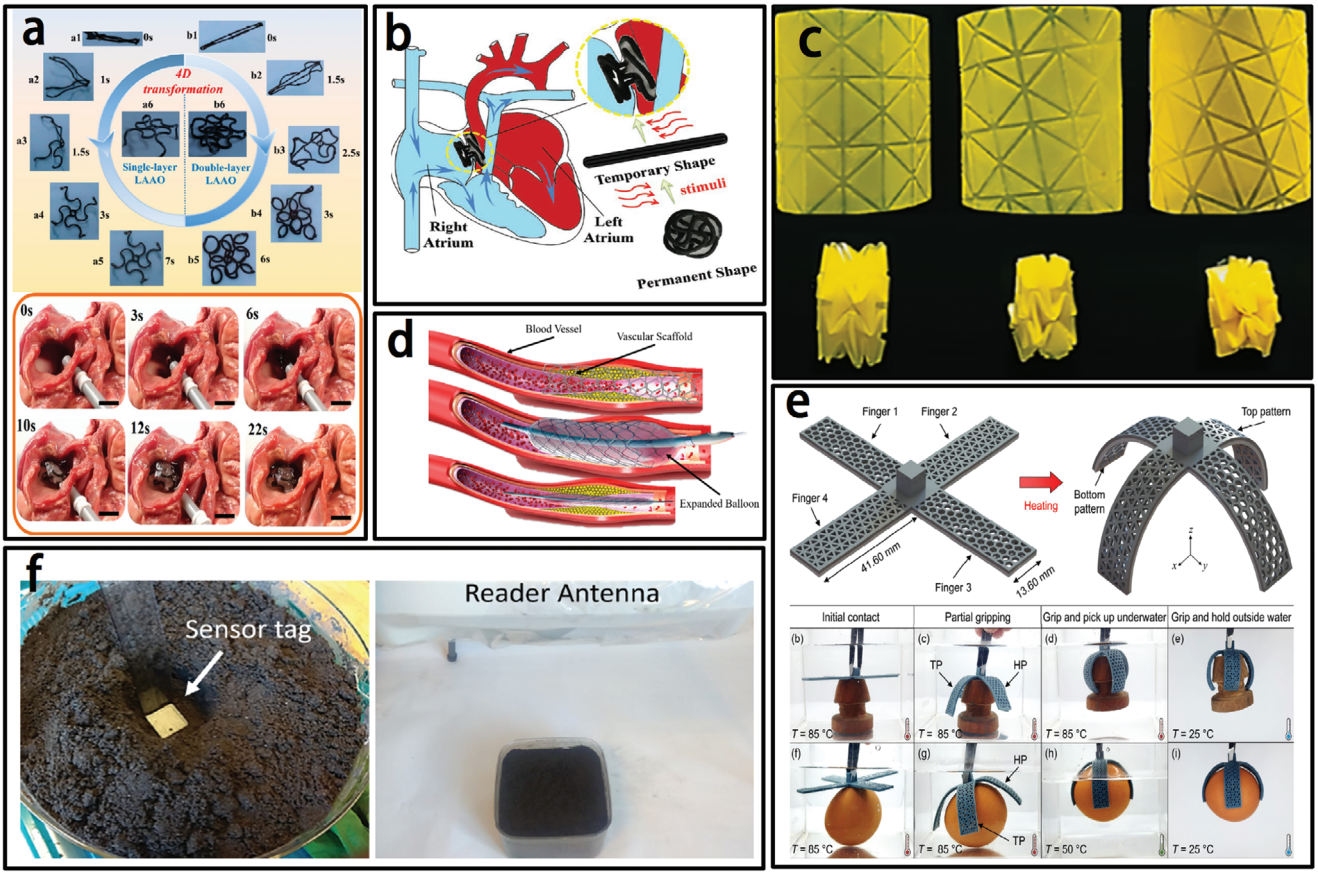


Figure 5. 3D/4D-printed BSSA made of PLA and employing the FFF technique. a) 4D-printed bioinspired absorbable left atrial appendage occluder. Reproduced with permission.[69] Copyright 2021, American Chemical Society. b) Schematic illustration of the occluder prototype. Reproduced with permission.[75] Copyright 2019, Wiley-VCH GmbH. c) Origami derived self-assembly stent. Reproduced with permission.[81] Copyright 2022, Elsevier. d) A vascular stent made of shape memory alloy and balloon-assisted vascular implantation. Reproduced under the term of CC-BY license.[123] Copyright 2023, The Authors, published by MDPI. e) PLA-based gripper made of the bioinspired pattern. Reprodcued under the term of CC-BY license.[124] Copyright 2022, The Authors, published by MDPI. f) Biodegradable radio frequency-based environmentally favorable 3D-printed sensor. Reproduced under the term of CC-BY license.[137] Copyright 2022, The Authors, published by Springer Nature.

controlled 4D transformation process under the trigger of a magnetic field. Jia et al.[61] prepared a biodegradable PLA flexible vascular stent with self-expanding properties using the FFF technique. For implantation, the 4D-printed soft actuator can be crimped into a provisional shape with a reduced diameter. The SMP PLA stent, when implanted in the body, can be thermally triggered to return to its original shape under the influence of body temperature. Lin et al.[75] designed a biodegradable, remotely controlled, and customized SMP soft occlusion actuator by combining programmable SMPs with 3D printing technology employing the FFF method (Figure 5b). The occlusion device may facilitate rapid endothelialization by promoting cell adhesion, proliferation, and tissue growth. The biodegradable occlusion device could supplant metal occlusion devices in the future.

By merging nanocarbon black/PLA composites with bioinspired gradient micro-gap structures and the 4D printing technique, Chen et al.[132] suggested an integrated sensor actuator. The inbuilt sensor-actuator may actively contact things when heated up and self-detect the touching state via varying resistance. Wang et al.[109] created an inexpensive, electrically driven, reversible actuation and sensing method based on PLA and FFF. Multiple applications of this newly designed actuator were demonstrated to illustrate the potential of electroactive polymers in soft, biodegradable sensors and actuators. Zhao et al.[81] discussed the design and manufacturing of self-assembly stents using the origami concept to achieve large shrinkage ratios (Fugure 5c). The researchers used 4D printing to prepare stents with different unit cells and investigated the effect of the helical angle on the shrinkage ratios of the stents. Zhang et al.[123] reported the use of SMPs based on PLA for designing and fabricating a novel porous vascular scaffold to treat vascular restenosis employing the FFF method (Figure 5d). The SMPs were characterized for their thermal, mechanical, and shape memory properties, and it was found that they could be perfectly adaptable in fabricating the vascular scaffold for vascular implantation.[123] The proposed scaffold structure regains its initial shape with a recovery ratio of 98% (recovery temperature of 47 °C) in 16 s. Zhao et al.[82] 4D printed a bioinspired tracheal scaffold using PLA and Fe_3O_4 nanoparticles employing the FFF method. The fabricated scaffold changed shape when exposed to a magnetic field. A highly compressible soft scaffold with a shape memory feature was cre-

ated by Langford et al.[71] using PLA. They created a 3D geometry based on the tessellations seen in origami, which enables precise control over the direction of compression and the material's ability to restore its original form. Rumley et al.[102] presented a method for creating entirely biodegradable, high-performance soft electrohydraulic actuators for soft robotics using sustainable materials, such as ester-based liquid dielectrics and NaCl-infused gelatin hydrogel. They created a completely biodegradable, hydraulically amplified, self-repairing electrostatic actuator. They created an entirely biodegradable gripper with three electrohydraulic soft-actuated joints inspired by spiders that could take up and release objects of various sizes. The gripper was mounted on a 3D printed mount made of PLA and affixed to a commercially available robotic arm that could be programmed. Alshebly et al.[124] presented the development of bioinspired and biodegradable 4D-printed actuators using different patterns made of PLA and employing the FFF technique (Figure 5e). The study analyzed the influence of patterns on the strain and developed a hand-like shaped gripper to demonstrate the feasibility of utilizing the proposed designs in practical applications.

Recent advancements in thermoplastic materials used as filaments for FFF 3D printing have enabled the simple fabrication of 3D-printed electrodes for electrochemical applications using a commercially available conductive filament. The use of 3D printers for this purpose enables the simple incorporation of electrodes into complex and intricate 3D structures to construct sensors with ease.[198,199] In this regard, Gaal et al.[135] demonstrated the potential of the FFF 3D printing technique to fabricate biodegradable soft electrodes using graphene-based PLA filament for the e-tongue sensor used for soil analysis as an alternative means to reduce the complexity of conventional methods. Gopalakrishnan et al.[137] developed a biodegradable radio frequency-based, environmentally favorable sensor by 3D printing biodegradable PLA (Figure 5f).

In addition to PLA, other biodegradable materials are utilized in the FFF technique for the fabrication of soft robotics. PCL,[60,65,77] gelatin-based hydrogel,[98,143] pharmaceutical-grade PVA,[105,106] and polyethylene oxide (PEO)[60] are among these materials. PLA, PCL, polyurethanes, PEG, soybean oil epoxidized acrylate (SOEA), and modified hydrogels are the most frequently used biodegradable polymers for 4D printing.[200] Innovative material science research has created new opportunities for the 3D printing of biodegradable flexible sensors. Utilizing the absorbent properties of bio-polymers such as gelatin or alginate, these lines of research were able to create sensorized hydrogels. Hardman et al.[143] used the FFF method to fabricate a biodegradable, biocompatible soft sensor employing gelatin-glycerol hydrogel. They presented the first investigation into adapting a desktop 3D printer and optimizing its control parameters to fabricate sensorized 2D and 3D structures that can withstand >300% strain and exhibit a highly linear and synchronous response to strain.

Intelligent cardiovascular stents that can incorporate additional components and sensors for healthcare surveillance and diagnosis are presently being developed. Some research has been conducted regarding the integration of 3D-printed sensors and actuators to accomplish closed-loop control of 3D-printed flexible robots. Accordingly, Park et al.[77] fabricated a biocompatible and biodegradable polymer stent with an integrated wireless pressure sensor. Because it can be dissolved and assimilated by the body over time, the PDLA polymer was used as a biodegradable drug coating material. To fabricate the pressure sensor (**Figure 6**a), PDLA powder was dissolved in a tetrahydrofuran solution to form a thin film, which was then deposited on the sacrificial layer. Using 3D printing technology and the biocompatible material PCL, a complex lattice structure was created.

Hygroscopic actuators, among other actuation mechanisms, represent a renewable energy solution for small-scale soft robotics with embodied energy.[201] Cecchini et al.[60] created a soft robot that mimics the adaptability and movement of Geraniaceae seeds, which can move on their own across and into the soil in response to changes in humidity (Figure 6b). This study also investigated the internal structure and biomechanics of pelargonium appendiculatum wild seeds to develop a model for the design of a soft robot. In this study, 4D printing technology was used to fabricate a seed-like soft robot using biodegradable and hygroscopic polymers.

Heiden et al.[98] presented a sustainable and cost-effective FFF process for creating soft robotic actuators using biodegradable gelatin-based hydrogel ink. The printed actuators feature integrated sensor networks and are capable of omnidirectional movement and real-time control for automated obstacle detection and removal (Figure 6c). The results demonstrate the potential of this approach for creating soft robotics with a reduced environmental footprint and accessible recycling procedures. Also, they showed the application of biodegradable printable ink to soft sensors by the fabrication of waveguide sensors.

2.1.2. DIW

DIW is another MEX AM technology that makes it possible to make meso- and microscale 3D objects with complicated shapes and structures.[202] DIW is a type of ink deposition in which viscoelastic ink is pushed out of a small nozzle at controlled flow rates and laid down layer by layer to make 3D objects. Owing to its relatively high resolution, DIW is widely utilized for the fabrication of functional applications, such as microfluidic devices,[203] actuators, and sensors.[204] DIW is the second most common technique for fabricating biodegradable flexible actuators and sensors. After extrusion, the 3D structure solidifies, creating a part with the right properties and characteristics. DIW, also known as robocasting (RC),[205] direct-write assembly (DWA),[206] or micro robotic deposition (μRD),[207] is often classified into three categories: extrusion-based, continuous droplet-based, and energy-assisted DIW.[208,209] However, due to ISO/ASTM 52900, those DIW techniques that employ the extrusion method are categorized as MEX-based DIW printing.

Regarding DIW technology, an ink with good rheological properties must be able to flow through the nozzle (i.e., have a low viscosity under stress) and hold its shape well during deposition (i.e., have a high elastic/storage modulus and a high yield stress). Due to its shear-thinning rheological behavior, the ink acts like a pseudo-solid after it is deposited. Unlike other methods (like FFF), shape preservation does not depend on the feedstock solidifying or drying.[210] Diverse materials may be used for the printing ink in this process so long as the precursor ink demonstrates the required rheological behavior, such as apparent viscosity, yield stress under shear and compression, and viscoelastic

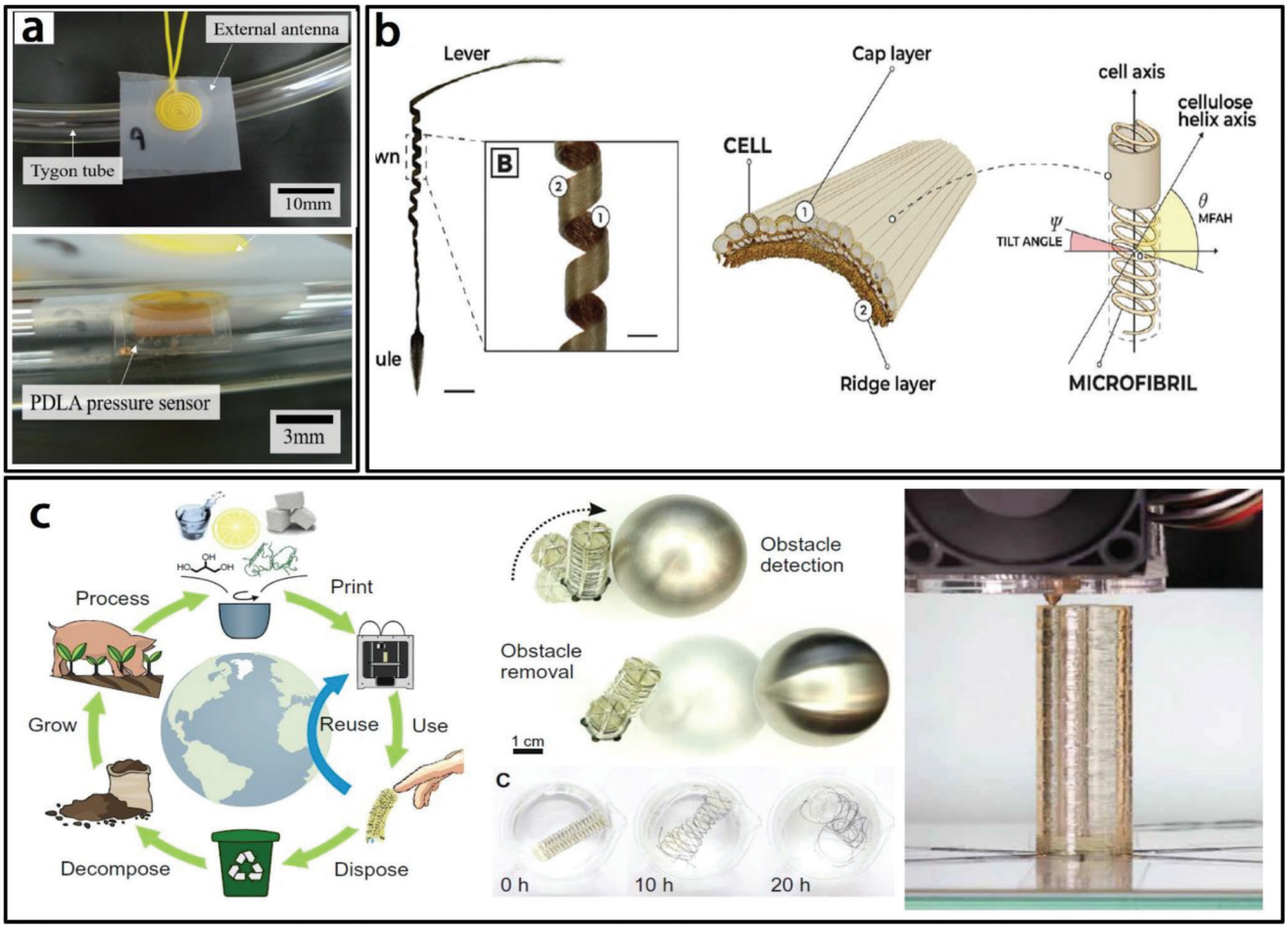


Figure 6. Printed BSSA using the FFF technique. a) PDLA-based pressure sensor. Reproduced with permission.[77] Copyright 2019, Elsevier. b) Humidity-driven seed-inspired soft robot. Reproduced under the term of CC-BY license.[60] Copyright 2023, The Authors, published by Wiley-VCH GmbH. c) 3D-printed biodegradable gelatin-based omnidirectional actuator. Reproduced with permission.[98] Copyright 2022, American Association for the Advancement of Science.

properties. Thus, DIW differs from other AM technologies in that it is not substantially constrained. Accordingly, diverse material classes can be utilized in this AM technology.[211] The distinguishing characteristic of the DIW is its capacity to extrude continuous filaments at ambient temperature, as the printability is not dependent on temperature but instead on the rheological characteristics of the ink. DIW's capacity to generate innovative multi-material structures via the independent and simultaneous extrusion of distinct ink components exemplifies its flexibility.[212] Hence, the capability of DIW to produce multi-material structures in a single step reduces production time, energy, cost, and waste without sacrificing material attributes.

DIW is expanding its services by offering 4D printing as a way to make smart materials that can change shape and respond to stimuli.[115] In addition, the recent advancements in DIW have put forth a promising approach for producing thermoset-based, short-fiber reinforced composites.[213] It is important to note that in DIW, curing normally occurs shortly after deposition, after the inks have been extruded from the printing head. Curing guarantees that complicated pieces may be printed without dimension loss.[214] In the printing process, ink solidification may occur spontaneously or with the assistance of an external process, such as solvent evaporation, gelation, solvent-driven reactions, heat treatment, or photocuring.[202,208]

Regarding MEX technology, DIW methods and processing processes for 3D-printing of microelectronic actuators and sensors may fall into one of two categories: 1) tip-based direct writing (TBDW) and 2) filament-based direct writing (FBDW).[215] A dip-pen nanolithography (DPN) technology is used for the TBDW technique. After being dipped into a material, the tip of an atomic force microscope (AFM) can move materials to a substrate that has an affinity for the material. This phenomenon happens because of capillary effects. This technology is especially beneficial for nanoscale applications since it can build features with a line width as narrow as 12 nm. Thermal dip-pen nanolithography is a variant of DPN that employs an AFM tip compatible with heat to melt the material previously deposited on the AFM tip.[216]

Alginate/methylcellulose (Alg/MC),[62] PLA,[72,80,95,141] poly(ethylene adipate) (PEA),[95] polylactide-co-trimethylene carbonate (PLMC),[64] carrageenan-based nanocomposites,[152,153] multi-walled carbon nanotubes (MWCNTs),[141,143] chitosan hydrogels,[67] PCL,[63,68,72] sodium alginate,[68] bio-polyurethane

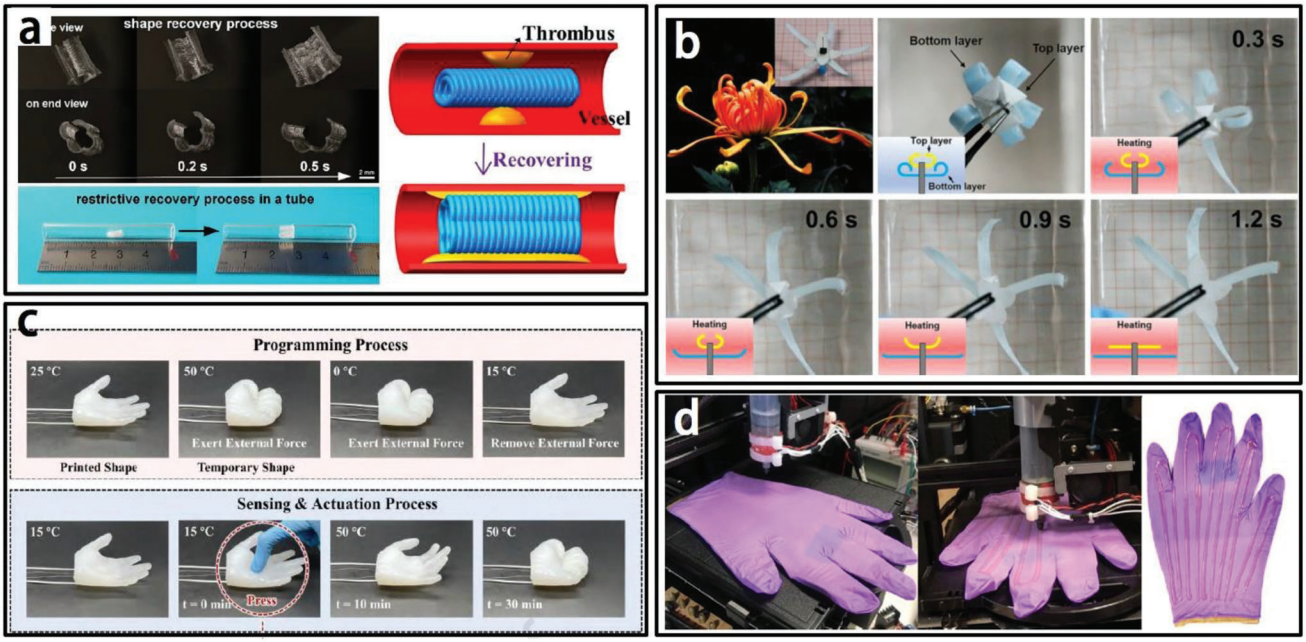


Figure 7. 3D/4D-printed BSSA fabricated by the DIW technique. a) 4D printed shape-changing intravascular stent using PLMC. Reproduced with permission.[64] Copyright 2019, Wiley-VCH GmbH. b) 4D-printed chrysanthemum using PLA/PCL shape memory composites with controllable sequential deformation. Reproduced with permission.[72] Copyright 2021, Springer. c) 4D-printed bionic hand using biodegradable shape memory double-network hydrogel. Reproduced under the term of CC-BY license.[114] Copyright 2023, The Authors, published by Elsevier. d) Self-healing ionic gelatin/glycerol hydrogel-based strain sensor. Reproduced under the term of CC-BY license.[146] Copyright 2022, The Authors, published by Springer Nature.

(BPU),[114] carboxymethyl chitosan (CMCS),[114] protein-based hydrogels,[70] propylene glycol di acetate (PGDA),[74] cellulose-based biopolymers,[115,136,157] carboxymethyl cellulose (CMC),[114,134] gelatin hydrogels,[146] and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)[148] are among biodegradable materials used to make appropriate ink for DIW technique.

Also, as mentioned, PLA is employed as a biodegradable material in making ecofriendly ink for the DIW process. PLA is a polymer synthesized from D, L-lactic acid monomers via liquid polycondensation. Biomedical uses of this biocompatible SMP have been studied for a decade. This polymer's strong stiffness at body temperature,[217] long breakdown time,[218] and side effects of biodegradable materials restrict its use in flexible medical devices. Several studies have synthesized poly(DLLA-co-TMC) (PLMC) and optimized its thermal, physical, mechanical, and biodegradable characteristics by changing monomer ratios. Wan et al.[64] discussed the use of this biocompatible material, PLMC, to create 4D shape-changing soft actuators through DIW. The printed structures in one, two-, and three-dimensions exhibit shape-changing behavior with fast responses around body temperature. The fast response time shows potential in the fields of surgical sutures, nonwoven fabric, and self-expandable stents (**Figure 7**a).

Due to research to develop ecofriendly advanced polymer composites, Park et al.[219] have developed biodegradable poly (lactic acid) multiwalled carbon nanotube nanocomposites (PLA/MWCNTs) using a solvent casting process and subsequent hot pressing. The inclusion of nanomaterials, such as carbon nanotubes, can considerably enhance the composite's electrical properties in addition to its mechanical properties. Accordingly, Guo et al.[141] designed and fabricated a soft liquid sensor comprised of a PLA/MWCNT nanocomposite with an innovative freeform helical geometry using the DIW technique.

Bodkhe and Ermanni[95] have reported solution-based DIW of a multifunctional particulate composite that combines shape-changing and sensing capabilities in a single printed soft structure. The printing ink consisted of a mixture of biodegradable PLA and PEA dissolved in dichloromethane, with the addition of piezoelectric barium titanate nanoparticles as sensing elements. The composites were utilized to print a variety of soft actuators and sensors, and their shape memory and sensing capabilities were studied. Ma et al.[72] used 4D printing technology to create biodegradable shape-memory composites based on PLA and PCL that can achieve controllable sequential shape change. The results showed that the composites have a good shape memory effect and have potential applications in bio-inspired robotics and biomedical devices. The authors also presented two applications of the SMP composites: a double-layer bionic flower (Figure 7b) and a drug-release device. They fabricated these soft actuators using the DIW technique.

Hydrogels are materials that are highly stretchable, transparent, biocompatible, and have ionic conductivity. These materials have potential applications in health monitoring, human motion detection, human–machine interfaces, and soft robotics. Biodegradable soft robots based on stimuli-responsive hydrogels have attracted attention because external stimuli can remotely control them, and they exhibit excellent adaptability to the

surrounding environments due to their softness and flexibility. However, their high-water content and organic nature make it difficult to ensure stability and durability over extended periods. Sensing is a crucial function of hydrogel bionic materials. Human tactile perception develops as a result of bio-ionic currents on the skin in response to mechanical stimulation, in contrast to electronic sensing. This ionic current is transmitted to the brain for sensing via the nerves. Accordingly, researchers infused the hydrogel with ions to create ion-conductive hydrogels.[220] When the ionic hydrogel was mechanically stimulated to undergo partial deformation, the hydrogel's ions shifted, resulting in an ionic gradient. This ion gradient may be converted into an electrical output signal. This bionic sensing ability enabled the use of ionic hydrogel in soft robots, prosthetics, and wearable devices.[221] In this regard, Song et al.[114] developed a biodegradable hydrogel-based bionic material that can sense mechanical stimuli and generate bio-ionic currents, mimicking human tactile perception (Figure 7c). BPU, CMCS, and carbomer were utilized to formulate the hydrogel ink for 4D printing. In addition, both the primary raw materials (BPU, CMCS, and carbomer) and the produced hydrogel were found to be biodegradable and harmless to the environment.

Hardman et al.[146] proposed the use of a versatile ionic gelatin glycerol hydrogel for soft sensing applications that is inexpensive, easy to manufacture, self-healable at room temperature, and can undergo strains of up to 454%. The material was proven to be stable over long periods, biocompatible, and biodegradable. Experiment results demonstrate the applicability of ionic hydrogels for DIW 3D-printed wearable devices and soft robotic technologies for strain (Figure 7d), humidity, and temperature sensing, with the ability to self-heal partially at room temperature.

The magnetic actuation of hydrogels with embedded nanomagnetic particles is one of the novel, recently introduced, noninvasive, and ecofriendly methods for controlling soft robots. The DIW of magnetic nanoparticles combined with alginate-methylcellulose hydrogel was reported by Podstawczyk et al.[62] to facilitate the fabrication of structures with magnetic gradients. Soft actuators made of hydrogel were also 3D printed by putting magnetic Fe_3O_4 nanoparticles inside an alginate-based ionic hydrogel made from algae.[222] The miniaturization of soft robots and untethered soft robots for various applications, such as drug delivery and local lesion treatment, has been recently reported. Jang and Park[67] employed 4D printing to fabricate an untethered milligripper using a biocompatible and biodegradable chitosan hydrogel and biocompatible citric acid-coated superparamagnetic iron oxide nanoparticles.

Zhang et al.[74] reported the 4D printing of a new biodegradable SMP called poly (glycerol dodecanoate) acrylate (PGDA) for potential biomedical implantation applications. The printed structures for vascular stents and vascular grafts were tested in vitro and in vivo, respectively. The material's suitable thermorheological properties enabled the printing of complex structures, and the printed constructs showed excellent shape memory properties, cycling stability, and fast recovery times. Macedo et al.[152] employed biodegradable carrageenan-based composites with barium titanate nanofillers to develop soft force-sensing devices using DIW. Mulakkal et al.[134] presented the development of a sustainable, biodegradable, and cost-effective ink for 4D printing. The ink contained a high total cellulose content and good dispersion of cellulose fibers within the hydrogel matrix. The cellulose fibers' strong inherent hydrogen bonds frequently caused the print nozzle to clog, but the addition of a cellulosic hydrogel solved this problem and made it possible to precisely extrude the composite.

Maity et al.[157] conducted research discussing the properties of cellulose, a biopolymer that is abundant and biodegradable, and its potential for use in various applications, including biomedical devices. The study focused on the piezoelectric property of cellulose, which can generate electricity from mechanical stress, and the pyroelectric effect, which generates an electrical charge from temperature fluctuations. The authors proposed an all-3D-printed pyro-piezoelectric nanogenerator based on cellulose nanocrystal (CNC) for hybrid energy harvesting and self-powered noninvasive cardiorespiratory monitoring. The device showed outstanding mechano-thermal energy harvesting performance along with sensitivity and is capable of accurate detection of the heart's pulse as well as respiration. The all-3D-printed nanogenerator sensor is biocompatible and economically advantageous due to its biomaterial-based supremacy and huge availability. They also demonstrated the application of the CNC-based sensor in a smart mask-based breath monitoring system.

In comparison to the widely studied stimuli-responsive SMP, bilayer films that undergo reversible deformation in response to external stimulation have attracted a great deal of interest in the fields of soft robotics, soft actuators, and soft sensors due to the flexibility of the deformation, the relative ease of preparation, and the diversity of materials. In this regard, Cao et al.[68] successfully fabricated a biodegradable and biocompatible bilayer film made of sodium alginate and polycaprolactone using the DIW printing technique. The bilayer film was found to exhibit self-rolling behavior in response to external stimuli such as heat and Ca^{2+} solution. The self-rolling behavior was found to depend on various factors, such as aspect ratio, thickness ratio, and pattern. The study suggests that the bilayer film has potential applications in creating well-defined tubular structures and biomedical devices such as vascular stents.

2.1.3. Extrusion Bioprinting

DIW is the most often used 3D printing technique for biological and medical purposes.[223] In 3D extrusion bioprinting, DIW is the most prevalent additive manufacturing technology based on the MEX technique. As described in this section, DIW is an additive manufacturing technology involving the extrusion of a filament of "ink" from a nozzle. Typically, the ink is supplied by a syringe or container and does not need a high temperature to be extruded through the nozzle for printing. Thus, cells and bacteria can survive the printing process.[224] Bioprinting refers to the use of AM technologies for the manufacture of designed constructions composed of biological components, such as cells, growth factors, and other biomaterials. Bioprinting is accomplished using a variety of AM methods, although it is especially suited to MEX and in particular DIW technologies, where it is known as "bioplotting."[164] Hydrogels are a significant type of bio-ink material that may be engineered to display shear-thinning behavior. Hydrogels are 3D polymers that may expand in the presence of watery fluids while retaining their form. This property is helpful

for MEX-based bioplotting. This approach typically utilizes cell-laden hydrogel as a bio-ink feedstock. Using hydrogels is a typical technique for making biocompatible and/or biodegradable components. These are water-insoluble polymers that are dispersible in water. Hence, hydrogels may be extruded in a gelatinous state. The water may be removed after extrusion, leaving behind a solid, porous medium. Such a medium might be biocompatible and favorable for cell development with minimal toxicity. Hydrogels may consist of naturally occurring polymers or manufactured polymers. Maybe natural polymers are more biocompatible than synthetic polymers, but synthetic polymers are stronger. Due to the utilization of hazardous chemicals, synthetic hydrogels are used in tissue engineering very rarely. Bioprinting systems are subject to some restrictions when fabricating tissue scaffolds. Although bioplotters may directly insert both material and cells in a scaffold, the diameter of the nozzle through which cells can be extruded is a limitation. Furthermore, tiny nozzles that generate large features often induce shear pressures on cells that dramatically diminish their viability.[225]

The polysaccharide alginate is the most commonly used bio-ink for extrusion 3D bioprinting due to its numerous cellular-friendly properties, such as gelation. Alginate lacks erroneous degradation and cell-binding motifs, which are limitations of alginate bio-inks that can be overcome by merging various low concentrations of natural or synthetic polymers.[226] If appropriate stimuli-response is incorporated, bio-printed bio-microstructures could be used as soft bio-micro actuators in soft robotics. Ding et al.[66] developed cell-laden scaffold tissues via 4D printing of biopolymers, including methacrylate alginate (MA), methacrylate gelatin (GelMA), and PEGDA, as well as an ultraviolet absorber, a photoinitiator, and living cells. To demonstrate the applicability of the biopolymer, they 3D-printed a gripper (**Figure 8**a) with numerous arms that deformed in response to external stimuli such as calcium ions and pH. Using bioprinting techniques, Kirillova et al.[112] created hollow self-folding cylinders with an average interior diameter as small as 20 μm. The self-folding tubes were composed of alginate and hyaluronic acid and were crosslinked with calcium ions and photocuring. They demonstrated the fabrication of (potentially) biocompatible/biodegradable shape-changing polymers (the polymers must be sensitive to Ca^{2+} ions for reversible shape transformations), which is accomplished by the presence of carboxylic groups in the chains and a gradient of crosslinking density in the polymers. Ding et al.[227] made a jammed single-component micro flake hydrogel from MA microgels of varying diameters and morphologies that were ionically crosslinked and oxidized. The authors showed that these jammed microgels can be easily extruded and printed without rheological filler components or support baths and that they have better mechanical stability than traditional granular hydrogels. Constante et al.[96] reported the 4D printing of bi-layer scroll-like scaffolds based on a combination of melt electrowriting of PCL fibers and bioprinting of MA. The combination of these two techniques allows for the controlled deposition of various compounds and the fabrication of high-resolution structures.

Soft ionic materials called eutectogels may be produced by immobilizing eutectic solvents inside polymer supports. These materials have several uses in soft robotics, wearable sensors, bioelectrodes, healthcare monitoring, and other biomedical fields. However, synthetic polymer-based eutectogels are not biodegradable, often have impaired biocompatibility, and are typically not recyclable. Mercadal et al.[145] investigated the use of tannic acid-decorated cellulose nanocrystals as dynamic nanofillers to enhance the mechanical properties and ionic conductivity of biodegradable eutectogels made from biopolymers, such as gelatin and a eutectic mixture composed of choline chloride and ethylene glycol (ethaline).

Huang et al.[76] used GelMA and poly(N-isopropyl acrylamide) hydrogel to create a temperature-responsive and biodegradable hydrogel-based actuator employing the bioprinting method. The actuator is capable of programmable deformation and has potential applications in biomimetic devices, artificial muscles, and soft robotics for biomedical purposes. The bilayer hydrogel actuator, composed of the active GelMA and poly(N-isopropyl acrylamide) layer and passive GelMA layer, shows partially reversible and large bending in response to thermal stimulation (Figure 8b).

Soft wearable electronics is a new technology that aims to enhance the quality of life of its consumers through health monitoring using wearable devices. This technology enables the design and engineering of mechanically deformable, compliant, and secure electronic coverings, flexible robots, and human–machine interfaces. In this regard, Heidarian et al.[144] developed a self-healing nano-polysaccharide hydrogel for use in flexible strain sensors (Figure 8c). Based on relative resistance changes caused by bending angles, the mesh-shaped hydrogel structure exhibited superior strain-sensing functionality.

Polyelectrolyte hydrogels are composed of highly polar polymer chains that form hydrophilic networks with desirable characteristics such as biocompatibility, biodegradability, and modifiable mechanical and electrical properties; thus, they may be promising materials for 3D-printed biomedical applications. Various polyelectrolytes, including gelatin, chitosan, and hyaluronic acid, have demonstrated their potential for 3D printing. Compared to the respective casted gel, the resultant chitosan polyelectrolyte gel exhibited superior swelling and stimuli-responsive bending properties (required for actuators). Also, chitosan-based electroactive polymer actuators exhibit greater ionic conductivity and mechanical efficacy than other biopolymer-based soft actuators.[228]

Zolfagharian et al.[79] investigated the use of 3D bioprinting in the fabrication of soft actuators from responsive materials such as chitosan-based hydrogel. Using bioprinting, Zolfagharian et al.[94] created a chitosan hydrogel self-folding flexible actuator that could rapidly respond to photo-thermal conditions. Several variables, including varied hinge widths and onset temperatures, have been observed to affect the folding angle and soft origami folding speed. Also in another study, Zolfagharian et al.[30] presented a novel application of 3D printing in the fabrication of biodegradable and biocompatible soft robots using polyelectrolyte hydrogels. The study focused on the actuation performance of chitosan and gelatin hydrogels, which are potential candidates for polyelectrolyte actuators. The researchers optimized the printing parameters to fabricate the desired geometrical model and analyzed the printing effects on actuation performance. Chitosan is a weak base containing numerous ionizable primary amine groups that are capable of inducing this reversible electrical response. Chitosan hydrogel sheets may be combined with different geometries to create intricate artificial

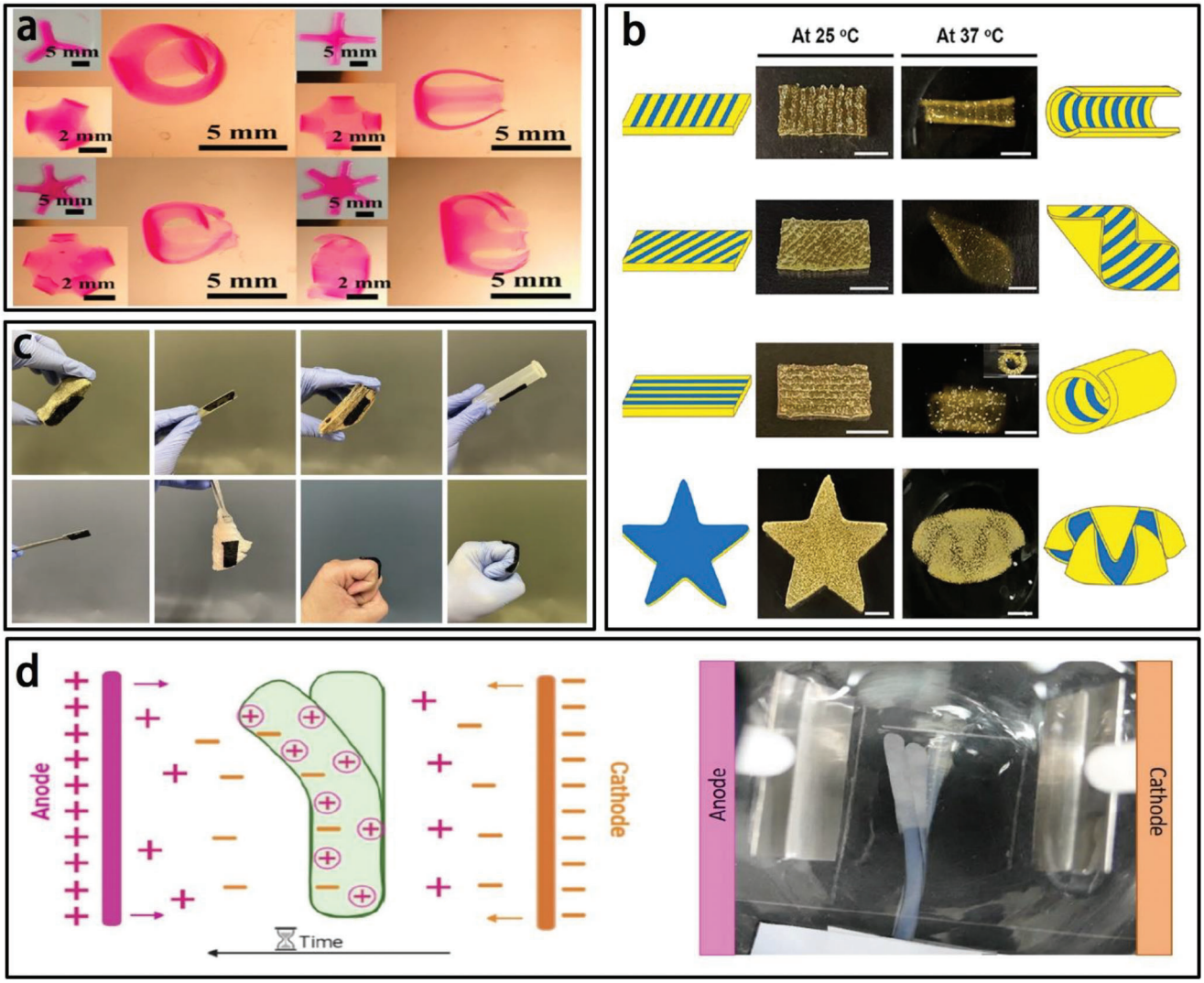


Figure 8. 3D/4D-printed BSSA fabricated by the extrusion 3D bioprinting technique. a) Bioprinted multiple-arm grippers and their deformed structures. Reproduced under the term of CC-BY license.[66] Copyright 2022, The Authors, published by Elsevier. b) The deformation of the hydrogel GelMA-based actuators when transferred from air at 25 °C to water at 37 °C. Reproduced with permission.[76] Copyright 2023, American Chemical Society. c) Soft strain sensor made of nanocellulose/nanochitin self-healing hydrogel. Adapted with permission.[144] Copyright 2022, Elsevier. d) pH-induced 3D printable chitosan-based soft actuator. Reproduced under the term of CC-BY license.[97] Copyright 2022, The Authors, published by MDPI.

3D deformations like fake claws, flowers, and horns, illustrating further shape changes brought on by pH. The hydrogels, on the other hand, are naturally able to bend in response to electrical stimulation because of the distinctive pH sensitivity of chitosan, which further qualifies them for usage as soft actuators and active scaffolds. Using bioprinting technology, Maiz-Fernández et al.[97] created a PH-induced chitosan hydrogel with high biodegradability and biocompatibility and discussed its possible use in soft actuators (Figure 8d). **Table 3** provides a summary of the BSSA manufactured with MEX techniques.

2.2. Vat Photopolymerization (VPP)

The genesis of 3D printing with economic viability may be traced back to 1986 when Charles W. Hull submitted a patent for stereolithography, a photopolymerization method.[229] VPP is an ISO/ASTM category for AM methods in which light-activated polymerization is used to selectively cure liquid photopolymer in a vat.[165] Using a vat of liquid photopolymer resin, the sculpture is created layer by layer or as a complete 3D object via VPP. When necessary, ultraviolet (UV) light is utilized to cure or harden the resin, while usually, a platform pulls the item downwards or upwards after each layer has been hardened. The curing light initiates and accelerates the polymerization process, which creates polymer chains or crosslinks them to form a solid resin.[230] The arrangement of various components, such as the light source, build platform, curing direction, and resin tank, distinguishes VPP technologies.[231]

In terms of curing techniques, VPP is classified into several sub-groups: 1) stereolithography (SLA), which is cured by a laser beam; 2) direct laser writing (DLW), which is cured with one

Table 3. Summary of the BSSA manufactured with MEX techniques.

Printing process	Year	Type	Actuation/sensing mechanism	Biopolymer	Potential applications	Refs.
FFF	2016	Actuator	Thermal	PLA	3D lightweight structures or devices, self-morphing structures	[116]
	2017	Actuator	Thermal	PLA	Delicate gripping applications, self-morphing structures	[125]
	2018	Sensor	Electrochemical	Graphene-based PLA	E-tongues, agriculture, soil quality sensing applications	[135]
	2018	Actuator	Thermal	PLA	Biomedical applications, vascular stents	[61]
	2018	Actuator/sensor	Pressure	PCL, PDLA	Biomedical applications, pressure sensing applications	[77]
	2018	Actuator/sensor	Electrothermal, force	Paper, PLA	Touch sensors, sliding sensors, miligrippers, paper robots, paper power generators, electronic pop-up books, animated origamis, foldable artifacts	[109]
	2019	Actuator	Thermal	PCL-T, poly-HDI-coated PCL	Muscle tissue engineering	[65]
	2019	Actuator	Thermal, magnetic	PLA-based magnetic nanocomposites (PLA-MNCs)	Biomedical applications, Implantable medical devices, bionic devices	[75]
	2019	Actuator	Thermal	Pharmaceutical-grade PVA	Drug delivery devices	[105]
	2019	Actuator	Thermal, magnetic	PLA/Fe_3O_4	Biomedical applications, minimally invasive medical applications	[82]
	2019	Actuator	Thermal	PLA	Delicate gripping applications, self-morphing structures	[128]
	2019	Actuator	Water	Pharmaceutical grade PVA	Medical applications, drug delivery devices	[106]
	2020	Actuator	Thermal	PLA	Soft energy-absorbing actuators, aeronautics components	[119]
	2020	Actuator	Thermal	PLA	Self-folding origami structures, aeronautic components, grippers	[120]
	2020	Actuator	Thermal	PLA	Self-morphing structures, self-deployment sandwich structures	[126]
	2020	Actuator	Thermal	PLA	Self-morphing structures, self-deployment sandwich structures	[133]
	2020	Actuator/Sensor	Strain, thermal	PLA	Humanoid soft robots, multifunctional sensors	[132]
	2021	Sensor	Strain	Gelatin-glycerol based hydrogel	Wearable soft robots	[143]
	2021	Actuator	Thermal, magnetic	PLA-MNCs	Biomedical applications, implantable medical devices, bionic devices	[69]
	2021	Actuator	Thermal	PLA	Biomedical applications, bone tissue engineering	[71]
	2021	Actuator	Thermal, Magnetic	PLA/Fe_3O_4	Biomedical applications, implantable medical devices, vascular stents	[78]
	2021	Actuator	Thermal	Paper, PLA	Electrical switch applications	[196]
	2022	Actuator	Pneumatic	Gelatin-based hydrogel	Grippers, surgical instruments, rehabilitation devices, swimming robots, waveguide sensors	[98]
	2022	Actuator	Thermal	PLA-PCL-based bio-polyurethane	Intelligent soft actuators, bionic materials, biomedical applications, drug delivery devices	[73]
	2022	Actuator	Electrohydraulic	PLA	Edible soft robots, electro adhesive pads, soft pumps	[121]
	2022	Actuator	Thermal	PLA	Delicate gripping applications, self-morphing structures	[124]
	2022	Actuator	Thermal	PLA	Vascular stents, biomedical applications, self-morphing structures	[81]

(*Continued*)

Table 3. (Continued)

Printing process	Year	Type	Actuation/sensing mechanism	Biopolymer	Potential applications	Refs.
2022	Actuator	Thermal	PLA	Delicate gripping applications, self-morphing structures	[127]	
2022	Actuator	Water	PLA	Agriculture, soil quality sensing soft robots	[137]	
2023	Actuator	Humidity	PCL, PEO shell, and CNC	Agriculture applications, soil exploration, environment monitoring	[60]	
2023	Actuator	Electrohydraulic	PLA	Grippers, rehabilitation devices, garbage-collecting robots	[102]	
2023	Actuator	Thermal	PLA	Biomimetic applications, stent repairments, biomimetic applications	[123]	
DIW	2015	Sensor	Liquid	PLA/MWCNT	Liquid sensing applications	[141]
	2016	Actuator	Water	Cellulose biocomposites	Medical/tissue engineering, load bearing, electronics, wearable devices, biomimetic devices, self-folding structures	[115]
	2017	Actuator	Thermal	PCL-based photocurable polymer	Biomedical applications	[63]
	2017	Actuator	Thermal, magnetic	PLA/Fe_3O_4	Biomedical applications, minimally invasive medical applications	[80]
	2018	Actuator	Water	CMC	Self-morphing structures	[134]
	2019	Actuator	Thermal	PLMC	Biomedical applications, shape-changing devices, smart nonwoven fabrics, self-expandable stents, drug delivery robots	[64]
	2019	Sensor	Humidity	Cellulose nanofibril	Humidity sensors, agriculture applications, soil exploration, environment monitoring	[136]
	2019	Sensor	Strain	PEDOT:PSS-PVA	Flexible strain sensors for soft electronics, wearable applications	[148]
	2020	Actuator/sensor	Magnetic	Alginate-methylcellulose based hydrogel	Magnetic sensors/actuators, biomedical applications	[62]
	2020	Actuator/sensor	Electrothermal	PLA and PEA	Micro positioning, wearable soft robots, electroactive scaffolds, artificial organs, adaptive electronics	[95]
	2020	Actuator	Thermal	PGDA	SMP-based scaffolds for use in vascular stents and grafts	[74]
	2021	Actuator	Thermal, pH, enzyme	Protein-based hydrogels	Biomedical applications, drug delivery devices	[70]
	2021	Actuator	Thermal	PLA and PCL	Intelligent soft actuators, bionic materials, biomedical applications, drug delivery devices	[72]
	2021	Sensor	Force	Silk, PHBV	Sutureless clips for intestine anastomosis, piezoelectric force sensors with self-powering properties, biomedical applications	[139]
	2022	Sensor	Force	MWCNT/Carrageenan-based nanocomposite	Soft sustainable electronics	[153]
	2022	Sensor	Strain	Gelatin glycerol hydrogel	Flexible strain sensors for soft electronics, wearable applications, bioelectrodes, healthcare monitoring, human motion detection	[146]
	2023	Sensor	Force	Carrageenan-based nanocomposite	Soft sustainable electronics	[152]

(*Continued*)

Table 3. (Continued)

Printing process	Year	Type	Actuation/sensing mechanism	Biopolymer	Potential applications	Refs.
2023	Actuator	Electromagnetic	Chitosan hydrogel	Miligrippers, positioning applications, biomedical applications, shape-changing devices, Invasive small soft robots in vivo	[67]	
2023	Actuator	Calcium ion, thermal	Sodium alginate and PCL	Biomedical applications, vascular stents, drug delivery devices	[68]	
2023	Actuator/ sensor	Thermal, force	BPU, CMCS	Bionic devices, wearable devices, soft smart prosthetics	[114]	
2023	Sensor	Thermal, mechanical	CNC-based biopolymer	Noninvasive cardiorespiratory monitoring, wearable devices, healthcare monitoring soft devices	[157]	
MEX-based bioprinting	2017	Actuator	Light	Chitosan-based hydrogels	Photothermal soft origami devices, positioning soft robots, drug delivery robots	[94]
	2017	Actuator	Calcium ion	MA and hyaluronic acid hydrogels	Muscle tissue engineering, regenerative medicine applications	[112]
	2017	Actuator	Electrical	Chitosan-based hydrogels	Environmental applications, biomedical applications	[79]
	2017	Actuator	Electrical	Chitosan-based hydrogels	3D biomimetic scaffolds, actuators in medical applications	[30]
	2021	Actuator	Calcium ion	MA and PCL	Muscle tissue engineering	[96]
	2021	Actuator/sensor	Calcium ion, pH	MA, GelMA, and PEGDA	Biomedical applications, bone tissue engineering	[66]
	2022	Sensor	Strain	Nano-polysaccharide self-healing hydrogel	Flexible strain sensors for soft electronics, wearable applications	[144]
	2022	Actuator	Thermal	Poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogel	Drug delivery devices, vascular stents, cardiovascular scaffolds	[104]
	2022	Actuator	Electromagnetic	alginate/Ca2+ based hydrogel	Biomimetic applications	[122]
	2022	Actuator	pH	Ionically cross-linked oxidized and MA	Tissue engineering, Regenerative medicine	[227]
	2022	Actuator	Electrical	Chitosan-based hydrogels	Three-dimensional biomimetic scaffolds, Actuators in medical applications	[97]
	2023	Actuator	Thermal	GelMA–poly(N-isopropyl acrylamide) hydrogels	Biomedical applications, biomimetic devices, artificial muscles	[76]
	2023	Sensor	Strain	Biocompatible eutectogels based on gelatin	Flexible strain sensors for soft electronics, wearable applications, bioelectrodes, healthcare monitoring devices	[145]

or more than one laser beam; 3) digital light processing (DLP), which is cured by digital projection; 4) continuous digital light process (CDLP), which is cured by LEDs and oxygen; and 5) Liquid crystal display (LCD) 3D printing, which is cured by an LCD. **Figure 9** illustrates the schematic representation of the diverse processes of VPP. Also, the characteristics of different types of VPP systems are listed in Table 2.

VPP has gained significant popularity as a 3D printing technology owing to its notable attributes such as superior printing resolution, dimensional stability, high-quality surface finish, and efficient processing. However, it is important to acknowledge that VPP technology faces limitations in terms of the range of resins and materials that can be processed and photo-cured. Although it is possible to synthesize customized resins on a research scale to get desired characteristics, this procedure becomes laborious and resource-intensive, resulting in increased costs related to raw ingredients and synthesis equipment. Therefore, it is essential to explore novel chemistries for resin materials, while simultaneously prioritizing the efficient use and optimization of existing resources. One potential method for accomplishing

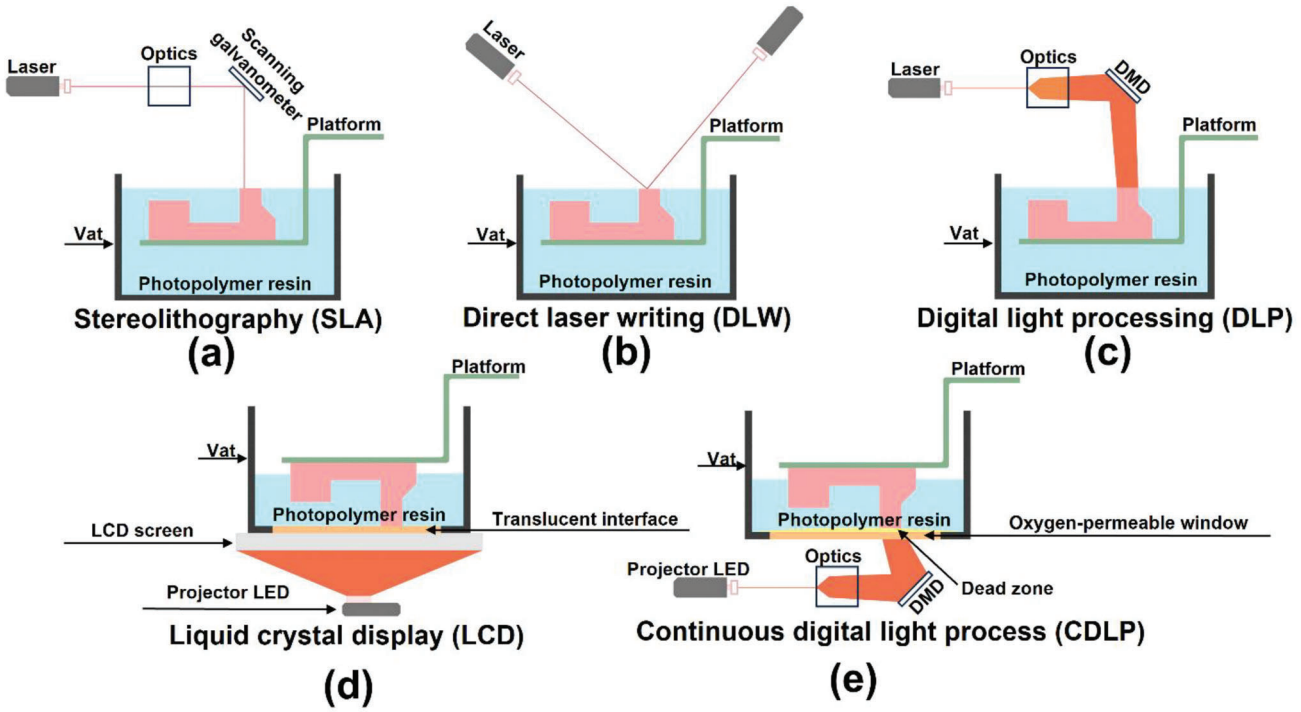


Figure 9. Schematic representation of the diverse processes of VPP. a) SLA, which is cured by a laser beam. b) DLW, which is cured with one or more than one laser beam. c) DLP, which is cured by digital projection. d) LCD 3D printing, which is cured by an LCD. e) CDLP, which is cured by LEDs and oxygen.

this objective is the use of a multi-material strategy, whereby the available or commercially accessible materials are leveraged to their fullest extent.[231]

While scanning laser beams are necessary for the SLA and DLW methods, the DLP method makes use of a large radiation beam that a digital micromirror device (DMD) patterns. In the DLW, photopolymerization happens at the intersection of two or more scanning laser beams, while in other setups, a single laser and various photoinitiator chemistries are used. With the SLA and DLP techniques, usually it is essential to recoat, or add a fresh layer of resin, but in the DLW approach, the component is produced under the resin surface, eliminating the requirement for recoating. Methods that eliminate the need for recoating are quicker and less complex.[232] Moreover, despite the other 4 configurations, CDLP is an alternative method of AM that uses the basic idea of oxygen-inhibited photopolymerization to make a continuous liquid interface of uncured resin between the growing component and the exposure window. This interface removes the need for a layer-by-layer iterative procedure, making continuous manufacturing possible.[233] The photopolymer mixture consists of monomers, oligomers, and photoinitiators. When photoinitiators are subjected to curing light, they release species that act as catalysts for the chain synthesis of monomers and oligomers. The chain-forming chemical-thermal process is irreversible, and prototypes cannot be returned to their liquid state.[234]

It is noteworthy that using a variety of biocompatible synthetic polymers, researchers have developed the construction of tissue scaffolds using VPP.[225,235] These polymers typically contain carbonate or ester groups that are hydrolyzable under physiological conditions.[236] Poly(propylene fumarate) (PPF), the most extensively documented printed photopolymer for tissue scaffolds, is biocompatible and shows potential for usage in scaffolds for hard tissue replacement.[237] Polymers such as poly(ε-caprolactone), poly(ethylene glycol) diacrylate, trimethylene carbonate, and poly(D, L-lactide) have also been developed.[238] Unfortunately, because of their restricted range of mechanical and chemical characteristics, these polymers are only suitable for particular kinds of tissue replacement scaffolds. TPETA,[83] GelMA,[84,85] Acrylamide (AAm),[117] PEGDA,[88–91,107,113,117,130,140,147] photocrosslinkable polycaprolactone dimethyl acrylate (PCLDMA),[87,103] photocurable PLA,[110] photocurable polycaprolactone diacrylate (PCLDA),[86,129] gelatin,[99] photocurable chitosan-based polymer,[34] pentaerythritol tetraacrylate (PETA),[107] photocurable alginate-based polymer,[100] poly(ethylene glycol) methyl ether methacrylate (PEGMA),[101] propylene glycol methyl ether acetate (PGMEA),[108] PEGgel,[92] and polyethylene glycol dimethacrylate (PEGDMA)[149] are among biodegradable materials used to make appropriate photocurable polymer for VPP technique. In the following sections, several facets of each VPP approach have been addressed in more detail.

2.2.1. SLA

SLA is the first AM ever invented. SLA employs a laser beam that traverses the surface of the forming layer, resulting in the local

polymerization of the photosensitive resin. The spot-by-spot curing of the resin enables the fabrication of intricately shaped components with great dimensional accuracy and surface quality. There are two main configurations to set up an SLA 3D printing machine: top-down VPP and bottom-up VPP. In top-down VPP, UV light follows the necessary route above the tank and solidifies the photopolymer in the top liquid bath by producing crosslinked networks. The bottom-up approach With VPP printers, the light source is placed underneath the resin bath, and the moving platform is constructed from the top down. The translucent bottom of the resin bath enables the laser light to flow through but prevents the cured portion from adhering to it. Compared to top-down VPP, bottom-up VPP takes less resin to fill the bath and may produce higher quantities.[160] An SLA-made component's mechanical characteristics, such as strength and Young's modulus, may be tailored across a broad range by adjusting the viscosity and the photoresin's photoreactivity.[239] For this kind of manufacturing, epoxy resin, polyester resin, and photosensitive polyacrylate resin are the most often utilized matrix materials.[240]

Also, researchers have developed a new printing method to improve the resolution of SLA-based printing and fix problems with the way it works now. Micro stereolithography (μSLA) is a new SLA method that has come about in the last two decades as a result of the development of certain resins, improvements in laser technology, and the addition of lenses that can make light spots so small. The basic principle of all vector-by-vector μSLA machines is very similar to that of the SLA technique: to achieve a higher resolution than SLA, the beam must be focused more accurately to minimize the spot size to a few microns, necessitating additional technological advancements in the designed μSLA machines.[241] μSLA has been developed to produce highly precise, 3D microstructures from a broad selection of functional materials, especially bio-compatible materials.[242]

Additionally, the biological and mechanical characteristics of photosensitive resins may be readily customized. The biocompatibility and biodegradability may be tailored by using different base monomers, and the elastic modulus and strength of the finished product can be adjusted by varying the degree of crosslinking. The main problems with photoreactive resins are toxicity and cell compatibility. These issues may be resolved with the right postprocessing techniques and a careful selection of the monomers used.[45]

When employing the VPP process to fabricate multi-material components, materials must be exchanged within the vat from one liquid resin to another. This method lengthens the production process and is very labor-intensive. Chan et al.[90] employed a 3D SLA printer to create multi-material biological soft actuators with a biological bimorph cantilever serving as the actuator and a base structure defining the asymmetric form for locomotion. The bio-bot was made of PEGDA hydrogel and powered by contractile cardiomyocytes. Given that the compression modulus of the PEGDA hydrogel material is comparable to that of human cartilage tissue, it has a promising future in the field of bioengineering. Mohammed et al.[117] implemented an optimized approach for infusing up to 2 wt% superparamagnetic iron oxide nanoparticles with a 10 nm diameter into a photo-resin composed of water, acrylamide, and PEGDA, with refined nanoparticle homogeneity and decreased agglomeration during printing. The 3D-printed starfish hydrogels (**Figure 10**a) displayed high mechanical stability and robust mechanical properties, with a maximum Young's modulus of 1.8 MPa and a limited 10% shape deformation when expanded. When a remote magnetic field is applied, each limb of the starfish can be magnetically activated. These hydrogels can be utilized in a vast array of applications, such as biodegradable soft robotics and magnetically stimulated actuators. Song et al.[131] fabricated a multi-material pneumatic actuator and microactuator using mostly biodegradable materials employing the SLA technique. This study showed how to create pneumatic actuators (Figure 10b) and microactuators with a resolution of as little as 200 micrometers utilizing combinations of materials with varying Young's moduli, such as 0.5 MPa and 1.1 GPa. These multimaterial actuators are simpler to assemble and offer better deformation controllability than single-material actuators.

Bioactuators, or biohybrid actuators, are among the several eco-friendly microactuator designs that have been created and researched recently. They are particularly intriguing since they use live cells, exhibit self-actuation, and have the potential to be used in vivo. For instance, incorporating the spontaneous contraction of cardiomyocytes into intricate polymer structures could be able to produce spontaneous motion with only the use of an ordinary cell medium and a natural energy source like glucose. Biohybrid robots made of soft materials and cells have recently shown that they are capable of detecting, reacting to, and adapting to environmental stimuli in real time, accomplishing lifelike tasks like swimming, walking, and pumping.[244] Also, soft robotic devices based on cells may have a transformative effect on our ability to design machines and systems that can dynamically detect and respond to a variety of complex environmental signals.[91] In this regard, Chan et al.[89] created a walking machine (Figure 10c) that mimics the in vivo musculoskeletal system using skeletons made using SLA 3D printing technology. They developed a bio-bot, or biological machine, with an actuation module for the purpose of movement. Using a multi-material SLA printer, a variety of biobots were produced. The bio-bot displayed an effective locomotion system that made the most of contractile forces to reduce frictional forces and kept the legs from moving backward when relaxing. A sheet of contractile cardiomyocytes was seeded onto the cantilever framework.

2.2.2. DLW

DLW, together with conventional SLA and selective laser sintering, make up a flexible family of laser-based 3D printing processes that allow the manufacture of customized structures directly from a 3D CAD file. Compared to those two, DLW provides greater resolution and does not require the necessity of recoating or layer-by-layer production; on the negative side, it is slower and requires expensive and specific equipment.[246] DLW with multiphoton polymerization (MPP) is an AM process that lets objects be put together with a precision of less than 100 nm. This process is based on the fact that photopolymers absorb photons in a nonlinear way. When a laser beam is carefully focused inside a transparent material, it can take in two or more photons and polymerize in a small area.[247,248] The DLW method is based on highly specific photochemical reactions that start in a small area near the laser beam's focal point. Due to the great spatial

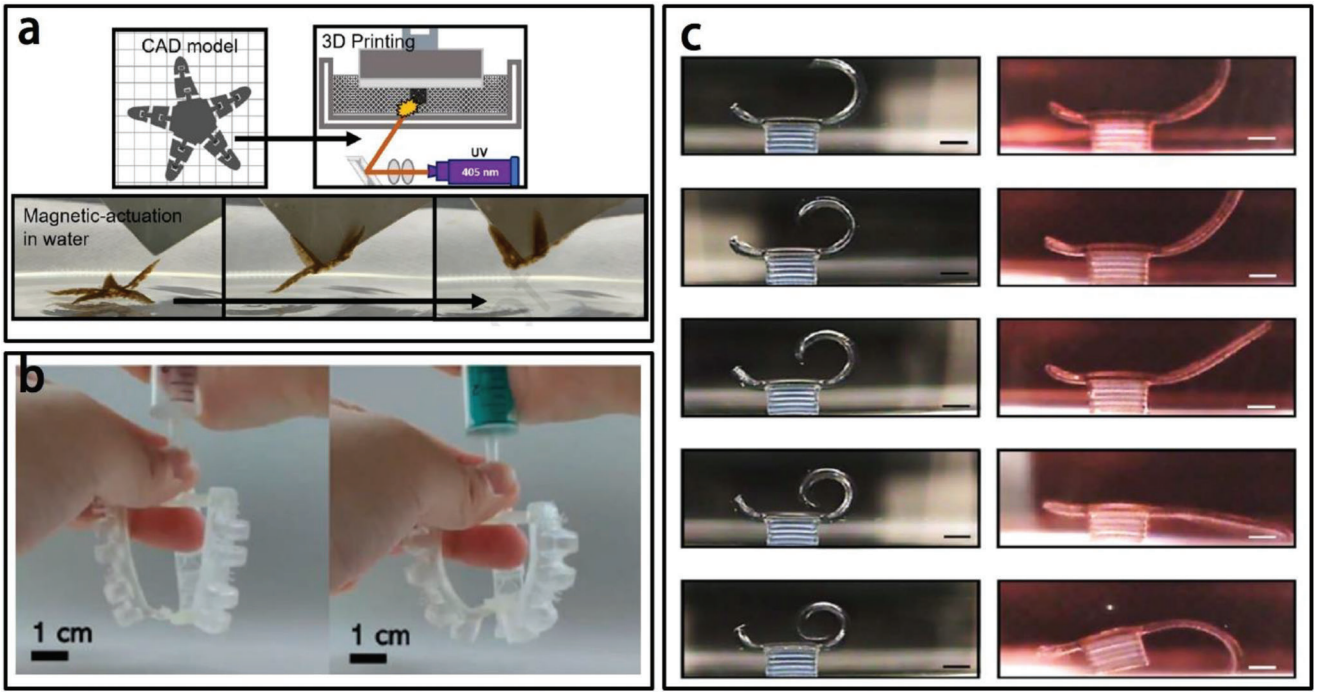


Figure 10. 3D/4D-printed BSSA fabricated by the SLA technique. a) SLA 3D-printed superparamagnetic stimuli-responsive starfish-shaped hydrogels. Reproduced under the term of CC-BY license.[117] Copyright 2023, The Authors, published by Elsevier. b) Locomotive "'bio-bots"' from hydrogels and cardiomyocytes using an SLA 3D printer. Reproduced under the term of CC-BY license.[89] Copyright 2021, The Authors, published by Springer Nature. c) 3D-printed PEG-AA-based elastomer pneumatic soft actuator. Reproduced under the term of CC-BY license.[131] Copyright 2023, The Authors, published by MDPI.

resolution of multiphoton absorption, the response is limited to such tiny locations. In the early 1990s, pioneering work on single-photon DLW was undertaken. Due to its ability to create fully 3D nanostructures, the first commercial employment of DLW using multi-photon polymerization took place in 1997, and the photonics community quickly accepted it and began to develop the DLW technology after that. The physical phenomenon that enables DLW to function is multiphoton absorption.[230,249]

Researchers have been utilizing two-photon polymerization (2PP/TPP) (also known as two-photon lithography (2PL/TPL), and two-photon absorption (2PA/TPA)) more often than any other DLW technique so far.[250–253] 2PP is proportional to the square of the intensity of light; hence, the polymerization drops fast with decreasing laser intensity. Significant differences exist between linear one-photon fluorescence and non-linear two-photon fluorescence. Due to the linear nature of one-photon (or normal) absorption, when a UV laser is directed at a solution containing a UV-absorbing molecule, the ensuing fluorescence may be seen along the laser's course inside the solution. Two-photon absorption, however, happens in a very narrow focal volume when a laser beam of high intensity is focused on the same material. Two-photon absorption is restricted to the laser's focus because it is a nonlinear optical phenomenon that happens at high laser intensities, which are only found at the laser's focus. This great spatial resolution is essential for the use of two-photon-induced procedures to employ DLW in the fabrication of high-resolution soft microrobots.[254]

In this respect, Kaynak et al.[83] presented a new approach to creating micromechanical soft actuators using acoustic signals as a power source. The researchers made tiny capsules with air bubbles inside them using 3D printing (**Figure 11**a). They printed all the structures as a monolithic piece from a single biocompatible soft biopolymer, trimethylolpropane ethoxylate triacrylate (TPETA), using 2PP.

Future biomedical applications, such as targeted distribution and diagnostics, have called for mobile micro- and nanorobots. Biocompatibility and biodegradability of micro- and nanorobots are essential components for their application to clinical practice. Making miniature robots with soft, non-cytotoxic, biodegradable parts will improve device absorption, optimize tissue contact, and reduce immunological reactivity. Wang et al.[84] reported the 3D microfabrication of biodegradable soft helical microswimmers by means of 2PP of the nontoxic photocrosslinkable GelMA (Figure 11b). GelMA microswimmers are degradable in their entirety by collagenases. Enzymes secreted by cells during culture can gradually break them down in addition to promoting cell attachment and proliferation. Bozuyuk et al.[34] introduced a double-helical, magnetically propelled microswimmer that actively releases the chemotherapeutic drug doxorubicin in response to external light stimulation. The microswimmers were created utilizing 2PP-based 3D printing of a magnetic polymer nanocomposite, a natural polymer derivative of chitosan. This magnetically actuated biocompatible and biodegradable chitosan-based microswimmer can be used for on-demand light-triggered drug release.

A wide range of materials can be used in DLW, such as various photo-polymers, bio-compatible materials, and even proteins and other biodegradable biomaterials.[255] Another technique for

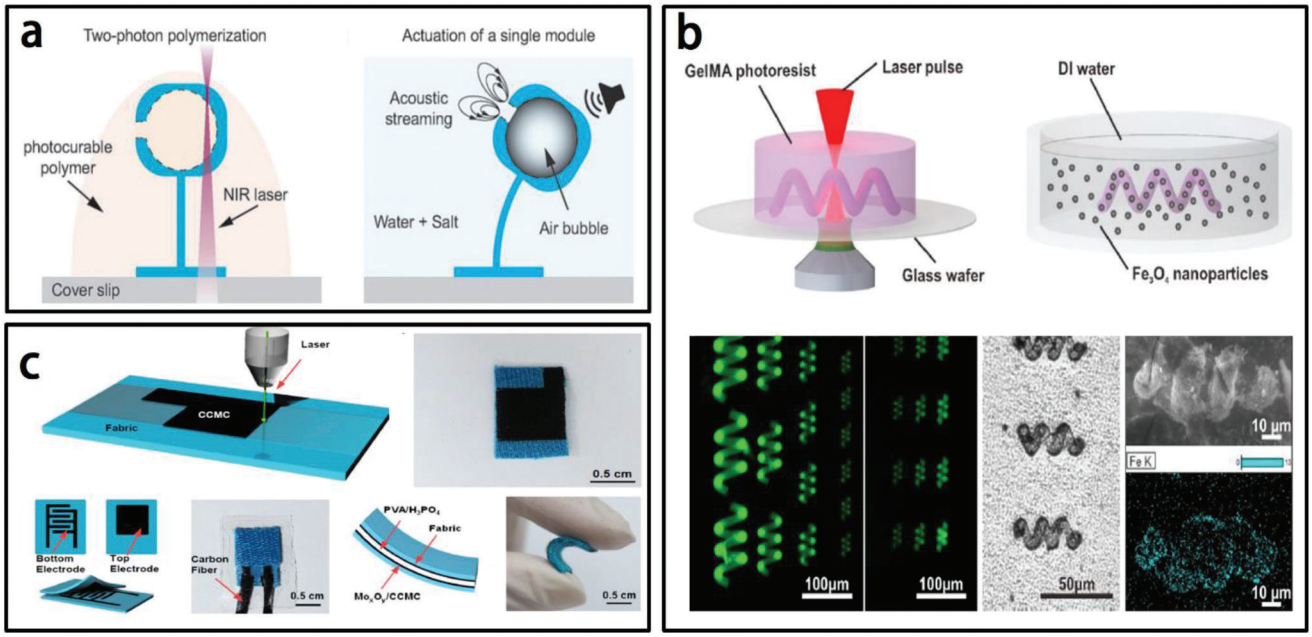


Figure 11. 3D/4D-printed BSSA fabricated by DLW technique. a) 3D-printed acoustically programmable soft microactuator using 2PP DLW technique. Reproduced under the term of CC-BY license.[83] Copyright 2023, The Authors, published by Mary Ann Liebert, Inc. b) Schematic of the fabrication of biodegradable GelMA helicalmicroswimmers. Reproduced with permission.[84] Copyright 2018, Wiley-VCH GmbH. c) Schematic illustrating the DLW of flexible electrodes on the fabric. Reproduced with permission.[154] Copyright 2020, American Chemical Society.

improving DLW resolution is to use stimulated emission depletion (STED) inspired 3D nanolithography. STED employs two light beams: the first is the excitation beam, and the second, ideally with a longer wavelength, is used to counteract the effects of exposure and depopulate excited chromophores by stimulated emission.[256]

2.2.3. DLP

DLP (referred to by some authors as mask projection stereolithography (MPSL), maskless projection slurry stereolithography (MPSS), or 3D slurry printing (3DSP))[257] employs a DMD as a dynamic mask to flash a 2D image across the whole platform and cure the full layer at once. The DMD is a digitally controlled array of revolving micrometer-size mirrors that reflect the light into or away from the liquid resin. DLP technology is therefore not limited to curing a single area at a time and may significantly shorten printing time with the projection of 2D patterning on the liquid resin surface and immediate layer growth. Additionally, DLP permits the application of grayscale lithography, which allows for inhomogeneous cross-linking density inside the layer by changing the light intensity distribution at each place.[231]

The DLP method also offers the ability to fabricate soft robots with extremely sophisticated 3D designs and a lengthy life span. Due to the high resolution of the DLP process and the flexibility of the employed material, it has been shown that soft actuator prototypes with good deformation capacity can be made using this method, even though the cured resin has a relatively low ultimate strain.[258] While other VPP systems have been used in 4D printing technology, DLP seems to be the most frequently utilized. Despite having a lower resolution than SLA, DLP offers faster printing rates.

Ge et al.[140] presented a new method for 3D printing complex structures made of hydrogels and other polymers. The method involves using a self-built DLP-based multi-material 3D printer and a water-soluble photoinitiator to covalently bond the hydrogel with other polymers. The resulting hybrid structures are highly stretchable and have high water content. They implied several applications taking advantage of this multi-material 3D printing approach, including hydrogel composites reinforced by a horseshoe and lattice structures, 3D-printed meniscus with spatially variable stiffness, 4D-printed cardiovascular stents (**Figure 12**a) with drug delivery functions, 3D-printed ionic conductors, and strain sensors with anti-dehydration elastomeric layers.

Poly(caprolactone) (PCL) and poly(-pentadecalactone) (PPDL), as well as their copolymers, are two of the most popular semicrystalline polymers for shape memory copolymer systems. This is because they are highly crystalline, have low toxicity, have mechanical properties that can be changed easily, and break down quickly.[259,260] Jiang et al.[129] discussed how the use of smart materials in 3D printing allows for the creation of structures with programmable and adaptable shapes, properties, or functionalities. They fabricated a 3D-printable resin that can produce single-network two-way shape memory smart materials. The materials can be easily tuned and hold promise for applications in soft robotics and medicine. They concluded that the 3D-printable resin developed in this study, comprising two polyurethane-based oligomers with distinctly different transition temperatures, can be used to fabricate single-network, two-way shape memory smart materials by DLP 3D printing. The PCLDA and PPDLDA switching segments were found to exhibit high mean shape

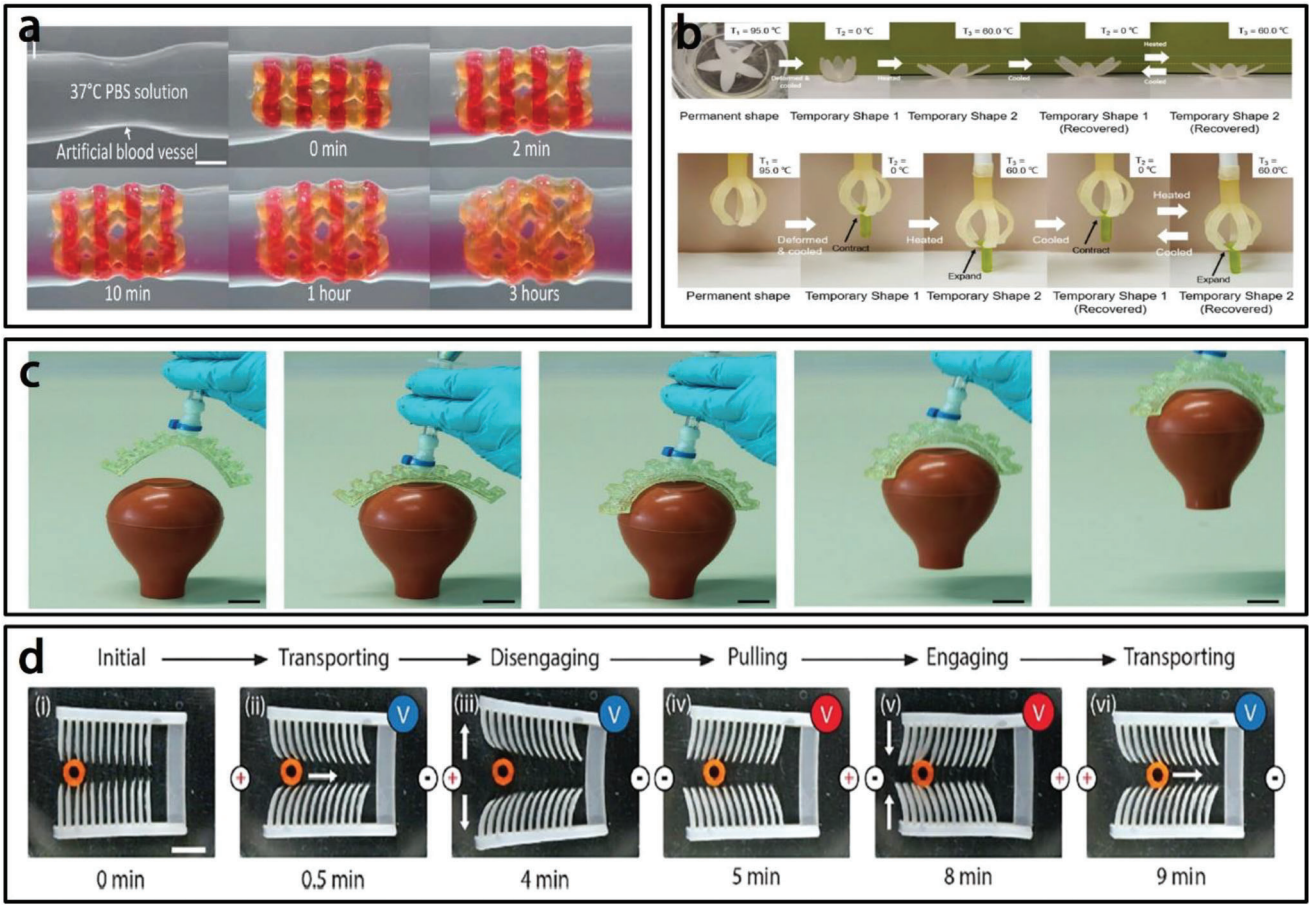


Figure 12. 3D/4D-printed BSSA fabricated by DLW technique. a) Printed SMP stent with drug-releasing function employing DLP 3D printing technique. Reproduced under the term of CC-BY license.[140] Copyright 2021, The Authors, published by American Association for the Advancement of Science. b) DLP 4D Printing of single-network SMP with two-way actuation properties. Reproduced with permission.[129] Copyright 2022, American Chemical Society. c) DLP 3D-printed pneumatic soft actuator with two fingers capturing a soft rubber pipette bulb. Reproduced under the term of CC-BY license.[92] Copyright 2022, The Authors, published by Wiley-VCH GmbH. d) 3D-printed electroactive hydrogel-based locomotive soft robot. Reproduced with permission.[113] Copyright 2018, American Chemical Society.

fixity ratios of >97% and high shape recovery ratios of >89%. They used this material for the fabrication of biodegradable soft actuators capable of gripping and releasing objects (Figure 12b).

Wang et al.[92] demonstrated the self-healing properties of PEGgel, and a 3D-printed self-healing pneumatic actuator was created using this material (Figure 12c). The enhanced mechanical properties of the PEGgel system can be transferred to other chemically and physically cross-linked polymer networks. Such a simple, 3D-printable, self-healing, and resilient soft material has the potential for extensive applications in ubiquitous electronics, soft actuators, and robotics.

By greatly enhancing continuity, compliance, and configurability, soft robotics powered by origami has the potential to radically revolutionize robotic functions.[261] According to Zhao et al.,[130] DLP may be used to create a variety of self-folding origami that can begin altering form as soon as desolvation in water initiates it. They discovered that a biodegradable sheet produced by DLP that was originally flat may change into one of two fundamental nonzero Gaussian curvature surfaces (a saddle or a dome). By creating a gripper in the form of a flower using PEGDA photocurable materials, they also demonstrated how this self-folding origami may be used in electronics and soft robotics.

Projection micro-stereolithography (PμSL) is another DMD-based VPP method capable of creating sophisticated 3D microstructures at microscale resolution. This process is done by passing the light reflected from the DMD device via a reduction lens before reaching the resin substrate. PμSL is beneficial for the fabrication of customized tissue scaffolds and other biological constructions for use in tissue engineering and regenerative medicine because of its capacity to generate complicated cellular shapes with exceptionally fine resolution. However, this method is limited to the ability to produce a small number of photocurable compounds with minimal cytotoxicity, appropriate cell adhesion, and degradability.[225] Moreover, since tissue scaffolds must be made from biocompatible and biodegradable materials,[262] the majority of AM systems cannot currently produce biocompatible and biodegradable materials. For instance, cells may be grown on scaffolds manufactured utilizing MEX methods, although these materials are often not readily soluble under physiological settings.

Zhang et al.[149] proposed a new type of conductive hydrogel that can be 3D printed using a PμSL technique. The hydrogel was found to be highly stretchable, conductive, and able to be completely degraded in alkaline solutions within seconds. The paper explored the influences of temperature, pH value, and chemical compositions on the conductivity and degradation performance of the hydrogel. The hydrogel can be used to create wearable devices that can monitor human body motions accurately and repeatedly. Based on printed hydrogel, they created a wearable gadget that could detect finger, knee, and phonating signals. This study suggested that the developed hydrogel sensors promise feasible applications in degradable, highly stretchable, and conductive wearable devices and transient electronics. Han et al.[113] demonstrated the use of 3D-printed electroactive hydrogels for soft robotic manipulation and locomotion. This study showed that complex 3D actuation of electroactive hydrogels, including gripping and transporting an object and bidirectional locomotion (Figure 12d), can be achieved through precise dimensional control enabled by a DLP-based micro 3D printing technique. The results suggest that 3D-printed electroactive hydrogel structures have potential applications in soft robotics and artificial muscle.

Furthermore, volumetric 3D printing (also known as holographic printing or multi-beam additive manufacturing) is another recently developed VPP DMD-based technique that provides high printing speeds and isotropic mechanical qualities.[263] In volumetric printing, the complete 3D object is simultaneously generated by irradiating a volume of photosensitive resin from numerous angles. Lithography-based metal manufacturing (LMM) is a recently introduced and developed AM method related to DLP technology. This process of 3D printing using light and resin makes small metal components for applications such as surgical instruments and micromechanical parts. Digital composite manufacturing (DCM), a new DLP-based composite printing method, has been also recently introduced by the Fortify manufacturing company. The DCM hardware is built on a DLP platform, which allows UV light to cure photopolymer resin layer by layer using a projector. This resin is comprised of magnetically aligned reinforcing additives in the DCM technique. The UV light then hardens the resin, with the additional material enhancing the part's structure.[268]

2.2.4. CDLP

CDLP is a novel form of vat photopolymerization that was developed by DeSimone and commercialized by CarbonTM in 2015.[269] CDLP improves upon conventional bottom-up VPP by removing the repetitive delamination stages from the bottom UV transparent window. CDLP (also known as continuous liquid interface production (CLIP) and digital light synthesis (DLS)[270]) technology is an advancement based on DLP technology. Unlike SLA and other DLP methods, CDLP utilizes digital projection with LEDs and an oxygen-permeable window in place of a conventional glass window.[271] A window that is permeable to oxygen permits molecular O_2 to diffuse into the bottom of the photopolymer vat. Its oxygen-permeable glass creates a "dead zone" as thick as a human hair, allowing the liquid resin to flow between the interface of the printed object and the window. This uncured resin flow significantly improves the resolution of the printed item and reduces the chance of printing failure caused by peeling force. The thickness of the "dead zone" may be fine-tuned by adjusting the photoinitiator type and concentration, incident photon flux, and resin curing dose. In addition, unlike the layer-by-layer process, CDLP machines are constructed with continuous movement of the build platform, enabling prototype printing at rates of several hundred millimeters per hour without interruption.[272] As a result of the CDLP, the issue of layer connection is avoided and the staircase effect is decreased.

Unfortunately, the polymerization reactions used in VPP photoresins are very exothermic, making heat dissipation a formidable problem at such print speeds.[273] Also, because gaseous oxygen is a thermal insulator, moving it across the print bed to make a "dead layer" in the CLIP technique limits cooling methods to the edges, where the heat is not dissipated quickly. Researchers have recently come up with a new VPP continuous printing system called high-area rapid printing (HARP) to solve this problem and improve the printed component surface quality. This method may guarantee the use of this technique in the fabrication of BSSAs in the future. To decrease interfacial adhesion at the build zone, the printer employs a UV-curable resin floating on a bed of flowing, immiscible fluorinated oil. The oil can be recirculated through a heat exchanger to cool or heat the build zone and keep the temperature of the print bed uniform across the whole surface.[274] Last but not least, because HARP doesn't need an oxygen-dead layer, it can be used with both oxygen-sensitive and oxygen-insensitive ink chemistries. This means that more resins, materials, and biopolymers can be used in this technique.[275]

2.2.5. LCD

LCD technology was just recently introduced as one of the most affordable 3D printing technologies. It has quickly become popular in this industry, making up almost one-fifth of the AM market.[276] LCD panels are a cost-effective and time-saving alternative to the DLP and laser-based systems typically employed in VPP. The light source for these printers is an LCD. This liquid crystal display is comprised of LCD panels that let parallel light pass through and illuminate the built area. This 3D printing process does not require the use of lenses or other devices to magnify light. This method gives this 3D printing technique an edge since the outcome is not influenced by pixel distortion. LCD, also known as masked stereolithography (MSLA) and daylight polymer printing (DPP), is very similar to DLP with the exception that it uses an LCD screen instead of a DMD, which has a significant impact on the 3D printer price.[267]

According to the literature, few studies have examined the precision of LCD 3D printing technology[277] as well as its application in the fabrication of BSSAs. LCD panels provide several advantages, including a boost in printing speed and precision, particularly when monochrome screens are used. LCD technology offers an imaging system that decreases the widening of output light, making pixel malformation less of an issue than in previous photo-induced printing techniques.

In a study, Xin et al.[110] presented the development of chiral metamaterials made of photocurable PLA using LCD printing with tunable, programmable, and reconfigurable properties.

Table 4. Summary of the BSSA manufactured with VPP techniques.

Printing process	Year	Type	Actuation/sensing mechanism	Biopolymer	Potential applications	Refs.
SLA	2012	Actuator	pH, glucose, electrical	PEGDA	Bio-bots, in vivo biomedical applications	[89]
	2012	Actuator	Calcium	PEGDA	Bio-bots, in vivo biomedical applications	[90]
	2012	Actuator	pH	Alginate-based polymer	Surgical microrobots, in vivo biomedical robots	[100]
	2014	Actuator	Electrical	PEGDA	Bio-bots, In vivo biomedical applications, biocompatible microelectronics, forward-engineered biological robots	[91]
	2017	Actuator	Thermal	PCLDMA	Endoluminal devices, biomedical soft robots	[87]
	2018	Actuator	pH	PEGMA	Surgical microrobots, in vivo biomedical robots	[101]
	2023	Actuator	Magnetic	AAm, PEGDA	Wearable electronics, robotic swimmers, aquatic grabbers	[117]
	2023	Actuator	Pneumatic	PEG-AA-based elastomers	Microsystem actuators, soft membrane actuators, surface motion actuators	[131]
DLW/2PP	2018	Actuator	Magnetic	GelMA	Microswimmers, targeted drug delivery, biomedical applications	[84]
	2018	Actuator	Magnetic, light	Chotisan-based polymer	Drug delivery robots, microswimmers	[34]
	2019	Actuator	Magnetic	GelMA	Microswimmers, targeted drug delivery, biomedical applications	[85]
	2019	Actuator	Magnetic	Gelatin	Surgical microrobots, in vivo biomedical robots	[99]
	2019	Actuator	Magnetic	PEGDA, PETA	Drug delivery robots, microswimmers	[107]
	2020	Sensor	Pressure	CMC	Fabric-based flexible sensors, human motion monitoring	[154]
	2022	Actuator	Acoustic signals	TPETA	In vivo biomedical applications, wireless implants	[83]
	2022	Actuator	Thermomechanical	PVA, PCL, PGMEA	Drug delivery robots	[108]
DLP/ PμSL	2017	Actuator	Water	PEGDA	Delicate gripping applications, self-morphing robots	[130]
	2018	Actuator	Thermal	PCLDMA	Human–machine interaction and rehabilitation applications, Wearable electronics	[103]
	2018	Actuator	Electrical	PEGDA	Artificial muscles, locomotion robots, grippers	[113]
	2020	Actuator	Thermal	PEGDA	Biomedical applications, drug delivery robots	[88]
	2021	Sensor	Strain	PEGDA	Soft electronics, biomedical applications, ionic conductors, Cardiovascular stents, drug delivery devices, strain sensors	[140]
	2021	Actuator	Thermal	PCLDA	In vivo and non-invasive biomedical applications, bone engineering	[86]
	2021	Sensor	Strain	PEGDA	Strain sensors, soft electronics	[147]
	2022	Actuator	Thermal	PCLDA, PPDLDA	Delicate gripping applications, self-morphing robots	[129]
	2022	Actuator	Pneumatic	PEGgel	Microsystem actuators, soft membrane actuators, surface motion actuators, biomedical applications, flexible electronics	[92]
	2022	Sensor	Strain	PEGDMA	Wearable soft electronics, flexible sensors, programmable functional human–machine interface	[149]
LCD	2020	Actuator	Thermal	Photocurable PLA	Tissue engineering, soft electronics	[110]

The metamaterials exhibit auxetic behavior and nonlinear "J"-shaped stress-deformation behavior and have potential applications in tissue engineering, soft actuators, and electronics. **Table 4** provides a summary of the BSSA manufactured with VPP techniques.

2.3. Material Jetting (MJT)

MJT is one of the most prevalent methods capable of producing and depositing controlled droplets at present. Typically, the deposited components solidify by evaporation of a solvent or

photocuring with an extra UV light. After one layer has been put down and hardened, the build platform is moved down by the thickness of one layer. This process is repeated until a 3D object has been completely manufactured.[280] MJT is a crucially viable manufacturing process for a wide variety of industrial and scientific applications because of its cost-effectiveness, high throughput, and scalability of production, as well as its capacity to enhance capability via multi-material printing.[281] MJT is usually known as 3D inkjet printing (IJP) due to the fact that it uses ink-jetting technology to create 3D objects. Also, MJT may be referred to as "droplet-based direct writing" in literature for building freeform structures or electronics with feature resolution in one or more dimensions below 50 μm. Due to its ability to print multiple functional materials at high resolution, MJT technology has enormous potential for the construction of miniaturized and complex systems. Of all AM technologies, MJT blends the greatest diversity of colors and materials into a single production system.[282]

The use of low-viscosity solutions in this printing method enables the deposition of a diverse array of materials, encompassing polymers, sol-gels, and dyes. On the other hand, MJT technology has the capability to print particle suspensions, enabling the deposition of insoluble substances such as metals, metal oxides, and ceramics in nanoparticle form. Additionally, live cells and other organic functional materials, such as graphene or carbon nanotubes, are readily printable by this technique. MJT has applications in fields such as flexible electronics, soft sensors, soft actuators, microfluidic systems, optoelectronic devices, and several other domains.[283] Regarding soft robotics, this technology is mostly used to 4D print multi-material structures out of stimulus-responsive materials. The three types of smart soft matter that are most often studied are SMPs, hydrogels, and liquid crystal elastomers. MJT printing is well-known and often utilized as a freeform manufacturing process in 3D printing as well as in the programming stages for 4D printing. The main reason why MJT was chosen as the process for microstructuring liquid crystal elastomer actuators is that it allows multimaterial ink to be printed in the plane in a single processing step, whereas other micropatterning techniques, like VPP, may require more steps to make the same structures.[284] The primary actuation techniques used for 4D-printed liquid crystal elastomers in MJT include heat treatment, light irradiation, alteration of solvent vapor concentration, among others.[285]

The movement of ink ingredients throughout the process is contingent upon their rheological properties. The fabrication of functional material-based components with incorporated nanoparticles poses challenges because of the tight requirements on ink quality, such as low viscosity. The aforementioned procedure has considerable use in biological contexts such as DNA microarrays and targeted drug delivery systems due to its biocompatibility, prevention of cross-contamination, and cost-effectiveness. Polymers based on polyethylene naphthalate and PET are often used in the fabrication of wearable electronic components and gadgets using the MJT printing process. The use of MJT technology is also employed in the bioprinting technique to construct dynamic scaffolds, including cells. This is achieved by the controlled deposition of smart polymers and cells via a nozzle.[46] The characteristics of different types of MJT systems are listed in Table 2.

Multi-material jetting (MMJ) through multiple individual nozzles allows for local control of color and stiffness. However, anisotropy may be an issue with this method because of how the UV light is exposed. In this technique, it is important to take into account how different materials react to the amount of UV energy, which depends on how the surfaces are oriented and how far they are from the UV source.[286] During the layer-by-layer printing process, porosity and anisotropy can occur, which can make the bonding between layers unfavorable or weaken it.[287] Also, MMJ techniques can be employed for the single-step fabrication of 4D multi-material objects. MJ techniques could be used to 4D print and thermomechanically program laminated structures with a variety of fiber orientations. Also, these 4D-printed objects can have complex 3D shapes, such as strips that are bent, coiled, or twisted, folded shapes, and complexly shaped structures with a curvature that changes in different places.[288] In terms of jetting technique, MJ may generally be divided into two categories: 1) continuous inkjet (CIJ) printing (Also known as continuous stream printing); and 2) drop-on-demand (DoD) inkjet printing. In CIJ printing, droplets are ejected continuously, but in DoD printing, a signal waveform, whether thermal or piezoelectric, allows for the ejection of droplets at a high frequency just when required. The ability to control an object's attribute voxel by voxel is a distinguishing characteristic of the DOD method. This capability to generate "digital materials" has been demonstrated through the production of objects with variable hues and levels of translucence, metamaterials, and functionally graded materials. Although there are several methods to classify MJ printing techniques (in terms of dripping mode, ink ejection, jet mode, throughput technique, etc.), this printing method may be categorized according to the various material jetting processes, taking into consideration both CIJ and DOD methods. Correspondingly, different MJ printing processes will be addressed briefly in the subsequent sections. PEDOT:PSS,[111,150,151] gelatin-based electrolyte,[111,118] silver nanoparticles (AgNPs),[158] poly(lactic-co-glycolic acid) (PLGA),[93] and zinc nanoparticles[156] are among the biodegradable materials used to make appropriate photocurable polymer for MJT technique. In the following sections, several facets of each MJT approach have been addressed in more detail.

2.3.1. Direct Inkjet Printing (DIP)

The fundamental principle of DIP technology is to employ a block of piezoelectric or thermal inkjet heads with numerous nozzles to deposit droplets of different photopolymer resins according to computer-generated deposition patterns. The nozzles in this system can switch between various materials, including support material. MJ processes usually need support, which is often 3D printed at the same time as the structure from a material that dissolves. During the post-processing procedure, the support material is subsequently removed. The DIP technique is an ideal alternative for producing realistic prototypes due to its high degree of detail, precision, and flawless surface finish. DIP enables manufacturers to print a design in numerous colors and with a variety of materials simultaneously. DIP is mostly used to produce polymer-based objects, although it is also capable of printing metals and ceramics.[289]

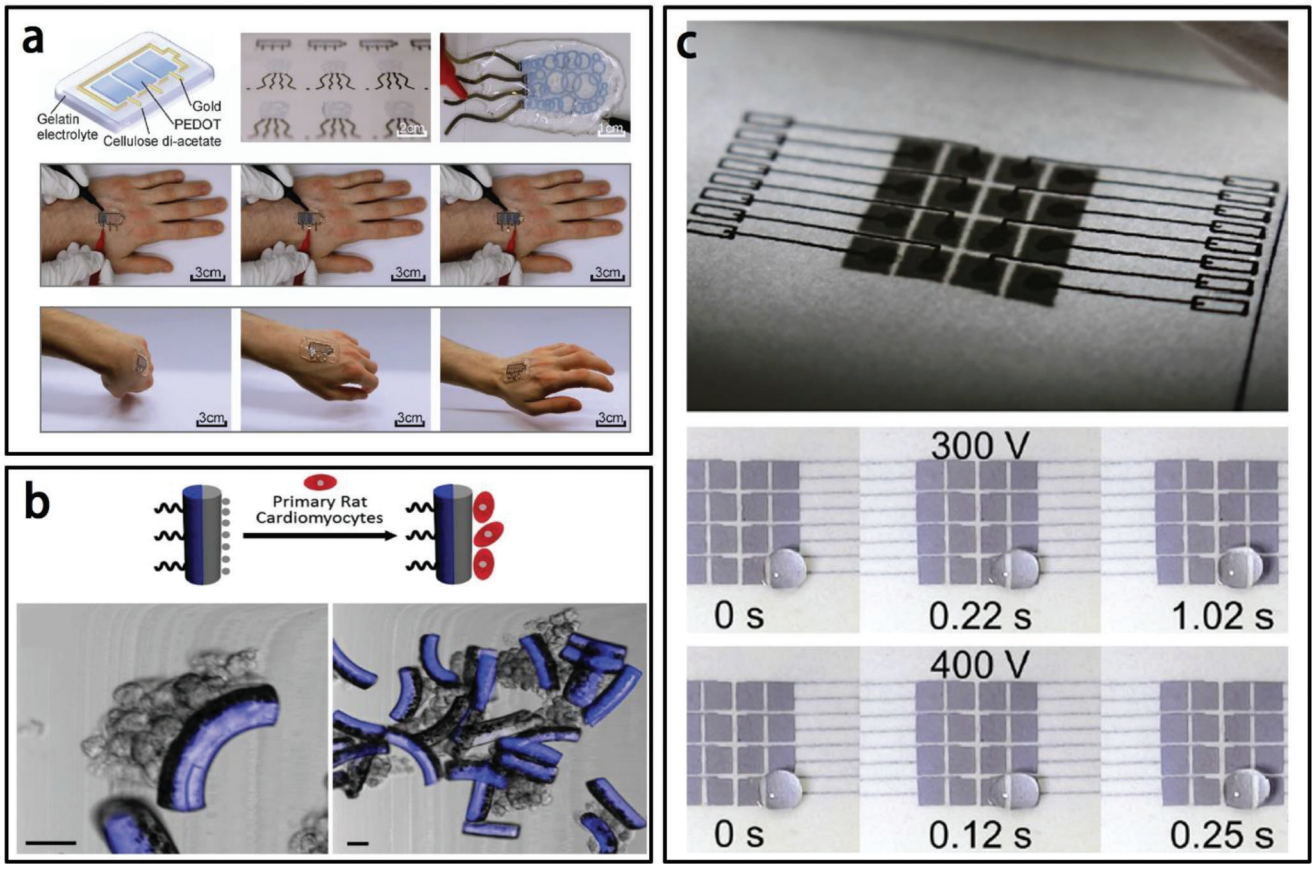


Figure 13. 3D/4D-printed BSSA fabricated by MJT technique. a) Biodegradable inkjet-printed electrochromic display for sustainable short-lifecycle electronics. Reproduced under the term of CC-BY license.[111] Copyright 2020, The Authors, published by Royal Society of Chemistry. b) PEG-based 3D-printed biohybrid microcylinders. Reproduced with permission.[93] Copyright 2015, Wiley-VCH GmbH. c) double-sided EHD-printed paper-based digital microfluidics chip. Reproduced with permission.[158] Copyright 2019, Elsevier.

DIP systems are further categorized as either continuous direct inkjet printing (CDIP) or drop-on-demand direct inject printing (DoDDIP). The ink is held in a reservoir that is delivered to the nozzles via CDIP. A charging electrode is used to draw ink from the nozzle to produce a droplet. Following droplet creation, deflection plates are used to steer the droplets to the desired substrate location. Although the droplets are not regulated by any input signal, the CDIP system creates droplets continuously with a specified frequency; thus, the wasted droplets are routed to the recycling system, where the ink is saved and reused.

The CDIP can be also classified into four groups: binary, multiple, hertz, and microdot drop deflection methods. The binary deflection system prints uncharged droplets into the matrix with one nozzle per dot. The multiple deflection mechanism deflects charged droplets onto the matrix, allowing various dot placements per nozzle. Multiple deposition speeds up the multiple deflection mechanism. Hertz is a binary-deflection CDIP technology with better color printing. The hertz mechanism controls ink droplet deposit by pixel ink volume. The microdot ejects large and tiny droplets from the nozzle, but only small droplets reach the electrical field for selective ejection.[290]

Of the well-known electron-conducting polymers in organic electronics, PEDOT:PSS has been implemented in a variety of biosensing applications and even in vivo studies. These common conducting polymers have been shown to be non-toxic and remarkably biocompatible; however, there is a lack of reports in the literature concerning the biodegradation of these materials.[291] Borghetti et al.[150] fabricated a strain soft sensor by depositing a conducting PEDOT:PSS ink on a polyimide foil using an ultralow-cost inkjet printer. To test the fabrication technique, a serpentine pattern was fabricated onto a PLA substrate using the proposed method. Pietsch et al.[111] presented a new type of soft electronic display (**Figure 13**a) that is made using biodegradable materials and can be printed using inkjet technology. This display is designed to have a short lifespan and can be easily disposed of without harming the environment. The researchers demonstrated the functionality of the display by creating a squid-shaped device that changes color when an electric current is applied. The results show that this type of sustainable electronics has the potential for use in applications where short-lived displays are needed, such as soft sensors, packaging, or temporary signage.

In contrast to continuous inkjet printers, the DoDDIP only ejects ink when necessary. The DoDDIP printer forms ink particles using a pressure pulse. The method applied to generate this pressure pulse determines the principal subdivisions of the DoDDIP printer, which include thermal, piezoelectric, acoustic,

electrostatic, electrohydrodynamic (EHD), and valve methods. The first two are prevalent in contemporary inkjet printing, while EHD is gaining prominence, and the remaining technologies are still in the developmental stage. In the EHD method, the ink to be deposited on the substrate is circulated from the ink storage canister to the orifice with the appropriate ink flow rate to generate a stable cone stream. The nozzle is supplied with a positive voltage, and the substrate holder is grounded. The induction of surface charges on the pendent meniscus emerging from the orifice outflow induces an electric tension on the surface of the ink.[292] If the electric field and flow rate are within a certain operating range, the surface tension stress over the ink surface will be overcome, resulting in the conical deformation of the droplet at the nozzle orifice. While moving the high voltage from zero to the required value, various spray modes occur, such as dripping, unstable, stable, and multi-jet modes.[293] For soft biomedical robots that seek to replicate tissue microarchitecture, it is essential to be able to print even smaller structural features on the micrometer or nanometer scale. EHD techniques such as solution electrospinning (SES), melt electrospinning (MES), and melt electrowriting (MEW) can facilitate such minuscule fiber diameters.[294]

Accordingly, Yoon et al.[93] presented the creation of cardiomyocyte-actuated biohybrid microcylinders using the EHD printing technique. The microcylinders (Figure 13b) were made of a biodegradable polymer and functionalized with PEG molecules to promote directional protein adsorption and cell growth. The successful binding of antifouling PEG on the surface was demonstrated through fluorescence-labeled bovine serum albumin incubation. The paper aimed to provide a foundation for the development of biohybrid microdevices that can be used for various biomedical applications. Choe et al.[118] presented a method for producing self-healing electrodes appropriate for dielectric elastomer actuators by incorporating conductive ions and hydrogen bonds into an eco-friendly gelatin-based composite. EHD was used to fabricate the electrodes, which were then attached to elastomers to construct dielectric elastomer actuators. The gelatin-based electrode was also used as a flexible strain sensor and demonstrated a sensitive dependence of electrical resistance on external joint movements.

Silver nanoparticles (AgNPs) have become an interesting component of biodegradable biopolymers, mainly due to their antimicrobial properties, which allow the development of active food packaging materials to prolong the shelf life of food products. Furthermore, the incorporation of silver nanoparticles into biopolymers may lead to the development of materials with improved physical and mechanical properties.[295] Numerous researchers have characterized the importance of the plant-mediated synthesis method in the development of stable, inexpensive, and environmentally friendly AgNPs in recent years.[296] In this regard, Jafry et al.[158] demonstrated the fabrication of a 2D array of electrodes on a single sheet of paper using double-sided EHD jet printing using silver nanowires and the dispensing of high-viscosity AgNPs (Figure 13c). The paper-based digital microfluidics chip is a low-cost, fully reconfigurable, and disposable point-of-care diagnostic platform for the environmental sensing of pesticides using organophosphorus hydrolase enzyme through colorimetric detection via smartphones.

2.3.2. Aerosol Jet Printing (AJP)

Similar to spray painting, AJP operates by spraying out an aerosol, a suspension of small liquid particles in the air. Unlike spray paint, however, this aerosol is deposited with extreme precision thanks to a series of steps that assure a narrow, focused beam of material. The printing ink is stored in the aerosol chamber where the procedure commences. This ink comprises printing material particulates suspended in a suitable liquid solvent. This aerosol chamber also contains the atomizer, which converts the ink into tiny airborne particles. From there, an inert gas conveying the aerosol is poured in. A virtual impactor removes excess gas to produce a denser aerosol spray once the stream has left the chamber. Lastly, a sheath gas stream is employed to assist the aerosol concentrate and avoid blockage. This variable-diameter aerosol stream departs the nozzle and is deposited on the desired substrate. This substrate is supported by a movable construction platform, and the extended focal distance of the aerosol helps it accommodate both 2D and 3D substrates. A controllable shutter precisely bars and releases the stream based on inputted CAD data in order to target deposition. After printing, thermal and photochemical processing (such as sintering and UV curing) can be used to accomplish the desired material properties and substrate adhesion.[297,216]

The pursuit of innovative techniques for low-cost, high-throughput soft sensors and microelectronics employing AJP methods represents a significant opportunity for recyclable and biodegradable solutions in soft robotics technology. In the printed electronics industry, direct-write techniques, such as AJP, are the predominant method for attaining advanced manufacturing designs. This technology is a viable candidate for the multi-layered, multi-material deposition of soft sensors and microelectronics due to the high build speed of AJP and its ability to accommodate multiple printhead modules.[298] Agarwala and Yeong[159] discussed the use of AJP to create conformal and soft antenna devices on biodegradable substrates. The process involves printing carbon nanotube ink directly onto a pre-treated PLC scaffold. This device has the potential to be employed in diverse soft robotic applications as a biodegradable electromagnetic sensor. Borghetti et al.[155] reported the manufacturing and experimental analysis of low-cost and eco-friendly paper-based gas sensors for food smart packaging employing AJP. The sensors were tested at different relative humidity values and ammonia concentrations, and a proportional resistance decrease was observed with increasing ammonia concentration. Also, a novel type of disposable gas sensor using AJP and flash lamp annealing on a cellulose-based material was manufactured by Cantu et al.[138] The sensors were tested for electrical resistance and showed a proportional increase in resistance with the concentration of NH_4OH present in the working volume. Lall and Narangaparambil[142] demonstrated the design and manufacture of a humidity sensor on a biodegradable paper substrate using AJP technology. The sensor had an interdigital capacitive architecture and could measure humidities in the range of 20% RH to 90% RH. The biodegradability of the substrate is important for the structural health monitoring of critical infrastructure. The sensor's long-term stability, repeatability, and hysteresis were also quantified. (**Table 5**) provides a summary of the BSSA manufactured with MJT techniques.

Table 5. Summary of the BSSA manufactured with MJT techniques.

Printing process	Year	Type	Actuation/sensing mechanism	Biopolymer	Potential applications	Refs.
DIP/EHD	2015	Actuator	Cardiomyocyte	PLGA, COT-PLA	Bio-bots, in vivo biomedical applications	[93]
	2018	Sensor	Microfluidic	Cellulose paper, AgNPs	Microfluidic sensors, health monitoring robots	[158]
	2020	Sensor	Strain	PEDOT:PSS	Smart connected soft robots	[150]
	2020	Actuator/sensor	Electrical	PEDOT:PSS, Gelatin-based electrolyte	Wearable soft electronic applications, health-monitoring robots	[111]
	2022	Sensor	Temperature	Zinc nanoparticles	Biodegradable antenna	[156]
	2022	Actuator/sensor	Electrical, Strain	Gelatin-based composite	Strain sensors, dielectric elastomer actuators, wearable soft robots, healthcare monitoring, human motion detection	[118]
	2022	Sensor	Strain	PGSA, PEDOT:PSS	Soft and stretchable electronic devices, health monitoring robots, wearable soft robots, body-mounted sensors, stretchable light-emitting devices	[151]
AJP	2019	Sensor	Electrical	PLC, CNT	Biodegradable antenna	[159]
	2022	Sensor	Gas	Cellulose paper, carbon ink	Food smart packaging soft robots	[155]
	2022	Sensor	Gas	Cellulose paper, carbon ink	Food smart packaging soft robots, agriculture	[138]
	2023	Sensor	Humidity	Cellulose paper, AgNPs	Structural health monitoring soft sensors	[142]

3. Discussions and Outlook

Numerous researchers have recently addressed the demand for a sustainable world utilizing disposable materials. Naturally synthesized biodegradable materials have superior biocompatibility; nevertheless, their inferior mechanical properties restrict their wide range of applications. Moreover, artificially synthesized biodegradable materials have superior mechanical properties compared to naturally occurring biodegradable materials. In spite of this, the majority of them are sensitive to temperatures, solvents, or water, posing additional difficulties in selecting appropriate fabrication methods. Developing suitable techniques, such as the use of biodegradable nanoparticles and fibers as reinforcement substances, could improve the mechanical properties of these readily biodegradable materials. Also, researchers can attempt to make biodegradable material from a non-biodegradable biocompatible polymer, such as PDMS, which is widely used in the fabrication of soft robotics. Moreover, to surmount the limitations of biodegradable soft robot fabrication, other widely used 3D printing techniques, such as SLS, can be used to create eco-friendly disposable soft robots. As more biopolymer materials become compatible with current 3D printing technology, additive manufacturing techniques will displace the conventional method of producing biodegradable soft robots.

FFF is the technique most commonly employed in the fabrication of soft sensors and actuators, both in the single printing cycle and in the printing of various 3D elements during the assembly of soft robots. Notably, PLA has been used the most in the manufacture of BSSA. Numerous authors have reported that this material can be used as an SMP in thermal,[61,71,73,81,82,116,119,120,123–128,132,133,196] electrothermal,[109] electrochemical,[135] magnetic,[69,75,78,82,197] and electrohydraulic-based[102,121] actuating soft systems. Several research groups have recently strengthened 3D-printed polymers by incorporating continuous fibers.[178] As reinforcements, biodegradable fibers such as wood,[183] cellulose, polysaccharides, and lignin[192,193] have been used, while PLA[186–188] has been the matrix of choice for printing with continuous fibers. The reinforcement of the biodegradable matrix with recyclable material will expand the mechanical properties of the materials used in soft robotic fabrication techniques utilizing AM technologies. In addition to PLA, other biodegradable materials are used in the FFF technique for BSSA fabrication. These materials include PCL,[60,65,77] gelatin-based hydrogel,[98,143] pharmaceutical-grade PVA,[105,106] and PEO.[60]

In contrast to FFF, shape preservation in DIW does not depend on the solidification or drying of the substrate.[210] Thus, DIW is significantly less constrained than other AM technologies. Consequently, a variety of material classes can be used with this AM technology.[211] The DIW is distinguished by its ability to extrude continuous filaments at room temperature, as printability is not contingent on temperature but rather the rheological properties of the ink. Alg/MC,[62] PLA,[72,80,95,141] PEA,[95] PLMC,[64] carrageenan-based nanocomposites,[152,153] MWCNTs,[141,143] chitosan hydrogels,[67] PCL,[63,68,72] sodium alginate,[68] BPU,[114] CMCS,[114] protein-based hydrogels,[70] PGDA,[74] cellulose-based biopolymers,[115,136,157] CMC,[114,134] gelatin hydrogels,[146] and PEDOT:PSS[148] are extensively used in DIW.

Regarding the biodegradability of current biopolymers, only a handful of articles have examined the degradation behavior of diverse materials in detail. Polymers such as PEDOT:PSS have been utilized in numerous biosensing applications and even in

vivo research. These common conducting polymers have been shown to be non-toxic and remarkably biocompatible; however, there are only a few reports in the scientific literature regarding their biodegradation. Further research on nanoparticles, such as silver and zinc nanoparticles, will enable the continued use of 3D printing systems such as aerosol jet printing to produce biodegradable sensors and electronics in a sustainable manner. Moreover, inkjet printing technologies are not yet fully compatible with biodegradable materials, despite their high resolution and throughput.

Hydrogels are another class of materials that are often used in the production of BSSA. Hydrogels are highly stretchable, transparent, biocompatible, and ionic conducting materials. Potential applications for these materials include health monitoring, human motion detection, human–machine interfaces, and soft robotics. BSSA based on stimuli-responsive hydrogels have attracted attention due to the fact that they can be remotely controlled by external stimuli and are highly adaptable to their surroundings due to their suppleness and pliability. Their high water content and organic nature, however, make it difficult to guarantee their stability and durability over extended periods. Hydrogel bionic materials have a crucial sensing function. In contrast to electronic sensing, human tactile perception develops as a consequence of bio-ionic currents on the skin in response to mechanical stimulation. This bionic sensing capability made it possible to use ionic hydrogel in soft robotics, prosthetics, and wearable devices.[221] Moreover, The magnetic actuation of hydrogels containing nano-magnetic particles is one of the novel, recently developed, non-invasive, and environmentally benign methods for controlling soft robots as well.[62]

It is noteworthy to mention that DIW is the most frequently used 3D printing method for biological and medical applications.[223] Typically, the ink is delivered by a syringe or other container, and it can be extruded through the orifice without requiring a high temperature. Consequently, bacteria and cells can survive the printing procedure.[224] Bioprinting refers to the use of AM technologies for the fabrication of biologically based structures, including cells, growth factors, and other biomaterials. Due to its many cellular-friendly properties, such as gelation, the polysaccharide alginate is the most commonly used bio-ink for extrusion 3D bioprinting. Alginate lacks incorrect degradation and cell-binding motifs, which are limitations of alginate bio-inks that can be circumvented by combining low concentrations of natural or synthetic polymers.[226] Bio-printed bio-microstructures could serve as soft bio-microactuators in soft robotics if the appropriate stimulus response is incorporated.

Several polyelectrolytes, such as gelatin, chitosan, and hyaluronic acid, have demonstrated 3D printing potential for the fabrication of BSSAs. Chitosan polyelectrolyte gel exhibits superior swelling and stimuli-responsive bending properties (required for actuators) compared to the respective casted gel. In addition, chitosan-based electroactive polymer actuators have greater ionic conductivity and mechanical effectiveness than other biopolymer-based soft actuators.[228]

Another widely used sustainable technique for the fabrication of BSSA is VPP. TPETA,[83] GelMA,[84,85] AAm,[117] PEGDA,[88–91,107,113,117,130,140,147] PCLDMA,[87,103] photocurable PLA,[110] PCLDA,[86,129] gelatin,[99] photocurable chitosan-based polymer,[34] PETA,[107] photocurable alginate-based polymer,[100] PEGMA,[101] PGMEA,[108] PEGgel,[92] and PEGDMA[149] are among biodegradable materials used to make appropriate photocurable polymer for VPP technique. Biocompatibility and biodegradability can be tailored by using different base monomers, and the modulus of elasticity and strength of the final product can be modified by altering the degree of crosslinking. Toxicity and cell compatibility are the primary issues with photoreactive resins. With the proper post-processing techniques and a cautious selection of monomers, these issues can be resolved.[243]

Bioactuators, also known as biohybrid actuators, are one of the many ecofriendly microactuator designs that have been recently created and researched using VPP. They are particularly intriguing due to their use of living cells, self-actuation, and prospective in vivo application. Recent research has demonstrated that biohybrid robots made of soft materials and cells are capable of detecting, reacting to, and adapting to environmental stimuli in real time, performing genuine tasks such as swimming, walking, and pumping.[244] Also, cell-based soft robotic devices may have a transformative impact on our ability to design machines and systems that can dynamically detect and respond to a variety of complex environmental signals.[91]

Mobile micro- and nanorobots are required for future biomedical applications such as targeted distribution and diagnostics. Biocompatibility and biodegradability of micro- and nanorobots are prerequisites for their clinical application. Miniaturizing robots with flexible, non-cytotoxic, biodegradable components will enhance device absorption, optimize tissue contact, and decrease immunoreactivity. In this regard, using the 2PP technique, the fabrication of these types of biodegradable soft micro- and nanorobots has been studied.

The DLP method also enables the fabrication of soft robotics with extremely complex 3D designs and long lifespans. Due to the high resolution of the DLP process and the flexibility of the employed material, it has been demonstrated that soft actuator prototypes with a high deformation capacity can be manufactured using this method,[258] despite the relatively low ultimate strain of the cured resin. Other VPP systems have been utilized in 4D printing technology, but DLP appears to be the most prevalent. DLP offers quicker printing speeds despite having a lower resolution than SLA. PCL and PPDL, in addition to their copolymers, are two of the most widely used semicrystalline polymers in shape-memory copolymer systems. This is due to their high crystalline structure, low toxicity, readily modifiable mechanical properties, and rapid decomposition.[259,260] Moreover, using VPP and significantly enhancing continuity, conformance, and configurability, soft robotics based on origami has the potential to revolutionize robotic functions.[261]

CDLP is a novel form of vat photopolymerization that enhances conventional bottom-up VPP by eliminating the repetitive delamination phases from the bottom UV transparent window. Unfortunately, the polymerization reactions used in VPP photoresins are extremely exothermic, making heat dissipation an insurmountable issue at such print velocities.[273] In addition, since gaseous oxygen is a thermal insulator, moving it across the print bed to create a "dead layer" in the CLIP technique restricts cooling methods to the edges, where heat is not rapidly dissipated. The use of biodegradable photocurable polymers can be adapted to this sustainable, cutting-edge AM method through additional re-

search. Also, LCD technology has recently been introduced as one of the most cost-effective 3D printing technologies. It has rapidly gained popularity in this industry, comprising nearly one-fifth of the AM market.[276] LCD panels are a time- and cost-efficient alternative to the DLP and laser-based systems that are typically employed in VPP. Few studies have examined the precision of LCD 3D printing technology[277] and its implementation in the fabrication of BSSAs, according to the literature. Regarding the commercialization of BSSA fabrication, LCD is a viable option to which scientists can adapt biopolymers and methods in order to create eco-friendly soft robots in a sustainable and cost-effective manner.

A big possibility for recyclable and biodegradable soft robotics technology lies in the development of novel ways for low-cost, high-throughput soft sensors and microelectronics using AJP approaches. Direct-write methods, including AJP, are the most popular way to create advanced production designs in the printed electronics sector. Due to the rapid build speed of AJP and its capacity for numerous printhead modules, this technique is a strong contender for the multilayered, multi-material deposition of soft sensors and microelectronics.[298] Due to their antimicrobial properties, AgNPs have become an intriguing component of biodegradable biopolymers, allowing the development of active food packaging materials using the MJ technique to extend the shelf life of food products. In addition, the incorporation of silver nanoparticles into biopolymers may result in the creation of materials with enhanced physical and mechanical properties.[295] In recent years, numerous researchers[296] have highlighted the significance of plant-mediated synthesis in the development of stable, inexpensive, and environmentally benign AgNPs.

In terms of manufacturing, the fabrication of biodegradable soft robots is limited to a few 3D printing technologies as well as biocompatible smart materials, as mentioned in this section. Although it is cost-effective and allows the printing of multiple materials, material extrusion-based 3D printing has significant limitations in terms of speed, throughput, resolution, nozzle clogging, and quality compared to light-assisted printing. On the other hand, light-assisted printing technologies may offer faster print speeds and higher print resolutions and circumvent the need for supports, but they are also expensive and do not support multiple materials, and the range of readily available biopolymers is limited. In order to guide the development of these techniques in the direction of accomplishing the goal of advanced soft robotics, it is essential to incorporate all the aforementioned key points and find solutions to the challenges and issues. Finally, commercial success depends on new innovations in biopolymers, 3D printing, and other rapid prototyping technologies to mass produce inexpensive and market-responsive ecofriendly flexible structures and robotics.

4. Conclusions

To create complex, biodegradable 3D soft robots for a variety of applications, highly precise fabrication methods and biodegradable material synthesis strategies have been developed. Due to their scalability and manufacturability, 3D/4D printing techniques have been favored in recent decades for the creation of multiscale and multifunctional 3D soft robotics. 3D/4D printing offers distinct benefits for the fabrication of biodegradable soft sensors and actuators with intricate structures. Hereupon, various applications of biodegradable, 3D-printed soft robotics were discussed in this paper. The current additive manufacturing techniques for the fabrication of biodegradable soft sensors and actuators were next addressed. Diverse facets of each 3D printing technique were reviewed in terms of applications, available materials, and advantages and disadvantages over other techniques. It is noteworthy to mention that the use of 3D printing in biodegradable soft robotics still presents significant obstacles, apart from those associated with all 3D printing parameters and the selection of appropriate biodegradable materials. This discipline is still in its infancy, and little commercial fabrication has occurred. Despite significant development, the majority of stimuli-responsive, biodegradable soft robots are still conceptual. Consequently, this lacuna should be covered with additional research, as it will be necessary to expand the biodegradable fabrication industries in the near future to prevent environmental impacts caused by mankind's activities.

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Conflict of Interest

The authors declare no conflict of interest.

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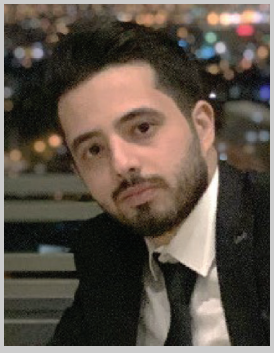

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