

Review

Photopolymerization in Light-Driven 3D and 4D Printing of Smart Materials: Types, Mechanisms, and Applications

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Abstract

The rapid development of 4D printing has revolutionized fields such as rapid prototyping, biomedical engineering, microfluidics, tissue engineering, and drug delivery. Central to this progress are shape memory polymers (SMPs), capable of recovering predefined shapes upon stimulation. Integrating SMPs with vat photopolymerization (VP) techniques enables high-precision, rapid fabrication of complex geometries, overcoming limitations of traditional manufacturing. This review provides a comprehensive overview of VP technologies, recent developments in photopolymerization, and the classification of SMP resins (natural and synthetic) in 4D printing. Applications span biomedical devices, soft robots, drug delivery and microbots, and anti-counterfeiting. This review also focuses on expanding the range of 4D printable photopolymers and addressing limitations of traditional UV-initiated systems. In this case, the core strategy of photopolymerization introduces liquid monomers and oligomers, combined with photoinitiators, which undergo radical or cationic polymerization upon exposure to specific wavelengths of light in different 4D printing applications. We also discuss current challenges, such as developing reversible SMPs, optimizing multi-material high-resolution processes, and outline future research directions. Several challenges remain in the light-driven 4D printing, including limited high-performance, reversible SMPs, difficulties in multi-material printing, and lack of standard testing methods. As photopolymerization advances with diverse chemical pathways like radical and cationic mechanisms, it enables the creation of stimuli-responsive materials for next-generation applications such as biofabrication and soft robotics.

Keywords: 4D printing, shape memory polymers, vat photopolymerization, biocompatible photopolymers, tissue engineering

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1 INTRODUCTION

Since the inception of additive manufacturing in the 1980s, commonly referred to as 3D printing, the technology has experienced rapid development, driven by advances in process precision, material diversity, and cost efficiency^[1-4]. Initially established as a means to fabricate complex, customized objects without the need for molds or extensive machining, 3D printing has evolved into a versatile platform with applications spanning rapid prototyping, microfabrication, tissue engineering, and integrated device manufacturing^[5-10]. Among the various techniques, photopolymerization-based approaches, including

stereolithography (SLA)^[11-14], two-photon polymerization (TPP)^[15], digital light processing (DLP)^[16-19], projection micro-stereolithography (PμSL)^[20], continuous liquid interface production (CLIP)^[21-23], and volumetric 3D printing (VAM)^[24-26] have attracted particular interest due to their capability to produce high-resolution, intricate geometries with smooth surface finishes. These methods operate by selectively curing liquid resins through light-induced polymerization, enabling layer-by-layer construction of complex multifunctional structures with tailored optical, chemical, and mechanical properties (Figure 1)^[27-30].

The core chemistry underpinning these processes

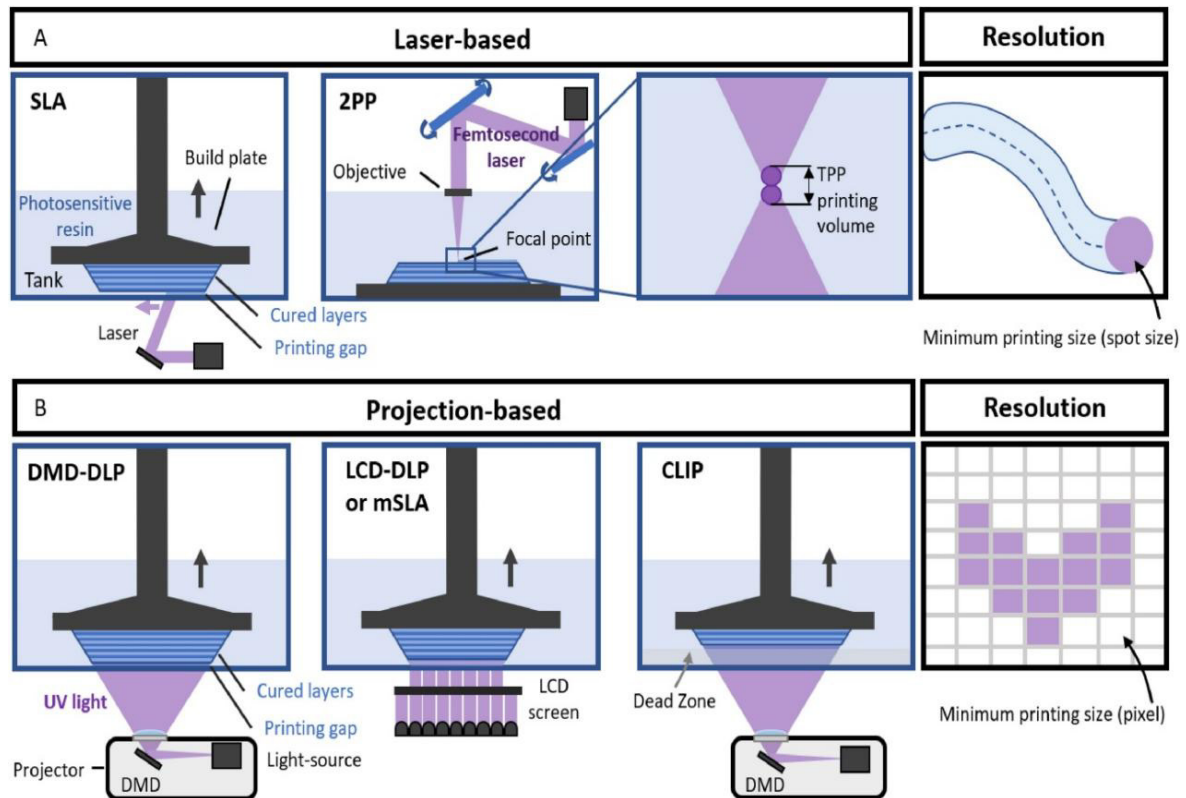


Figure 1. Schematic Representation of Vat Photopolymerization Techniques. (A) laser-based techniques, such as SLA and 2PP; and (B) projection-based techniques, such as DLP, Liquid Crystal Display-based masking projection (LCD-DLP), or masked stereolithography apparatus (mSLA), and CLIP. Reprinted with permission from Ref.^[30].

involves the use of monomers or oligomers in a liquid state, which undergo rapid polymerization upon exposure to specific wavelengths of light, typically ultraviolet (UV) or visible^[31-37]. Photoinitiator systems, comprising molecules with high molar extinction coefficients, absorb incident photons and generate reactive species (radicals or cations) that initiate chain growth via radical or cationic mechanisms^[38-43]. Although UV-based systems have been extensively utilized, they pose limitations such as limited light penetration depth^[32], potential cellular damage in bioprinting^[33,34], and side reactions caused by prolonged high-energy light exposure^[41,42]. These challenges have stimulated research into alternative photoinitiators and resins activated by longer wavelengths, including visible^[44-46] and near-infrared light^[47-50], to facilitate deeper curing^[51], milder operational conditions^[52], and enhanced biocompatibility^[53], particularly for tissue engineering^[54-57] and regenerative medicine applications^[58-61].

While conventional 3D printing excels at creating static objects with complex geometries, a paradigm shift emerged with the advent of 4D printing. This evolution fundamentally extends the capabilities of additive manufacturing by incorporating the dimension of time as a core design parameter^[62-66]. The key innovation of 4D printing lies in its ability to create objects that are not static end-products, but rather dynamic systems capable of undergoing pre-programmed, reversible shape or property transformations after the fabrication process is complete, in response to specific environmental stimuli.

This temporal dimension enables functionalities such as self-assembly, reconfiguration, and adaptive behavior, which are unattainable with traditional 3D printing alone. The 4D printing leverages stimuli-responsive materials, such as shape memory polymers (SMPs)^[67-70], hydrogels^[71-75], and nanocomposites^[75-80], which can undergo predetermined, reversible shape or property transformations upon exposure to external cues like temperature^[81-85], light^[86-89], pH^[90-92], magnetic fields^[93-96], or multi-stimulus environments^[97-101].

This integration of time-dependent responsiveness in 4D printing involves using stimuli-responsive materials that change their properties or shape in response to external triggers. These include SMPs^[67-70], which revert to a preset shape when heated; hydrogels^[71-75], that swell or contract based on environmental cues like pH; and nanocomposites^[75-80], which incorporate nanoscale fillers to enhance responsiveness. These materials respond dynamically to stimuli such as temperature^[81-85], light^[86-89], pH^[90-92], magnetic fields^[93-96], or combinations of multiple stimuli^[97-101]. This ability to respond over time enables the creation of adaptive structures capable of self-assembly, reconfiguration, and dynamic functions. Such features have significant implications for biomedical devices^[102,103], soft robotics^[104,105], aerospace components^[106-108], and reconfigurable systems^[109-112], allowing them to change shape or function autonomously in response to environmental changes.

SMPs have established themselves as pivotal materials

in the realm of 4D printing due to their intrinsic ability to undergo reversible shape transformations triggered by external stimuli. This property embodies the core concept of temporal programmability in 4D printing, enabling the development of dynamic systems for diverse applications such as minimally invasive surgical devices, deployable aerospace structures, and adaptive actuators. The advent of advanced VP-based techniques, including DLP, SLA, VAM, and 2PP, has facilitated the fabrication of SMP architectures with unprecedented geometric complexity and functional precision^[113-116]. Recent progress in the synthesis of functionalized, stimuli-responsive resins and the refinement of polymerization parameters has been instrumental in producing SMPs that exhibit a synergistic combination of rapid actuation, mechanical robustness, and biocompatibility, thereby broadening their potential for biomedical, aerospace, and soft robotic applications.

Recent advancements have heralded the emergence of "living" photopolymerization systems, notably those integrating photoredox catalysis with reversible addition-fragmentation chain transfer (RAFT) mechanisms. These innovative methodologies afford unprecedented temporal precision in polymer network formation, facilitating the fabrication of three-dimensional structures with dynamic and reprogrammable functionalities. Such systems pave the way for the development of materials endowed with reversible or adaptive properties, thereby unlocking new possibilities in the design of smart, stimuli-responsive architectures for advanced applications in soft robotics, biomedical devices, and adaptive materials. Moreover, the integration of controlled polymerization techniques into 3D printing workflows paves the way for advanced material architectures featuring gradient properties, multi-material compositions, and post-fabrication modifications, thereby expanding the functional scope of printed constructs^[116].

Despite these advancements, challenges remain in achieving fully reversible, multi-shape memory systems with long-term stability, enhancing multi-material integration, and scaling up manufacturing processes. Ongoing research continues to focus on designing novel photoresponsive monomers and oligomers, engineering fillers for enhanced responsiveness, and developing standardized evaluation methodologies to accelerate clinical and industrial translation.

This review aims to critically analyse the latest advancements in vat photopolymerization (VP)-based 4D printing technologies, with particular emphasis on the intricate photochemical mechanisms that govern polymerization processes. It explores the pivotal roles of photoinitiators in controlling reaction kinetics and achieving precise spatial and temporal resolution. Furthermore, the review delves into the design and engineering of complex material architectures that facilitate the fabrication of

stimuli-responsive structures capable of undergoing controlled, dynamic transformations over time. Emphasis is placed on the mechanisms underpinning the temporal and adaptive evolution of these structures, highlighting their potential to enable next-generation 4D printed systems with programmable, reversible, and reconfigurable properties for diverse applications in biomedical, soft robotics, aerospace, data security (encryption) and anti-counterfeiting. We explore the classification and properties of various substrate 'natural' and 'synthetic' resins, highlight key applications across biomedical, soft robot, and security sectors, and discuss current challenges and future perspectives in this rapidly evolving field.

2 SMPs AS ENABLERS OF 4D PRINTING: AN IN-DEPTH PERSPECTIVE

The identification of SMPs hinges critically on their intrinsic ability to undergo programmable shape transformations, which necessitate a deliberate shape-setting or "programming" procedure. This process typically involves three fundamental steps: first, establishing a desired initial configuration; second, applying an external mechanical stress while elevating the temperature to induce deformation; and third, cooling the material under maintained stress to lock in a temporary shape^[117-120]. Reheating the material then triggers a return to its original, permanent form. At elevated temperatures, thermal agitation enhances the entropy of the polymer chains, effectively reducing the activation energy barriers for chain mobility and facilitating molecular rearrangement. Conversely, during the cooling stage under stress, the mobility of polymer segments is restricted, stabilizing the deformed shape in a frozen state even after the external force is removed. The energy and internal stress stored during this phase are stored within the molecular network, forming the basis for the material's shape memory effect.

SMPs are generally classified into three categories based on their shape recovery behavior: one-way^[121,122], two-way^[123,124], and multi-shape systems^[125,126]. One-way SMPs are capable of reverting solely from a temporary to a permanent shape upon thermal stimulation. Two-way SMPs exhibit reversible shape changes, cycling between two distinct configurations in response to stimuli. Multi-shape SMPs, on the other hand, can transition among multiple configurations, enabling complex, programmable shape evolutions^[122] (Figure 2).

In thermoresponsive SMPs, the shape memory effect predominantly manifests when the temperature exceeds the polymer's glass transition temperature (T_g) or the melting point (T_m) of their crystalline domains. External triggers, such as heat, release the stored elastic energy, allowing the material to recover its original geometry^[127,128]. The programming cycle of an SMP can be repeated multiple times, provided the material's

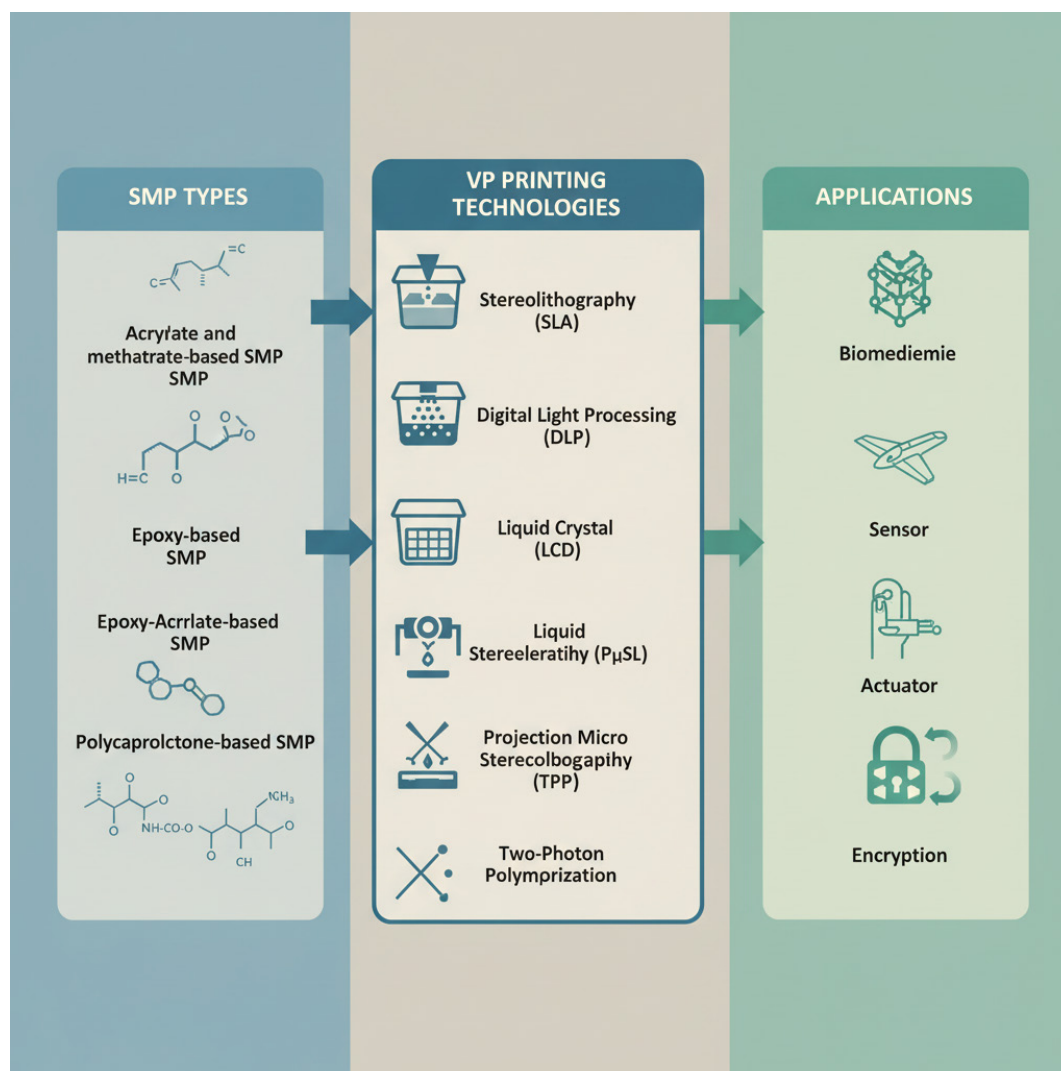


Figure 2. Schematic Overview of VP of SMPs. The Middle Showcases Various VP Printing Technologies (SLA^[11], TPP^[15], DLP^[16], PμSL^[20], LCD^[30]). Different SMP and Their Applications are Presented on Both Sides.

mechanical integrity remains intact. The defining feature that distinguishes SMPs from other shape-changing materials lies in their capacity for tailored temporary shapes, which can be designed on demand. This behavior is fundamentally explained via two primary theoretical frameworks: thermoviscoelasticity and phase transition models, each offering unique insights into the underlying mechanisms.

The *thermoviscoelastic theory* conceptualizes the polymer as an entangled network of microscopic springs randomly oriented at ambient conditions^[129,130]. When temperature increases, molecular segments gain mobility, leading to a thermoviscoelastic response where springs stretch and align under external forces^[131]. Cooling under stress constrains the chains, effectively “freezing” their configuration and storing elastic potential energy as the springs are locked in a deformed state. Upon reheating, this stored energy is released, culminating in shape recovery. This model adeptly captures the viscoelastic behavior of polymers across a broad temperature spectrum, emphasizing their mechanical responses under thermal cycling^[132].

In contrast, the phase transition theory interprets the shape memory phenomenon via transitions between active and frozen phases within the polymer's microstructure. During the shape-fixing phase, the material undergoes a transition from an active, deformable phase to a frozen, glassy state, effectively “locking in” the deformed shape by converting strain into a storable form^[133,134]. When subjected to subsequent heating, a pseudo-phase transition occurs, shifting the material back from the frozen to the active phase, thereby converting the stored strain into macroscopic shape change^[135]. The macroscopic shape recovery process is governed by the thermally induced variation in the volume fractions of these phases and the associated internal strains.

While the thermoviscoelastic approach excels at predicting mechanical responses over temperature variations, it offers limited explanatory power regarding the fundamental thermodynamics of shape memory. Conversely, the phase transition approach provides a robust microscopic understanding of shape change

but falls short of capturing the viscoelastic response under high-temperature or non-ideal conditions. To overcome these limitations, integrated models that combine the strengths of both frameworks have been developed^[136,137]. For instance, Guo et al.^[138] proposed a generalized constitutive model that synthesizes thermoviscoelastic and phase transition theories, effectively capturing the evolution of stored strain during deformation and recovery cycles. This model describes shape memory behavior in terms of phase volume fractions and the dynamics of stored energy, elucidating how mechanical deformation at elevated temperatures is encoded into the polymer network and subsequently released upon thermal activation. Similarly, Zeng et al.^[139] devised a three-dimensional finite-deformation model that accounts for anisotropic behaviors in SMP composites, decomposing the material into rubbery, glassy, and evolved phases. This approach considers the transformation of the deformation gradient during phase transitions, providing a comprehensive understanding of the shape memory mechanism at the microstructural level.

To facilitate quantitative analysis, several mathematical models and formulas have been employed to describe the complex interplay between thermal, mechanical, and phase-related phenomena in SMPs. For example, the thermoviscoelastic stress-strain relation can be expressed as (Equation 1):

$$P_i(\lambda_i^e(t), \lambda_i^s(t)) = P_i^e(\lambda_i^e(t)) + P_i^s(\lambda_i^e(t), \lambda_i^s(t)) + P_i^{vol}(\lambda_i^e(t)) \quad (1)$$

where P_i is the total uniaxial stress along direction i , P_i^e denotes equilibrium stress and P_i^s represents the Maxwell stress in direction i , and P_i^{vol} accounts for the stress because of combined volumetric response as a result of both elements. The *elastic deformation* of $\lambda_i^e(t)$ and $\lambda_i^s(t)$ associated with single molecular springs and Maxwell elements is characterized by their respective stretch ratios, respectively, integrating the time-dependent and temperature-dependent responses^[140].

The *phase transition dynamics* are captured through the evolution of the volume fractions of the frozen (φ_f) and active (φ_a) phases, which serve as internal variables. The free energy of an SMP can be modeled as (Equation 2):

$$W(F, T) = \varphi_f W_f(F_f, T) + \varphi_a W_a(F_a, T) \quad (2)$$

where W_f and W_a denote the free energies associated with the respective phases, and the phase fractions evolve with temperature and strain according to thermodynamic principles of F_f and^[141].

The integration of these theoretical frameworks opens new horizons for designing SMPs tailored for advanced 4D printing applications, where complex, programmable, and reversible shape transformations are essential. The advent of high-resolution VP techniques has further catalyzed this progress, enabling the fabrication of sophisticated SMP architectures with unprecedented precision. The development of photocurable SMP

resins, optimized for VP processes, has unlocked a multitude of potential applications, from deployable aerospace components to responsive biomedical devices, highlighting the transformative impact of these smart materials in the realm of 4D printing.

3 ADVANCED PHOTOPOLYMERIZATION-BASED 3D/4D PRINTING TECHNIQUES

Understanding the fundamental photopolymerization techniques is essential before delving into photochemistry and photoinitiators (Section 4). These light-based methods, operating within a resin vat, enable precise layer-by-layer fabrication of complex geometries by inducing localized polymerization. Key techniques include SLA, DLP, PμSL, TPP, CLIP, and volumetric 3D printing. Each offers distinct advantages in resolution, speed, and feature control, forming the foundation for fabricating the dynamic, multi-material, and functionally graded structures central to 4D printing. This section provides an overview focusing on their operational principles and relevance to advanced applications, particularly 4D printing.

3.1 Laser-Scanning and Projection Techniques: SLA and DLP

SLA, pioneered in the 1980s, established the foundation for high-resolution VP^[142-145]. It utilizes a focused laser beam (commonly UV or visible wavelengths) directed by galvanometric mirrors to trace patterns onto the resin surface^[146-159]. This cures it point-by-point, which is a key strength regarding its high resolution (typically down to ~50μm, potentially sub-10μm in advanced systems) and excellent surface finish^[160,161]. These attributes make SLA particularly suitable for applications demanding intricate features, such as biomedical scaffolds, micro-optics, and microfluidic devices^[162-166]. Recent developments include compatibility with ceramic or metal-filled resins, expanding its utility^[162-164] (Figure 3).

DLP significantly enhances fabrication speed compared to point-scanning methods like SLA^[165-169]. It employs a digital micromirror device (DMD) to project entire 2D layer images onto the resin surface using a high-intensity light source (e.g., LED), curing each layer simultaneously. Typical feature resolutions range from 50-100μm, with layer thicknesses between 25-100μm. A key advantage of DLP for advanced manufacturing, including 4D printing, is its ability to project grayscale images. This enables precise control over curing depth and degree within a single layer, facilitating the creation of structures with gradient mechanical properties or complex internal architectures essential for stimuli-responsive behavior^[170-172]. This speed and grayscale control make DLP ideal for high-throughput prototyping, microfluidics, and soft robotics components.

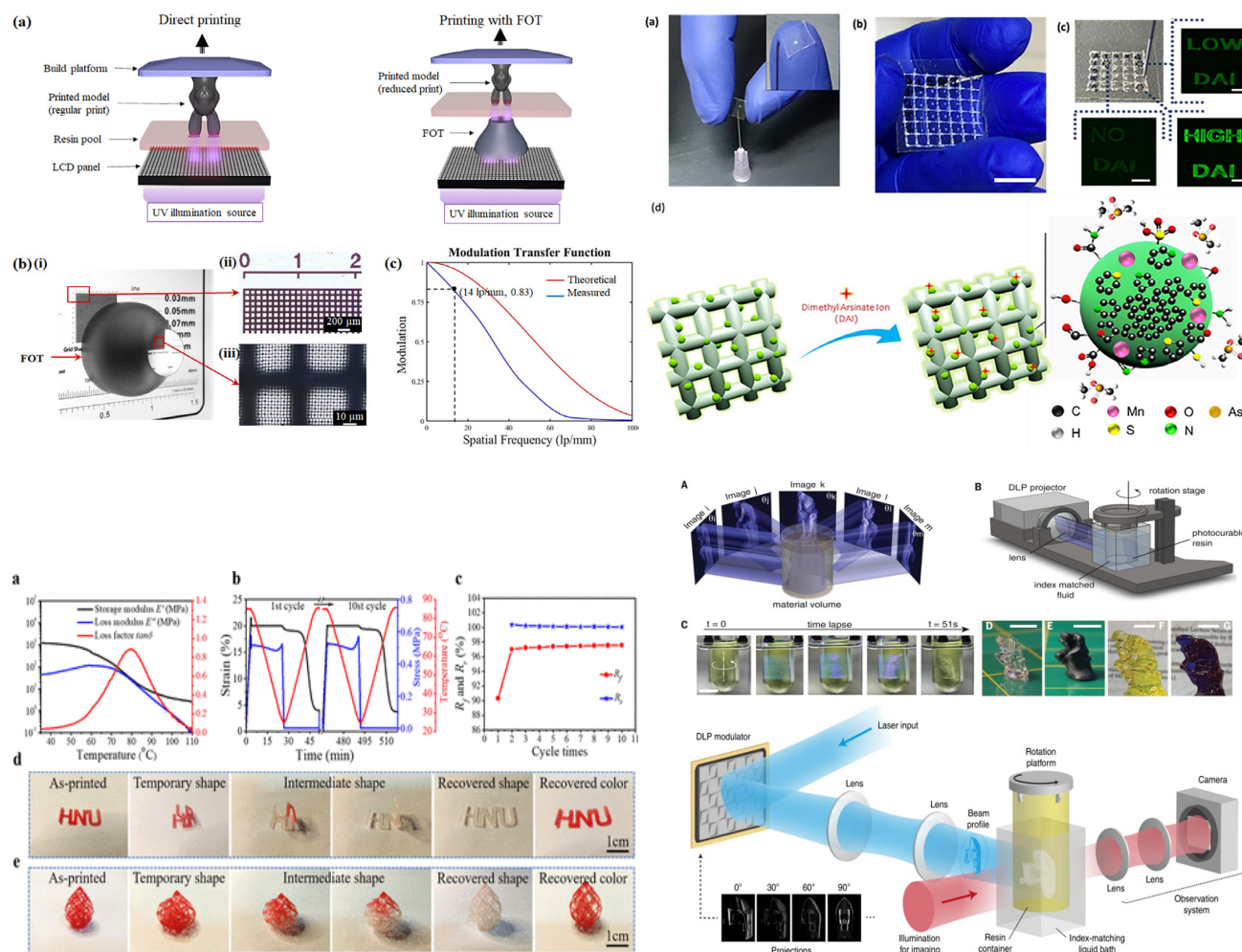


Figure 3. Top-left: Schematic illustration contrasting the conventional (direct) printing setup with an improved fiber-optic taper (FOT)-based system. The traditional approach (left) projects image layers directly through LCD screens into the resin vat, whereas the enhanced configuration (right) directs the LCD image through a fiber-optic taper before reaching the resin. During printing, the build platform advances upward to form the 3D structure. Additionally, the figure shows a photograph of the FOT positioned on a calibration grid with 0.1 mm divisions, an optical micrograph of the grid under 5 $\times$ magnification, and a detailed micrograph of the FOT's smaller facet at 100 $\times$ magnification revealing discrete fiber cores. Theoretical and experimental modulation transfer functions (MTF) of the FOT are also presented as a function of spatial frequency at the larger facet. Copywriting^[162]. **Top-right: The figure displays a micro-sensor fabricated to match the size of a microneedle tip.** It demonstrates a single-platform device capable of detecting DAI across different concentrations. The fluorescence intensity varies according to the presence and number of DAI, with measurements shown for absent, low, and high concentrations. A proposed sensing mechanism utilizing TPAF micro/nano structures is illustrated. Scale indicators are provided: 1 cm for the images in (b) and (c), and 100 μ m for the micrograph of the sensor. Copywriting^[173]. **Bottom-left: This set explores the shape recovery behavior of SMP.** It includes Dynamic Mechanical Analysis (DMA) curves, a shape memory cycle test, and the assessment of shape fixity (Rf) and recovery (Rr) over ten cycles. Additionally, two 3D printed structures are depicted: the "HNU" letters and a hollow form demonstrating effective shape recovery performance. Copywriting^[172]. **Bottom-right: The diagrams depict the principle of tomographic light superposition in volumetric printing, along with the setup of a DLP projector-based tomographic VP system.** A time-lapse sequence shows a print completed in 51 s, accompanied by photographs of Thinker models^[24]. Further images illustrate support-free printing capabilities with polymer objects created via tomographic VP^[25]. Two references are included: (J) laser-based tomographic VP system, and (K, M) polymer objects of Notre Dame and Benchy, with corresponding micro-CT scans (L, N). These images are adapted from sources published in 2019 and 2020, with permissions from the respective publishers.

3.2 TPP: Pushing the Limits of Nanoscale Fabrication

Building upon SLA's foundation, TPP employs ultrafast femtosecond pulsed lasers, typically in the near-infrared spectrum (~ 700 – 1000 nm), to induce two-photon absorption within a highly localized focal volume^[174–179]. The nonlinear nature of two-photon absorption confines polymerization to a micron-scale volume, enabling the creation of nanostructures with resolutions down to a few hundred nanometers, well below the diffraction limit of conventional optics. The process involves focusing a high-

peak-power pulsed laser into a resin doped with appropriate photoinitiators that can absorb two photons simultaneously. When the photon flux exceeds a threshold, polymerization occurs exclusively at the focal point, allowing precise 3D structuring within the resin volume without the need for layer-by-layer stacking. This technique is invaluable for fabricating nanodevices^[172,180], tissue engineering scaffolds^[181] with cellular-scale features, and photonic structures^[182,183]. However, TPP's intrinsic trade-off is a slow build rate, often in the order of micrometers per hour, making it suitable primarily for research, prototyping, or applications requiring nanoscale detail^[184].

3.3 PμSL: Micro-Resolution with Enhanced Control

PμSL refines DLP principles by integrating reduction optics, such as high-magnification lenses, to focus the projected image onto the resin surface, achieving resolutions as fine as 0.6μm. This precise control over light delivery enables the fabrication of micro-architectures with nanometer-scale features, vital for microelectromechanical systems, micro-optics, and tissue scaffolds with cellular resolution^[185-187]. PμSL employs a digital projector or DMD, with the optical pathway optimized to concentrate light into a small spot, allowing for high-precision, high-resolution microfabrication^[188]. The layer thickness can be finely controlled, often below 10μm, facilitating the construction of complex, multi-material microsystems with integrated gradients and functional heterogeneity.

3.4 Liquid Crystal Display (LCD) Masked Photopolymerization: Cost-Effective Flexibility

LCD-based resin curing offers a low-cost alternative by replacing DMDs with commercially available LCD^[189-194]. These displays modulate light transmission based on electric signals, controlling the exposure pattern dynamically^[189-193]. Using a high-intensity UV or visible light source, the LCD acts as a mask, allowing for flexible patterning at resolutions typically around 50-100μm^[190]. While less expensive and easier to implement, LCD systems face challenges such as lower light transmission efficiency^[195], potential light leakage^[196], and slower curing speeds^[197] compared to DLP or SLA. Nevertheless, they serve well for educational purposes, rapid prototyping, and applications where cost constraints outweigh ultra-high-resolution requirements.

3.5 VAM-based 3D Printing

VAM is an emerging 3D printing technology that fabricates objects by curing the entire volume of a medium simultaneously, rather than layer-by-layer. First introduced in 2017, VAM enables rapid production, often in seconds to minutes, without the need for support structures, facilitating the creation of complex, overhanging, and internal features with high precision^[198-202]. This is achieved by selectively delivering energy throughout the medium to initiate polymerization or other solidification reactions, resulting in uniform, high-quality parts in a single step. The core concept involves generating an energy dosage distribution field within the medium, representing the spatial energy delivery pattern crucial for controlled solidification^[200]. VAM's unique capacity for layer-less, volumetric fabrication results in parts with superior surface finish, mechanical homogeneity, and minimal residual stresses. Its ability to overprint around existing structures makes it particularly suitable for creating integrated components with embedded functionalities, such as

sensors or electronic circuits^[201,202]. Moreover, the process involves no external mechanical forces, which preserves delicate or soft materials, making it highly advantageous for applications requiring material integrity. The precise control over environmental conditions further broadens the range of compatible materials, especially those sensitive to oxygen or moisture, enhancing its potential in fields like bioprinting and tissue engineering^[200,204].

The technology offers significant advantages, including rapid manufacturing speeds that can facilitate real-time production and reduce inventory costs. Its layerless approach produces continuous, monolithic structures with improved mechanical properties and reduced surface defects. The capacity for overprinting enables the embedding of pre-existing components, paving the way for advanced integrated devices in electronics^[201,205], robotics^[206], and biomedical application^[201,205]. Additionally, the absence of mechanical interference during printing preserves the integrity of fragile or living materials, making VAM particularly promising for biomedical applications such as tissue engineering^[204], regenerative medicine^[208], and bioprinting of complex biological structures^[209].

VAM also contributes to sustainable manufacturing by minimizing material waste, as only the necessary volume of resin or polymer is cured. Its ability to produce intricate geometries rapidly supports agile prototyping, customization, and development of complex devices that are difficult or impossible to create with traditional methods. Although still in early stages, VAM shows potential for multi-material printing, which could further enhance its application scope in multifunctional device fabrication. The dominance of tomographic VAM, utilized in over 83% of research, underscores its central role in the field. Countries like the USA and Switzerland lead global research efforts, reflecting broad international interest.

3.6 Multi-Material and Functionally Graded Printing: Towards Complex, Adaptive Structures

Traditional VP systems are primarily limited to single-material or multi-voxel discrete material assemblies, but recent innovations aim to overcome these constraints. Grayscale DLP (g-DLP) introduces the capacity for *gradients* in material properties by modulating the intensity of light within a single exposure^[210-216]. By varying gray levels, g-DLP controls the degree of cure, enabling the fabrication of functionally graded materials with spatially varying stiffness, transparency, or thermal properties within a continuous structure.

Additionally, two-stage curing systems, employing separate resin formulations or dual-curing mechanisms, allow for the creation of multi-material parts. For instance, a resin can be selectively cured in different regions with

distinct chemical compositions, producing objects with embedded soft-rigid interfaces or complex biological mimetics^[217,218]. Complementing these approaches, centrifugal multi-material 3D printing leverages rotational forces to enable large-area, multi-material transitions with high precision^[219,220]. By sequentially depositing different resins and using centrifugal forces to clean residual resin, CM systems create heterogeneous objects with sharply defined interfaces — ideal for soft-rigid hybrids, electronic packaging, or multi-functional devices^[221].

The confluence of these advanced photopolymerization techniques has dramatically expanded the landscape of additive manufacturing, offering unmatched resolution, speed, and material complexity. Their integration into 4D printing frameworks enables the fabrication of structures capable of dynamic, reversible, and multi-functional shape transformations. As innovations continue, such as hybrid multi-material systems and gradient architectures, the potential for responsive, adaptive, and intelligent materials in biomedical, aerospace, and robotics applications becomes increasingly tangible. Despite its promise, challenges such as limited commercial equipment, the need for specialized hardware, and the absence of standardized evaluation criteria remain. Addressing these issues will be essential for the widespread adoption of VAT. Moving forward, VAT's rapid, high-resolution, and support-free fabrication approach positions it as a transformative technology with significant implications across biomedical engineering, aerospace, electronics, and beyond.

4 RADICAL-DRIVEN PHOTOPOLYMERIZATION USED FOR 4D PRINTING: THE (METH)ACRYLATE PARADIGM

A photoinitiator or a photoinitiator system with a high absorption coefficient is essential to efficiently convert photolytic energy into reactive species, either radicals or cations, that initiate polymerization through radical or cationic mechanisms^[222]. Typically, photoinitiators exhibiting strong molar extinction coefficients at shorter wavelengths, primarily in the UV range below 400 nm, are employed to trigger these photochemical reactions^[223]. While UV-based photoinitiation is well-established in 3D printing, several limitations hinder its broader application: (1) UV photons have limited penetration depth, restricting the achievable layer thickness to approximately 100 micrometers, which slows down the overall printing process, especially for larger structures; (2) in bioprinting contexts, UV exposure poses risks of cellular damage, potentially causing chromosomal abnormalities or genetic instability; and (3) prolonged UV irradiation can lead to undesirable side reactions, including degradation of reactants and products^[224,225].

As a result, there is active research aimed at developing

photopolymerization systems that can be activated using longer wavelengths of light. The goals of this research include creating safer, milder operational conditions; increasing penetration depth to enable thicker layers and faster printing speeds; and designing systems compatible with living tissues to advance applications like tissue engineering^[226]. Such advancements seek to overcome the inherent limitations of traditional UV-based systems, opening new possibilities for efficient, biocompatible 3D printing technologies^[227-229].

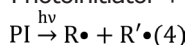
4.1 (Meth)acrylate Photocurable Systems and Radical Initiation

(Meth)acrylate monomers and oligomers constitute the backbone of many photopolymerizable formulations used in 3D/4D printing. Their polymerization proceeds predominantly through a radical chain-growth mechanism, encompassing three pivotal stages: radical generation, initiation, and propagation.

4.1.1 Radical Generation and Initiation

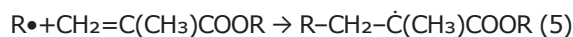
A photoinitiator or photoinitiator system with a high absorption coefficient is essential to efficiently absorb light energy (photons) and convert it into highly reactive chemical species called free radicals^[222]. These radicals are the starting points for building the polymer chain. Typically, photoinitiators used are chosen because they absorb strongly at shorter wavelengths, primarily in the UV range below 400 nm, to trigger these photochemical reactions^[223] (Equations 3 and 4).

Step 1: Creating radicals from light (photolysis): When the photoinitiator molecule absorbs a photon of light ($h\nu$), it breaks apart (cleaves) to produce two free radical fragments. This cleavage is often a specific type called Norrish Type I α -cleavage. Common photoinitiators operating this way include Irgacure 1173 and DMPA (Irgacure 651)^[222]. Photoinitiator absorbs light and splits into two radicals. The general reaction is:



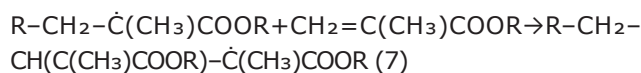
where PI is the photoinitiator molecule, and $\text{R}\cdot$, $\text{R}'\cdot$ are the radicals formed.

Step 2: Starting the chain - radical attacks monomer (initiation): The newly formed free radicals ($\text{R}\cdot$ or $\text{R}'\cdot$) are highly reactive. They immediately seek out and attack the carbon-carbon double bonds ($\text{C}=\text{C}$) present in the liquid (meth)acrylate monomers. When a radical attacks the double bond, it forms a new chemical bond with one carbon atom of the monomer, leaving the other carbon atom as a *new* radical site. This creates a slightly larger molecule with a reactive radical end, called the "initiating radical" or "chain-initiating radical". A radical reacts with a monomer's double bond, creating a new, larger radical (Equations 5 and 6):



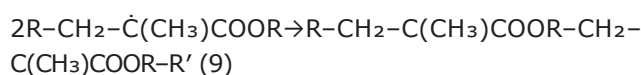
$R\bullet + C=C \rightarrow$ Radical addition to monomer (6)

Step 3: Building the chain - adding more monomers (propagation). The new radical (e.g., $R-CH_2-\dot{C}(CH_3)COOR$) formed in initiation is still highly reactive. It now attacks *another* monomer molecule's double bond. This process repeats itself over and over again. Each time a radical adds to a monomer, it consumes the double bond and creates a *new* radical on the end of the growing chain. This rapid, sequential addition of monomers is called chain propagation. The chain radical keeps adding monomers, making the chain longer (Equations 7 and 8):



Radical chain + monomer $\rightarrow$ Extended radical chain (8)

Step 4: Stopping the chain - radical meets radical (termination). The chain propagation continues until two growing radical chains encounter each other. When two radicals meet, they react to permanently stop the chain growth. This can happen in two main ways. (i) Combination: The two radicals simply join together, forming a single bond between the ends of the two chains. (ii) Disproportionation: One radical takes a hydrogen atom from the other, resulting in one chain with a double bond and one saturated chain. Two radicals react, stopping growth and forming a stable polymer chain (Equation 9):



The radical combination then leads to disproportionation, halting chain growth (Equation 10):



This entire sequence – initiation, propagation, and termination – happening simultaneously throughout the illuminated resin converts the liquid monomers into a solid, crosslinked polymer network. Millions of chains grow and link together, solidifying the material. This rapid network formation is crucial for achieving the high resolution needed in 3D printing, as it quickly "freezes" the shape defined by the light pattern. However, this speed and the conversion of double bonds into single bonds also cause significant shrinkage stress and can lead to network heterogeneity, which are challenges for dimensional accuracy and final material properties.

4.1.2 Applications and Material Compatibility

Methacrylate-based resins are highly versatile, compatible with a broad spectrum of commercial and custom 3D/4D printing^[67,230-232]. They have been employed in fabricating SMPs^[233,234], siloxane-based

hybrids^[230], highly stretchable elastomers^[235], and biofunctional materials^[236]. Typical monomers include polyethylene glycol diacrylate (PEGDA)^[237], urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA)^[238], bisphenol A-glycidyl methacrylate (Bis-GMA)^[239], and trimethylolpropane triacrylate (TTA)^[240], each contributing specific properties such as flexibility, biocompatibility, or mechanical robustness (Figure 4).

4.1.3 Limitations and Challenges

Despite their success, (meth)acrylate resins exhibit inherent drawbacks. Notably, volumetric shrinkage during polymerization induces internal stresses, potentially causing warping or deformation in layered objects^[241,242]. This shrinkage varies with monomer structure; aromatic and cycloaliphatic acrylates tend to exhibit lower contraction compared to TEGDMA, which is more reactive but prone to higher shrinkage stress^[243-244]. Strategies to mitigate these issues include employing high molecular weight oligomers with reduced reactive group density, although at the expense of increased viscosity requiring thermal management, or utilizing alternative polymerization mechanisms like step-growth processes that inherently produce less shrinkage^[245].

High kinetic chain lengths associated with multifunctional acrylates can lead to network heterogeneity and brittleness, compromising mechanical integrity. Incorporating chain transfer agents, such as addition-fragmentation chain transfer (AFCT) agents, can promote more homogeneous networks, decrease residual stresses, and improve toughness^[246]. Oxygen inhibition remains a persistent obstacle, especially in open vat systems; additives like tertiary amines or triphenylphosphine can alleviate this, although they may introduce side effects such as discoloration or interference with cationic polymerization pathways. Alternatively, photopolymerization via thiol-ene chemistry offers oxygen tolerance and reduced stress, expanding application horizons.

4.2 Alternative Radical Systems: Thio-ene and Thio-yne Chemistry

4.2.1 Thiol-Ene and Thiol-Yne Reactions

Thiol-ene and thiol-yne systems present a class of step-growth radical that proceed via addition reactions between thiol groups and reactive carbon-carbon double or triple bonds, allowing them greatly appropriate for applications in 3D/4D printing^[247-250]. These reactions offer several advantages over traditional (meth)acrylates, including rapid polymerization, reduced shrinkage stress, and enhanced biocompatibility^[251-253]. The presence of thiol groups acts as hydrogen donors, effectively scavenging oxygen and enabling ambient air curing.

In thiol-ene formulations, the step-growth mechanism facilitates network formation at high conversion levels

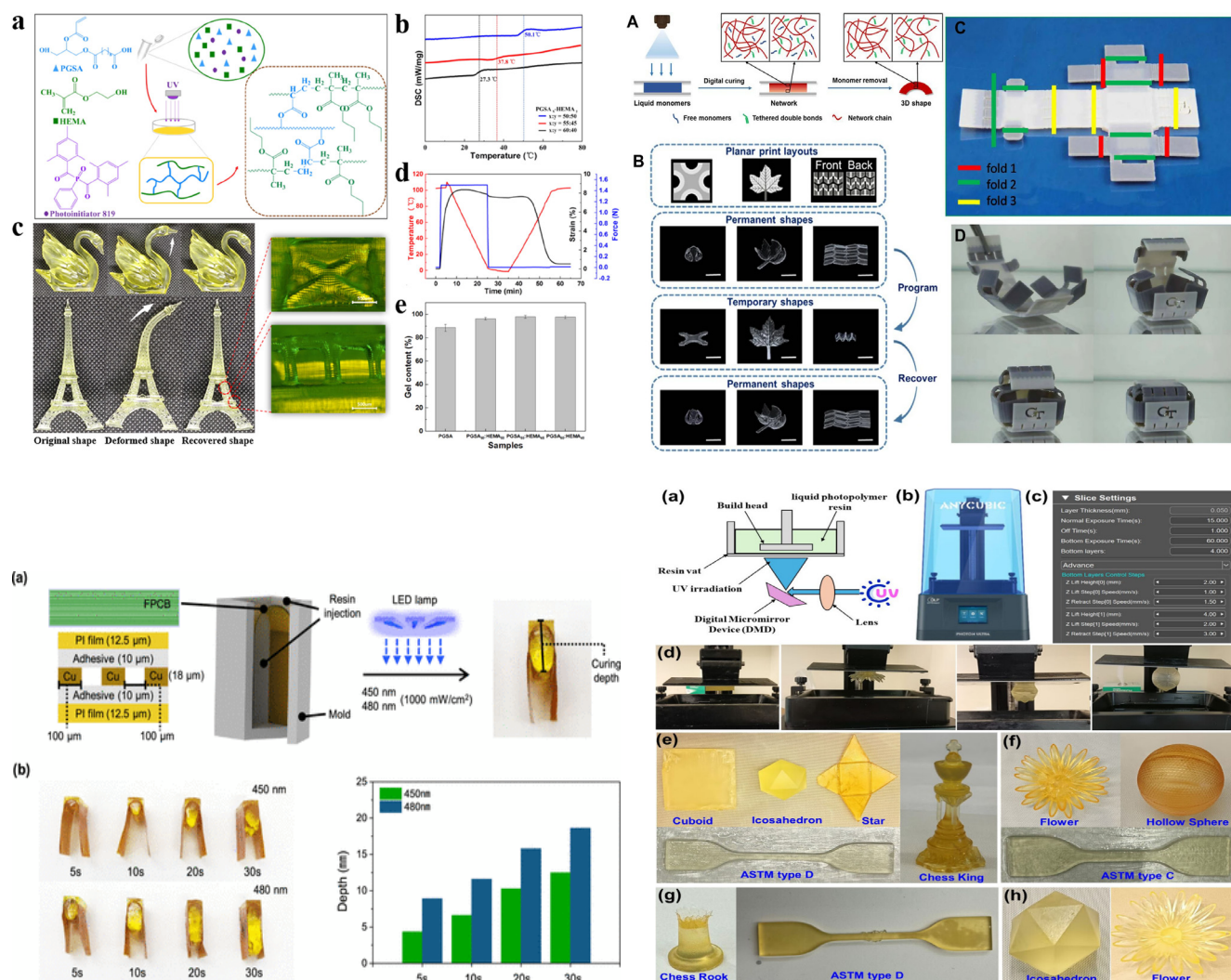
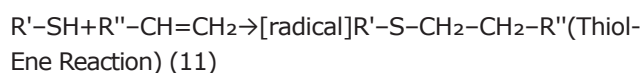


Figure 4. (Top-Left): Schematic representation of the photocrosslinked PGSA network. The differential scanning calorimetry (DSC) curves for PGSA are shown, illustrating its thermal properties. A shape memory demonstration features a DLP 3D printed swan and Eiffel Tower model; the inset provides a microscopic view of the detailed structure at 500μm scale. The shape memory effect (SME) curve, obtained from cyclic thermal-mechanical testing of PGSA55, is also included, along with the measured gel content of the PGSA composite^[234]. This figure is adapted with permission from Ref.^[234] published in 2023. **(Top-Right): (A) Diagram illustrating the experimental setup used to evaluate resin cure depth.** The FPCB consists of a layered structure, including a 12.5μm thick PI film, a 10μm adhesive layer, and copper traces measuring 100μm in width with 100μm spacing. The FPCB was bent and placed into a mold, after which resin was injected and applied to the surface. The resin was then exposed to light at wavelengths of 450nm and 480nm with an intensity of 1000mW/cm² to initiate curing, and the cure depth was subsequently measured. **(B)** Results of resin curing under 450nm and 480nm illumination at 1000mW/cm², with different exposure durations^[236]. This figure is adapted with permission from Ref.^[236] published in 2023. **(Bottom-Left) An image of a 3D printed self-folding box fabricated with multiple materials at different hinge locations demonstrates multi-material integration.** Additionally, a schematic illustration depicts the self-locking mechanism that responds to environmental changes such as temperature variations, enabling the structure to lock or unlock accordingly^[239]. This figure is adapted with permission from Ref.^[239] published in 2025. Assessment of the multicomponent system on a real flexible printed circuit boards (FPCB). **(Bottom-Right): (A)** The operational concept of DLP 3D printing, **(B)** the Anycubic Photon D2 3D printer model, **(C)** the parameter settings used for slicing during the printing process, **(D)** example images of printed objects positioned on the platform, and **(E, F)** 3D printed samples of soybean oil-based photocurable resins (ESBO_HEA), while **(G, H)** display objects made with ESBO_HEA, both using pure and 20% trimethylolpropane triacrylate (TMPTA) formulations, respective^[240]. This figure is adapted with permission from Ref.^[240] published in 2024.

with minimal internal stresses, making these systems suitable for applications demanding high toughness and low residual stress^[254]. The general reaction involves the radical-mediated addition of a thiyl radical (derived from a thiol) across a C=C bond Equation (11):



This reaction describes how a thiol group (R'-SH) reacts with an alkene (a molecule with a C=C double

bond, R''-CH=CH₂). A radical initiates the addition, attaching the thiol to the double bond, forming a new thioether linkage (R'-S-CH₂-CH₂-R''). This process links molecules together into a network.

Similarly, thiol-yne reactions involve the addition of thiol groups to alkynes (triple bonds), which can undergo multiple addition steps, creating densely crosslinked and more mechanically robust networks.

Similarly, thiol-yne reactions extend this chemistry

further, where alkynes undergo multiple addition steps, resulting in densely crosslinked networks with superior modulus and toughness Equation (12):

$R'-SH + R''-C\equiv C-R''' \rightarrow R'-S-CH=CH-R''' \rightarrow \text{additional additions}$
(Thiol-Yne Reaction) (12)

Here, R' , R'' , R''' are organic groups, $h\nu$ is photon energy. A thiol reacts with an alkyne ($R''-C\equiv C-R'''$), first forming an intermediate with a double bond. This intermediate can undergo further reactions with thiols, resulting in a tightly connected network with high strength and flexibility. The multiple addition steps enable the formation of highly crosslinked structures, leading to materials with superior mechanical properties. In summary, these step-growth reactions enable the formation of uniform, resilient polymer networks with flexible linkages, offering advantages such as improved mechanical performance and reduced shrinkage during curing.

4.2.2 Chain Transfer Agents and Network Homogenization

In efforts to tailor network architecture, chain transfer agents, such as AFCT reagents, are incorporated into photocurable systems. These agents facilitate controlled radical transfer during polymerization, promoting uniform crosslinking, reducing brittleness, and alleviating shrinkage-induced stresses^[255]. Recent innovations involve designing non-reversible AFCT reagents, such as vinyl sulfonates, to accelerate reaction rates and enhance network homogeneity, thereby producing tougher, more reliable 3D-printed structures^[256]. Zhang et al.^[257] used a rapid, visible light-mediated RAFT polymerization process that is suitable for open-air 3D printing. The system is non-toxic, metal-free, and environmentally friendly, making it ideal for biomaterial fabrication. They incorporated RAFT agents into photosensitive resins to control the mechanical properties of printed materials and enable post-functionalization. Additionally, they achieved photoinduced spatiotemporal control of the network structure, facilitating the production of both 3D and 4D stimuli-responsive materials. This work expands the possibilities for creating functional and smart materials through additive manufacturing.

4.2.3 Cationic Photopolymerization: Epoxy and Vinyl Ether Systems

Cationic photopolymerization of epoxy and vinyl ether systems offers efficient, oxygen-tolerant curing processes suitable for advanced manufacturing^[257-260]. The initiation relies on photo-generated Lewis acids, enabling precise control over polymerization kinetics and network formation. These chemistries produce highly durable, thermally stable polymers with potential for 4D printing applications. Their inherent reactivity and tunability facilitate the development of smart, stimuli-responsive structures^[261].

4.2.4 Cationic Initiation and Monomer Chemistry

Cationic polymerization, initiated via decomposition of photoinitiators like aryl iodonium or sulfonium salts, involves the generation of strong electrophilic species capable of opening epoxide rings or vinyl ether bonds^[262-265]. This pathway is characterized by a chain-growth mechanism featuring high reactivity and insensitivity to oxygen inhibition, making it advantageous for large or complex geometries^[266,267]. Commercially relevant monomers include epoxy resins such as bisphenol A diglycidyl ether (DGEBA) and cycloaliphatic epoxides, which polymerize rapidly under UV exposure^[268].

The initiation involves the photolytic cleavage of a photoinitiator, generating a strong Lewis acid or electrophile (Equation (13)):

$ArI + h\nu \rightarrow Ar^+ + I^-$ (Aryl Iodide Photolysis) (13)

This electrophile then attacks the epoxide ring, opening it and forming a carbocation intermediate (Equation (14)):

$\text{Epoxide} + Ar^+ \rightarrow \text{Open-chain carbocation} \rightarrow \text{Polymer network}$
(Cationic Polymerization) (14)

The reactivity and network properties depend on monomer structure; cycloaliphatic epoxides, due to their ring strain, undergo faster polymerization, resulting in high crosslink density and thermal stability. Vinyl ethers, with their high reactivity and low shrinkage, further expand the toolkit for cationic curing^[268]. Dual curing strategies combining cationic and radical pathways enable the fabrication of complex, multi-responsive structures with tailored mechanical and thermal properties^[269].

5 NATURAL BIOMATERIALS FOR 4D PRINTING

5.1 Gelatin Methacryloyl (GelMA)

Derived from collagen, gelatin is a naturally biodegradable peptide that has gained significant attention in tissue engineering due to its excellent biocompatibility, modifiability, and presence of cell-recognition motifs such as RGD sequences^[270-274]. Its thermoresponsive behavior, transitioning from a liquid to a gel upon temperature decrease, allows for versatile applications including surface coatings and three-dimensional hydrogel matrices. In extrusion-based bioprinting, minimal chemical modification is required, as gelatin's natural gelation mechanism suffices to increase viscosity for structural stability. Conversely, in light-mediated processes, gelatin must be chemically functionalized to facilitate rapid and spatially controlled crosslinking. This is achieved through the synthesis of GelMA, initially described by Van de Bulcke et al.^[275] involving

conjugation of methacryloyl groups to amino groups within gelatin molecules via reaction with methacrylic anhydride. Recent advancements have focused on optimizing reaction parameters to achieve consistent degrees of substitution, enabling precise control over hydrogel stiffness and degradation. When exposed to specific wavelengths of light in the presence of a photoinitiator, GelMA undergoes free radical polymerization, resulting in a covalently stabilized hydrogel suitable for cell culture and tissue engineering applications.

The application of light-based fabrication enhances the ability to fine-tune GelMA hydrogel properties by adjusting parameters such as degree of substitution, polymer concentration, and irradiation conditions^[270,276-278]. This enables replicating the stiffness range of various tissues, from neural tissue to cartilage. For example, Ma et al.^[279] demonstrated that DLP could modulate GelMA stiffness to model different stages of liver disease by controlling exposure time, impacting embedded cell behavior (Figure 5).

Smart 4D printed hydrogels based on GelMA are capable of undergoing reversible shape transformations under stimuli, making them suitable for integration with 3D printing to produce structures that evolve over time. These time-dependent shape changes can also be engineered through deliberate design, where the initial deposition of materials is combined with predefined structural patterns. These 4D hydrogels that swell or contract anisotropically can be used to create complex, morphing architectures, with shape-shifting behavior controlled by manipulating network density gradients and fiber orientation during fabrication.

Luo et al.^[280] demonstrated a straightforward technique involving the 3D printing of biphasic hydrogels composed of alginate with GelMA or polydopamine (PDA). These printed constructs could be programmed to alter their shape upon dehydration and exposure to near-infrared light. The scaffolds exhibited maximum angular deformation within a specific concentration range of 14-18%. The shape change induced by NIR irradiation remained stable during 14 days of cell culture, with human embryonic kidney cells showing viability rates above 80% inside the alginate-GelMA matrix. This study emphasizes the potential of NIR-sensitive, shape-morphing bioinks based on alginate for applications in 4D bioprinting.

In another example, Yang et al.^[281] employed an electric-field-assisted extrusion process to produce aligned GelMA fibers containing myoblasts, targeting skeletal muscle regeneration. They fine-tuned variables such as cell density, electric field intensity, and stimulation duration to produce viable, highly oriented fibers with enhanced differentiation capabilities. Additionally, they utilized a 4D printing strategy with a gelatin hydrogel substrate, onto which cell-laden GelMA microfibers were deposited, forming bundled structures that closely resemble natural

muscle tissue. These engineered constructs demonstrated the ability to replicate complex muscle architecture and show promise for applications like muscle-on-a-chip systems for drug testing and tissue regeneration.

Zhang et al.^[282] developed a biomimetic microvascular model by creating hydrogel-based hollow tubes inspired by the curling behavior of dried apple peels. Using GelMA and methacrylated hyaluronic acid, they fabricated various vascular structures, such as Y-shaped branches, loops, and rings with diameters from 50 to 500 μm , through 3D printing or molding techniques. The hydrogel flakes, initially rectangular, contracted inward during drying, causing them to curl similarly to apple peels. This curling was driven by differential cross-linking density, which resulted in uneven swelling and contraction during the drying process. When soaked in water, these structures curled into tubular shapes, and subsequent culture with human umbilical vein endothelial cells demonstrated their capacity to promote microvascularization and improve skin flap survival, highlighting their potential for tissue engineering.

Although GelMA's biological properties are advantageous, its mechanical strength is limited due to its proteinaceous composition, making it susceptible to enzymatic and hydrolytic degradation. To mitigate this, GelMA is often combined with other biomaterials to form composite scaffolds. Since its development, GelMA has been extensively utilized to engineer three-dimensional constructs mimicking hepatic, cardiac, and neural tissues^[270].

5.2 Thiol–Ene Cross-Linking of Gelatin

While methacrylation remains predominant for gelatin functionalization, traditional free-radical polymerization faces challenges such as network heterogeneity, oxygen inhibition, and complex reaction dynamics^[283,284]. An alternative approach employs thiol–ene click chemistry, which proceeds through a step-growth mechanism under mild conditions, producing homogeneous networks with high efficiency, rapid reaction kinetics, and minimal oxygen sensitivity. This chemistry involves the addition of thiol groups to alkene functionalities, particularly norbornene, favored due to its high reactivity driven by ring strain. Munoz et al.^[284] demonstrated the synthesis of gelatin functionalized with norbornene groups (GelNB), enabling stable covalent cross-linking with dithiol or tetra-thiol cross-linkers like PEG4SH upon UV exposure. This approach allows independent control over hydrogel stiffness by adjusting cross-linker type, concentration, and stoichiometry, resulting in customizable mechanical and swelling properties. These step-growth networks are compatible with various 3D/4D printing technologies and support high cell viability due to their mild reaction conditions.

The study found that cross-linking GelNB with tetra-functional PEG4SH, compared to DTT, influenced hydrogel

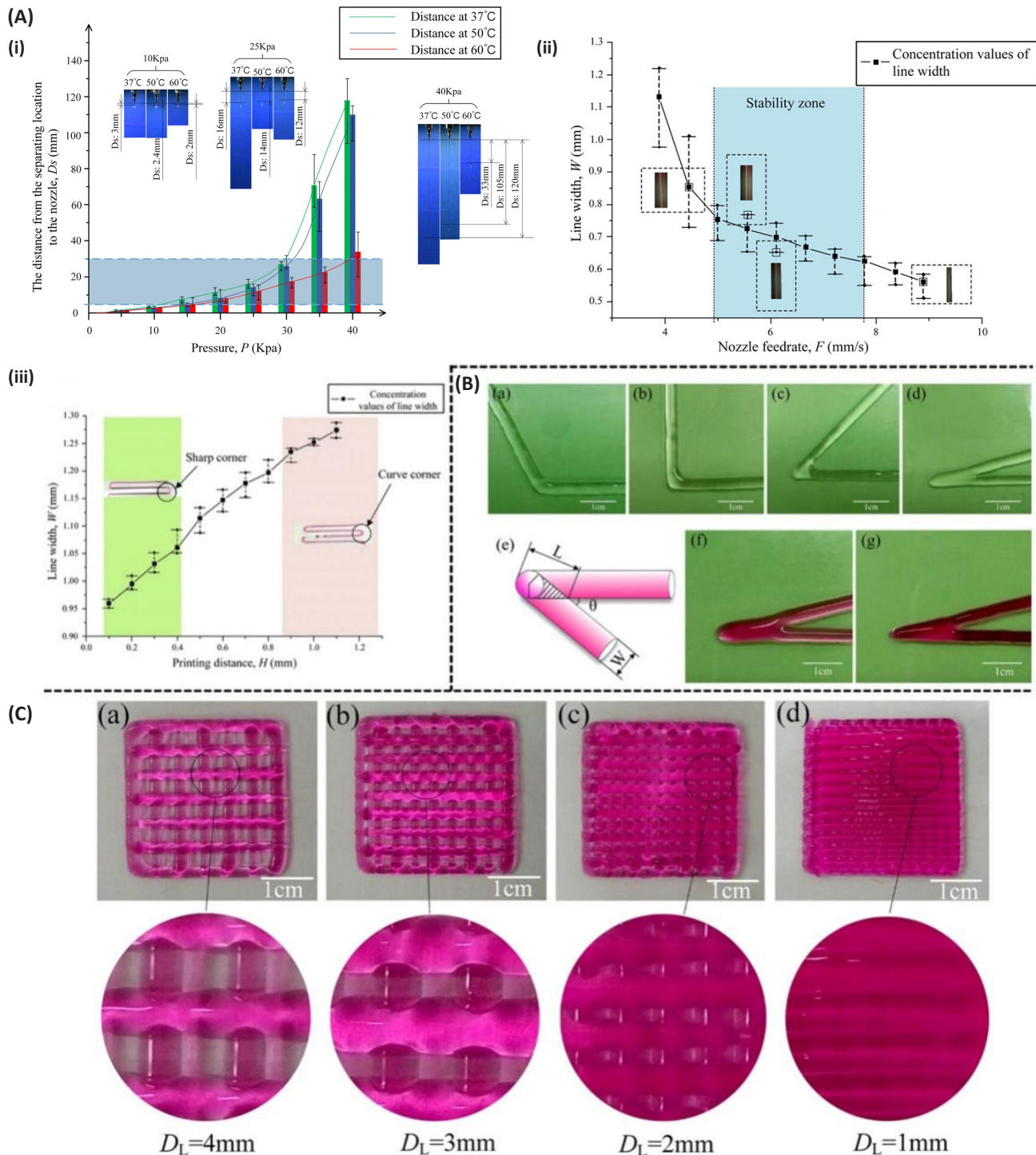


Figure 5. Several Key Parameters, Including Extrusion Pressure, Nozzle Feed Rate, and Printing Angle, Play Crucial Roles in Determining Printability. (A) Effects of printing parameters in extrusion bioprinting: (i) The relationship between extrusion pressure and filament length was examined at three different temperatures (37 °C, 50 °C, and 60 °C) while maintaining a constant nozzle diameter of 0.4 mm. (ii) The influence of nozzle feed rate on filament width showed that higher feed rates produce thinner filaments; a stable printing range was identified between 5 and 8 mm/s. (iii) A linear correlation was observed between filament width and layer height (the distance from nozzle to substrate), indicating a proportional relationship. (Reprinted with permission under a Creative Commons CC BY 4.0 license from Ref.^[276], Copyright 2016 Nature Portfolio.) (B) Reducing the printing angle negatively affected print quality due to filament overlap, with the most significant deterioration observed at sharp angles. (Reprinted with permission under a Creative Commons CC BY 4.0 license from Ref.^[276], Copyright 2016 Nature Portfolio.) (C) The top layer's squeezing and radial diffusion decrease scaffold porosity and resolution, but increasing the line distance (DL) can enhance these qualities. (Reprinted with permission under a Creative Commons CC BY 4.0 license from Ref.^[276], Copyright 2016 Nature Portfolio.)

properties by altering step-growth efficiency. Keeping GelNB concentration and alkene-thiol ratios constant, PEGSH increased the equilibrium shear modulus to 5kPa from 0.4kPa with DTT and affected swelling behavior^[285]. Unlike chain-growth polymerization systems like GelMA,

where stiffness correlates with bioink concentration, thiol-ene step-growth networks allow mechanical tuning through cross-linker functionality and thiol-alkene ratios independently of concentration. Recent developments include thiol-ene photoclickable gelatin bioinks for DLP

and extrusion 3D printing. Bertlein et al. synthesized allylated gelatin (GelAGE) cross-linked with DTT, using either UV photoinitiator (Irgacure 2959) or visible-light initiator (Ru/SPS). Mechanical properties were adjusted by varying GelAGE to DTT ratios. GelAGE's low viscosity at high concentrations (10–20%w/v) at room temperature enabled the creation of porous, high-fidelity lattice structures with 250µm struts. For extrusion, a less degraded, high-concentration (30%w/v) GelAGE maintained thermal gelation and shear-thinning at low temperatures (4–7 °C). This produced 500µm resolution constructs with high cytocompatibility of encapsulated porcine erythrocytes^[286].

5.3 Collagen-Based Biomaterials

Collagen, the predominant structural protein in the extracellular matrix, provides critical mechanical and biological cues in tissues^[287–289]. Type I collagen, with its characteristic triple-helical structure, assembles into fibrils that confer tensile strength and form dense fibers in connective tissues such as tendons, bones, and muscles. Its innate ability for fibrillogenesis under physiological conditions has been exploited to produce soft hydrogels^[288]. However, native collagen hydrogels are mechanically fragile, prompting the use of chemical or enzymatic cross-linking agents (e.g., glutaraldehyde, genipin, transglutaminase) to enhance stability and control degradation^[290]. Common methods for cross-linking collagen typically involve chemical and enzymatic approaches, such as using glutaraldehyde, genipin, or transglutaminase^[291–293]. However, these techniques often present limitations, including prolonged cross-linking durations, limited control over localized mechanical properties, and potential cytotoxic effects of the cross-linking agents. In 3D printing applications, pure collagen bioinks have predominantly been employed in nozzle-based systems, relying on fibrillogenesis to facilitate rapid self-assembly and prevent structural collapse during printing. For example, the freeform reversible embedding of suspended hydrogels (FRESH) technique, demonstrated by Hinton et al.^[294] involves extruding collagen type I into a supportive slurry bath composed of HEPES and gelatin. This approach maintains the structural suspension of the printed material while ensuring optimal pH and temperature conditions for collagen self-assembly. Similarly, Lee et al.^[295] showcased the potential of FRESH to fabricate porous collagen scaffolds that mimic patient-specific geometries of the human heart. Although FRESH can achieve a spatial resolution of approximately 200 µm, challenges such as nozzle clogging become more significant when working with higher concentration bioinks necessary to replicate tissue-specific mechanical properties.

To address these limitations, researchers have developed strategies to modify collagen type I for light-based 3D printing techniques, which offer faster

fabrication speeds, complex geometrical design capabilities, and enhanced control over material properties. For instance, Drzewiecki et al. synthesized collagen methacrylamide (CMA) by reacting collagen with methacrylic acid, via EDC and NHS activation in MES buffer for 10min, followed by a 24-hour reaction in acetic acid^[296]. This process preserves the natural fibrillogenesis and thermoreversible properties of collagen while enabling photo-cross-linking upon UV exposure at 365nm^[297]. Using this approach, CMA hydrogels are formed by self-assembly at 37 °C, then solidified with UV light through a photomask to create specific geometries. Cooling the construct to 4 °C melts non-photopolymerized regions, resulting in stable structures with a fivefold increase in storage modulus compared to thermally gelled controls, achieving resolutions around 350µm^[295,296].

For higher resolution fabrication, multiphoton 3D printing techniques have been applied to collagen bioinks. Bell et al.^[297] utilized acid-solubilized collagen type I mixed with 5'-phosphorylated flavin mononucleotide, a biocompatible photosensitizer suitable for low pH solutions. Using a titanium-sapphire femtosecond laser, they produced complex microarchitectures, including multilayered woodpile structures with struts approximately 12.5µm wide and pore sizes as small as 12µm. This work demonstrates that unmodified collagen type I can be precisely printed at the micrometer scale, expanding the potential of collagen biomaterials for intricate 3D free-form fabrication methods^[297].

5.4 Hyaluronic Acid (HA) and Derivatives

HA is a non-sulfated glycosaminoglycan that exists naturally within the extracellular matrix and is found in numerous tissues throughout the body, including epithelial, connective, and neural tissues^[299]. In vivo, HA plays vital roles such as maintaining tissue hydration, lubricating joints, forming a scaffold that facilitates cell migration, regulating wound healing processes, and supporting endothelial cell proliferation and angiogenesis^[300,301]. Similar to gelatin and collagen, HA can be cross-linked into hydrogels without the need for chemical modifications. For instance, research has demonstrated that HA can be cross-linked under alkaline conditions using agents like bisepoxides or under acidic environments with chemicals such as glutaraldehyde and multifunctional hydrazides. These cross-linked HA hydrogels exhibit enhanced mechanical strength and stability compared to their native form, making them suitable for various 3D printing techniques, including extrusion-based methods^[302].

In light-based 3D printing systems, HA can be chemically modified to introduce photo-cross-linkable groups. This is typically achieved by attaching (meth)acrylate functionalities through reactions with compounds

like glycidyl methacrylate, resulting in glycidyl methacrylate-modified HA (GM-HA). These derivatives can then be covalently polymerized into permanent hydrogels via free-radical photopolymerization, using light in the presence of a photoinitiator. The mechanical properties and cross-linking density of GM-HA hydrogels can be finely tuned by adjusting parameters such as exposure time and photoinitiator concentration, allowing for customizable gel characteristics suitable for advanced tissue engineering applications^[302,303].

5.5 Decellularized Extracellular Matrix (dECM)

dECM retains the complex biochemical composition and architecture inherent to native tissues, serving as an ideal scaffold for regenerative purposes^[304,305]. The decellularization process involves a combination of physical disruption, chemical detergents, and enzymatic treatments to remove cellular material while preserving structural proteins and glycosaminoglycans (GAGs). The resulting ECM can be processed into various formats, such as powders, hydrogels, or organ-specific scaffolds, depending on the application. For bioprinting, enzymatic digestion (e.g., with pepsin) produces a solubilized form suitable for extrusion. To improve mechanical stability and printability, dECM can be combined with other biomaterials or chemically modified, including photocross-linking strategies. Recent innovations include powder-based formulations that can be reconstituted into bioinks compatible with high-resolution light-based printing techniques, enabling the creation of complex, tissue-specific structures with preserved biochemical cues. The extracellular matrix (ECM) within tissues provides essential structural support, comprising fibrous proteins and GAGs that influence critical cellular activities such as proliferation, differentiation, and migration. Each tissue or organ system features a unique ECM composition, creating specialized microenvironments tailored to support specific cell populations *in vivo*. Achieving tissue specificity in biomaterials development is crucial; designing materials that closely mimic the complex biochemical makeup of the native ECM enhances cell function, phenotype, and maturation. One prominent top-down strategy involves creating dECMs derived from native tissues. This process entails treating tissues with mechanical, enzymatic, and chemical methods to remove cellular components while preserving the ECM's structural and biochemical integrity. Physical methods include snap freezing to form ice crystals for cell disruption, washing with hypertonic or hypotonic solutions, and agitation to facilitate removal of cellular debris. Chemical and enzymatic approaches involve washing with acidic, alkaline, ionic, or nonionic detergents, as well as treatments with enzymes like trypsin or nucleases to eliminate residual DNA and RNA. It is essential that these protocols thoroughly remove cellular remnants to prevent immune responses. Numerous procedures have been established for processing various

tissue types, including heart, lung, liver, adipose tissue, brain, muscle, and intestine. The resulting dECM scaffolds can be fabricated into diverse formats, such as whole decellularized organs, porous foam scaffolds, thermally gelled hydrogels, or powdered forms, tailored to different tissue engineering applications^[304,306].

A common method to prepare dECM for use as bioinks in 3D printing involves digesting the material with pepsin to produce a solubilized form suitable for extrusion. Because of its inherent thermal gelation properties, dECM can be easily deposited using conventional extrusion-based printers and then solidified at body temperature (around 37 °C)^[307]. However, native dECM hydrogels are often mechanically weak and lack sufficient structural integrity, limiting their utility as standalone scaffolds. To address this, additional supportive materials, such as polycaprolactone (PCL), are frequently incorporated during printing to maintain shape fidelity. Alternatively, increasing the viscosity of dECM bioinks can improve extrudability and reduce reliance on nondegradable supports. For example, Skardel et al.^[308] developed a multi-component liver dECM bioink capable of two-stage polymerization, facilitating smooth extrusion and adjustable mechanical properties. This involved mixing solubilized liver dECM with thiolated gelatin, hyaluronic acid, PEG acrylate, and PEG alkyl components. Primary cross-linking between thiol groups and PEG acrylate enabled extrusion, while subsequent UV irradiation triggered secondary cross-linking, stabilizing the construct and increasing its stiffness.

In another approach, Jang et al.^[309] incorporated vitamin B2 (riboflavin), a biocompatible photo-cross-linker, into heart dECM bioinks to improve printability and achieve mechanical properties close to native cardiac tissue. The process involved depositing the viscous dECM, followed by layer-by-layer UVA irradiation to cross-link the material, and then thermally gelating the entire structure at 37 °C for added stability. Most dECM bioinks developed to date are primarily compatible with extrusion-based 3D printing, offering moderate resolutions of around 100µm and simple lattice geometries^[310]. These limitations in speed and complexity hinder scalability. To overcome this, recent advancements have focused on adapting dECM bioinks for DLP systems, enabling rapid fabrication of high-resolution, complex structures. For instance, Yu et al.^[311] devised a multi-step process to create a photo-cross-linkable dECM-GelMA bioink. This involved mild pepsin digestion, lyophilization, and cryomilling to produce a dry, powdered form that can be reconstituted into a homogeneous liquid suitable for DLP printing. Using this method, tissue-specific microarchitectures, such as striated and hexagonal patterns mimicking heart and liver tissue, were printed with resolutions up to 30µm. The mechanical properties could be easily tuned by varying the exposure time during printing, allowing the scaffold's stiffness to match that of native tissues.

Table 1. Comparative Properties of Natural Biomaterials for 4D Printing

Property	GelMA	Collagen (Type I)	Alginate	HA	dECM
Biocompatibility	Excellent	Excellent	Good	Excellent	Excellent
Mechanical Strength	Moderate; tunable via cross-linking	Low (fragile alone)	Variable; tunable via cross-linking	Variable; tunable	Variable; depends on formulation
Cross-linking Methods	Photocrosslinking (UV/Vis), chemical	Enzymatic, chemical, photo-	Ionic (Ca ²⁺), chemical	Photo-crosslinking (methacrylate)	Enzymatic, chemical, photo-
Stimuli Responsiveness	Light, enzymes	None inherently	Ionic (Ca ²⁺), pH	Light	None inherently
Degradation Behavior	Enzymatic (collagenases)	Enzymatic	Hydrolytic, enzymatic	Enzymatic	Enzymatic, mechanical
Applications	Tissue engineering, 4D hydrogels	Soft tissues, scaffolds	Cartilage, vascularization	Wound healing, cartilage	Organ scaffolds, tissue models

For example, this approach was employed to develop a liver dECM-GelMA model for studying hepatocellular carcinoma, where regional variations in stiffness were used to replicate healthy versus cirrhotic liver tissue environments.

5.6 Alginate

Alginate, a naturally derived polysaccharide from alginic acid, has established itself as a fundamental biomaterial in the cutting-edge realm of bioprinting, including advanced techniques such as 3D/4D printing^[312-315]. Its widespread use in extrusion-based and inkjet-based bioprinting stems from its biocompatibility, ease of gelation, and capacity for modification. Extracted mainly from calcium, magnesium, and sodium alginate salts, sourced from the cell walls and intracellular spaces of brown algae, alginate's intrinsic ability to undergo ionic cross-linking makes it highly attractive for fabricating complex, functional tissue constructs with minimal chemical intervention^[313-315].

The rapid gelation triggered by multivalent cations such as calcium enables precise spatial and temporal control during the printing process. By fine-tuning parameters like alginate concentration, molecular weight, and cross-linker ratios, researchers can tailor the mechanical properties and porosity of the resulting hydrogels, optimizing them for specific tissue engineering needs. This tunability is especially vital in 4D bioprinting, where the time-dependent transformation of printed constructs, such as shape-shifting, self-assembly, or functional adaptation, is desired^[316-318]. Modifying alginate with chemical groups, such as through methacrylation via EDC/NHS chemistry to produce photo-cross-linkable macromers, has further expanded its utility^[320-324]. These modifications facilitate photopolymerization, yielding hydrogels with superior stability and mechanical strength that can withstand biological environments over time.

Photo-cross-linked alginate hydrogels demonstrate excellent cytocompatibility, supporting cell viability and function, making them suitable scaffolds for regenerative

applications. For example, encapsulated chondrocytes within these hydrogels have shown promise for cartilage repair, while nucleus pulposus cells have been maintained effectively for intervertebral disc regeneration^[324,325]. As the field advances, integrating alginate with other smart biomaterials and bioactive cues promises to enable the fabrication of living, adaptive tissues capable of responding to environmental stimuli, ushering in a new era of personalized, functional regenerative therapies through 4D printing. In this, a composite hydrogel system combining carbonized alginate (CAI) and methylcellulose (MC) has been engineered to produce customizable, branched vascular channels. These hydrogels are capable of moisture-triggered shape changes, facilitating the formation of complex, perfusable networks that promote the survival of both endothelial cells and fibroblasts^[324].

Researchers have utilized multicomponent methacrylated alginate with other biopolymers-based hydrogels to develop self-folding hydrogel tubes through 4D bioprinting techniques. A notable approach reported by Kirillova et al.^[325] employed two distinct shape-morphing hydrogels, including alginate and HA modified with methacrylate groups to create photocrosslinkable structures. These hydrogels, crosslinked with biocompatible green light to preserve cell viability, can form hollow, tubular constructs with high resolution, controllable architectures, and adjustable diameters. The method enables the fabrication of complex, self-folding tubes suitable for vascular tissue engineering, supporting the differentiation of mouse bone marrow stromal cells into various cell types. This innovative approach facilitates the creation of intricate architectures with significant potential for vascular network formation^[325]. Table 1 offers a side-by-side comparison of key properties of popular natural biomaterials used in 4D printing. It highlights differences in biocompatibility, mechanical strength, cross-linking techniques, responsiveness to stimuli, degradation mechanisms, and typical biomedical applications. Such a comparison helps in selecting the most suitable material based on specific requirements for tissue engineering, wound healing, or organ scaffolding.

6 SYNTHETIC BIOMATERIALS FOR 4D PRINTING

This section provides an overview of the current state of research concerning photo-cross-linkable synthetic biomaterials utilized in light-based 3D/4D printing technologies, with a particular focus on their roles in tissue engineering and regenerative medicine. Synthetic polymers, including polyethylene glycol (PEG), poly(glycerol-co-sebacate) (PGS), poly(glycerol-co-sebacate methacrylate) (PGSM), PEGDA, and polyurethanes (PUs) are highly versatile materials that can be engineered to meet specific property requirements by precisely controlling parameters such as molecular weight distribution, monomer composition, functional groups, and end groups. This level of control enables the development of tailored biomaterials with optimized mechanical, chemical, and biological properties.

In the context of 4D printing, synthetic polymers serve as promising candidates due to their tunable characteristics. Synthetic polymers are particularly advantageous for enhancing and customizing the mechanical properties of natural polymer hydrogels, which often face limitations in strength and durability^[250,326-329]. For light-based printing techniques, PEGDA is a widely favored prepolymer material^[327]. Its popularity stems from its ability to produce high-resolution features owing to its low swelling ratio and high cross-linking density, which ensures structural stability^[328]. Moreover, PEGDA's compatibility with various photoinitiators and its rapid curing process make it ideal for fabricating complex, fine-scale architectures.

Additionally, PEG itself is a highly studied biomaterial due to its relative bioinertness, which minimizes undesired biological interactions and fosters biocompatibility^[327]. Its chemical structure can be easily modified to incorporate functional groups, allowing for increased bioactivity, cell attachment, or controlled degradation^[330]. These modifications expand the utility of PEG-based materials in 4D printing applications, enabling the creation of smart, stimuli-responsive constructs that can adapt their shape or properties in vivo or in response to environmental cues. The integration of synthetic biomaterials into 4D printing technologies holds significant promise for advancing regenerative medicine, providing dynamic, customizable scaffolds capable of evolving in harmony with biological systems.

6.1 PEG and Its Derivates

Synthetic polymers such as PEG have revolutionized biomaterials science by offering highly controllable and reproducible properties, unlike their natural counterparts^[331]. This level of customization stems from the ability to precisely manipulate their molecular architecture, functional groups, and chain length at

both the monomeric and polymerization stages^[332,333]. PEG and its derivatives, including PEGDA^[327,328,334,335], PEGDMA^[336-339], and multi-branched PEGs^[340,341], are among the most extensively employed synthetic polymers in 4D printing for biomedical research and applications.

PEG-based hydrogels are lauded for their remarkable biocompatibility, largely due to their inert nature and minimal immune response. These properties have led to their approval by regulatory agencies such as the FDA for use in various clinical settings^[342,343]. A key advantage of PEG hydrogels is their tunability: by adjusting parameters like polymer chain length, concentration, and degree of functionalization, scientists can modulate physical characteristics such as stiffness, porosity, and degradation rate to suit specific tissue engineering requirements. Their non-adhesive nature makes them ideal scaffolds, serving as neutral platforms that can be functionalized with bioactive molecules or peptides, like Arg-Gly-Asp-Ser (RGDS), to promote targeted cell attachment and signaling^[344].

The capacity for photopolymerization further enhances their versatility. PEG macromers functionalized with acrylate or methacrylate groups can be rapidly cross-linked under mild conditions, using low-intensity UV or visible light, facilitating the fabrication of complex 3D/4D architectures with high precision^[336]. This property is particularly advantageous for light-based bioprinting techniques, which enable the creation of cell-laden constructs with intricate geometries while maintaining high cell viability.

Beyond static structures, PEG hydrogels are also pivotal in the emerging field of 4D bioprinting. By incorporating stimuli-responsive elements, such as temperature, pH, or enzymatic activity, these hydrogels can be programmed to undergo dynamic shape transformations or functional changes over time^[345]. This capability opens new frontiers in regenerative medicine, where scaffolds can adapt to their biological environment, promote tissue maturation, or facilitate controlled drug release^[346].

Furthermore, PEG's modular nature allows for the combination or copolymerization with other monomers or biomolecules, resulting in hybrid materials with bespoke properties, such as enhanced mechanical strength, degradation profiles, or bioactivity, that are essential for mimicking complex biological tissues^[327,329,347-349]. This adaptability has led to a broad spectrum of applications, from fundamental cell biology studies and in vitro tissue models to advanced regenerative therapies and implantable devices.

PEG-based hydrogels exemplify the potential of synthetic biomaterials in modern biofabrication. Their chemical versatility, combined with advanced

manufacturing techniques like light-assisted and 4D bioprinting, positions them at the forefront of creating dynamic, functional, and personalized tissue constructs, paving the way for innovative solutions in regenerative medicine and beyond.

6.1.1 PEG-Based Hydrogels for Cell Biology

In regenerative medicine and cellular biology, there is a growing recognition of how physical and geometric cues within the cellular microenvironment influence cell behavior, including proliferation, differentiation, and organization. The prevailing hypothesis suggests that the mechanical and spatial properties of the surrounding matrix can direct cellular alignment, induce patterned stresses, and ultimately modulate cell fate decisions^[350]. Due to their inherently non-adhesive and inert surface, PEG-based hydrogels are uniquely suited as scaffolds for investigating these phenomena, as they provide a neutral platform free from confounding chemical signals. This allows researchers to isolate the effects of geometry and physical forces on cell behavior.

For example, Qu et al.^[350] developed an innovative approach utilizing DLP bioprinting to create PEGDA constructs with precise geometric patterns. They printed three distinct designs, stripes, symmetric forks, and asymmetric forks, on a glass substrate, then seeded adipose-derived stem cells (ADSCs) within these confined geometries. The non-adhesive PEGDA walls served as physical boundaries that constrained cell growth, leading to varied multicellular arrangements. These geometric constraints generated different levels of cellular stress and alignment, which in turn directed the ADSCs toward specific differentiation pathways without the need for exogenous biochemical cues such as growth factors or specialized media.

Beyond static geometries, PEG's versatility extends to the fabrication of complex three-dimensional structures that can actively influence cellular organization and behavior. For instance, researchers have employed 3D-printed microwell arrays to facilitate multicellular spheroid formation and embryoid body development, providing a controlled microenvironment for tissue modeling. Additionally, fractal-inspired patterns have been designed to mimic the hierarchical organization found in natural tissues, enabling the study of how cells interpret complex spatial cues^[351].

In addition to these fixed structures, PEG's amenability to high-resolution and flexible fabrication techniques makes it possible to create dynamic scaffolds for real-time studies of cell mechanics. Zhang et al.^[352] demonstrated this by utilizing PEGDA combined with two-photon laser direct writing to produce suspended web-like microstructures with tailored mechanical properties, such as positive and

negative Poisson's ratios. These microscale architectures allowed for the investigation of how cells respond to unconventional mechanical stimuli. Notably, they observed atypical cell division behaviors on structures exhibiting negative Poisson's ratios, suggesting that this mechanical property could serve as an influential parameter, alongside elastic modulus, in directing cell fate and behavior.

Furthermore, the adaptability of PEG-based materials in advanced bioprinting and microfabrication techniques enables the creation of stimuli-responsive, reconfigurable scaffolds. These structures can change shape or mechanical properties over time, opening avenues for 4D bioprinting applications, where dynamic environmental cues guide tissue development and regeneration. The capacity to engineer such complex, responsive systems underscores PEG's potential as a foundational material in the next generation of cell and tissue engineering platforms, facilitating more nuanced investigations into the interplay of physical forces and biological responses at the microscale.

VP offers ultra-precise 3D printing for intricate tissue scaffolds, but developing biocompatible, soft resins remains a challenge. Urigoitia-Asua et al.^[335] introduced a groundbreaking 4D biomaterial designed for lung modelling, an optically responsive, thermoresponsive resin compatible with LCD-based VP. Composed of VCL, PEGDA, and gold nanorods (AuNRs) with an 800nm plasmon band, this hybrid material enables near-infrared light-triggered cyclic swelling and shrinking with a 6% contraction rate. Using this resin, they crafted detailed, alveolar-like scaffolds featuring 400µm honeycomb cavities. Lung epithelial cells readily formed monolayers, showing stronger adhesion on surfaces functionalized with positively charged AuNRs. Additionally, light-induced mechanical stimulation activated cellular mechanotransduction, offering a dynamic platform to mimic breathing forces. In another study, Hao et al.^[328] developed and 3D-printed millimeter-scale, micro-patterned PEGDA microscaffolds that self-assemble through tessellation, tailored for osteochondral cartilage repair. Using an in vitro model with simulated cartilage lesions, they tested various scaffold designs and delivery solutions. Hexagonal microscaffolds (750µm x 300µm) achieved the highest coverage, 73.3%, when injected with a 1% methyl cellulose solution. When chondrocytes were embedded within a collagen hydrogel, they successfully integrated with the scaffolds and remained viable for at least 14 days, demonstrating the potential for reconstructing layered cartilage tissue. This innovative 4D-printed, injectable approach shows promise for advancing osteochondral regeneration in clinical settings.

van Altena et al.^[353] introduced a cutting-edge high-resolution µDLP 3D printing protocol to create soft hydrogel scaffolds with mesoscale gyroid-based architectures specifically designed for 3D neural cell

culture. This innovative bioink combined PEGDA for structural integrity and GelMA to boost biocompatibility and facilitate cell attachment through RGD motifs. Utilizing lithium phenyl (2,4,6-trimethylbenzoyl) phosphinate (LAP) as the photoinitiator and tartrazine as a photoabsorber, they achieved remarkable feature resolutions down to 12.4µm, ensuring high fidelity, reproducibility, and mechanical robustness. The resulting hydrogels exhibited tunable Young's moduli ranging from 770kPa to 2.25MPa, aligning well with the mechanical softness of brain tissue, and supported cell viability of approximately 80%, with about 55% of cells successfully adhering to the scaffold surfaces. They engineered two distinct gyroid-based geometries: a fully porous structure optimized for culturing dissociated neuroepithelial stem cells, and a hollow variant designed to house pre-formed neural organoids. Both configurations facilitated strong cell attachment and organoid sprouting, underscoring their potential as advanced platforms for neurobiological research and tissue engineering. Recent developments in 4D printing have highlighted its potential for creating dynamic, shape-changing structures using programmable materials. Notably, Podstawczyk et al.^[354] developed thermo-responsive hydrogels composed of laponite (LAP), an interpenetrating network of poly(N-isopropylacrylamide) (PNIPAAm), and alginate (ALG) for direct printing of shape-morphing constructs. These hydrogels feature honeycomb patterns that enable self-rolling into tubular shapes when exposed to specific temperature stimuli. The shape transformation is driven by shear-induced anisotropy introduced during the 3D printing process, allowing the hydrogels to be programmed for different actuation behaviors at varying temperatures. For example, at 12°C, the printed hydrogel discs spontaneously roll into tubes, whereas at 42°C, they initially unfold and then curve in the opposite direction. Dual photocrosslinking of PNIPAAm further enables reversible shape changes, facilitating inverse temperature-dependent folding and unfolding. Such self-assembling motions are promising for applications in soft robotics and biomedical engineering, particularly for fabricating hollow structures like tubes, which can be utilized in active implants and minimally invasive procedures. This research underscores the potential of stimuli-responsive hydrogels in advancing 4D printed biomedical devices^[354]. Gao et al.^[327] developed a 3D-printable PAEK-based ink for DIW, addressing the challenge of fabricating high-performance SMPs. By incorporating N-vinyl-2-pyrrolidone (NVP) and PEGDA into PAEK oligomers, they enabled versatile cross-linking through photopolymerization, resulting in materials with excellent mechanical and shape memory properties. The photocured PAEK exhibited a tensile strength of 42.6MPa, high thermal stability ($T_d=246^{\circ}\text{C}$), and shape fixation and recovery ratios exceeding 93% and 100%, respectively. These properties allowed the material to act as a high-temperature actuator for gripping and releasing tasks. This work presents a promising approach

for manufacturing durable, shape-memory components via DIW, with potential applications in challenging environments^[327].

Seo et al.^[336] developed a 4D hydrogel structure using hydroxybutyl methacrylated chitosan (HBC-MA) combined with SLA 3D printing to mimic dynamic tissue movements. The HBC-MA enabled temperature-responsive expansion and contraction due to water absorption/desorption, resulting in structures that can change shape reversibly with temperature changes. Compared to control PEG-DMA structures, the HBC-MA-based 4D constructs demonstrated significant volume change and shape memory behavior, confirmed through morphological, swelling, and mechanical analyses, including bending ratio measurements. This approach advances the creation of dynamic, tissue-mimicking structures for biomedical applications^[336].

6.1.2 PEG-Based Hydrogels for Tissue Engineering and Regenerative Medicine

PEG-based hydrogels are renowned for their excellent biocompatibility and minimal immunogenic response in vivo^[355,356], making them widely applicable in tissue engineering^[357] and regenerative medicine^[327,336,358], including applications such as injury repair^[359], wound healing^[360,361], and tissue modelling^[335] (Figure 6). For example, recent advancements were the 3D printing of biomimetic spinal cord scaffolds using a combination of PEGDA and GelMA to treat severe spinal cord injuries^[357]. These scaffolds feature precisely fabricated linear microchannel arrays designed to promote axonal regeneration and directional growth within the injury site. The inclusion of PEGDA provided adjustable mechanical properties that closely matched the elasticity of the native spinal cord, while GelMA supported cell attachment. This material synergy was shown to significantly reduce foreign body reactions compared to other scaffolding materials like agarose, leading to notably better functional recovery in treated animals. Similarly, PEG-based hydrogels have been utilized to 3D print nerve guidance conduits aimed at peripheral nerve regeneration^[362]. The exceptional printability of PEG hydrogels allows for scalable production of patient-specific scaffolds, customized based on imaging data from MRI, CT scans, or CAD models.

In a relevant study, Testore et al.^[357] have highlighted the growing interest in electroconductive hydrogels (ECHs) for tissue engineering, particularly for regenerating electrically active tissues. These hydrogels require tunable electrical, mechanical, and biological properties to effectively mimic native tissues. Recent developments include photo-crosslinked PEGDA-gelatin hydrogels with varying PEGDA:gelatin ratios (1:1, 1.5:1, and 2:1wt./wt.) and incorporation of poly (styrene sulfonate) (PEDOT): poly (styrene-sulfonate) (PSS) (0.0–0.5%w/v). Notably,

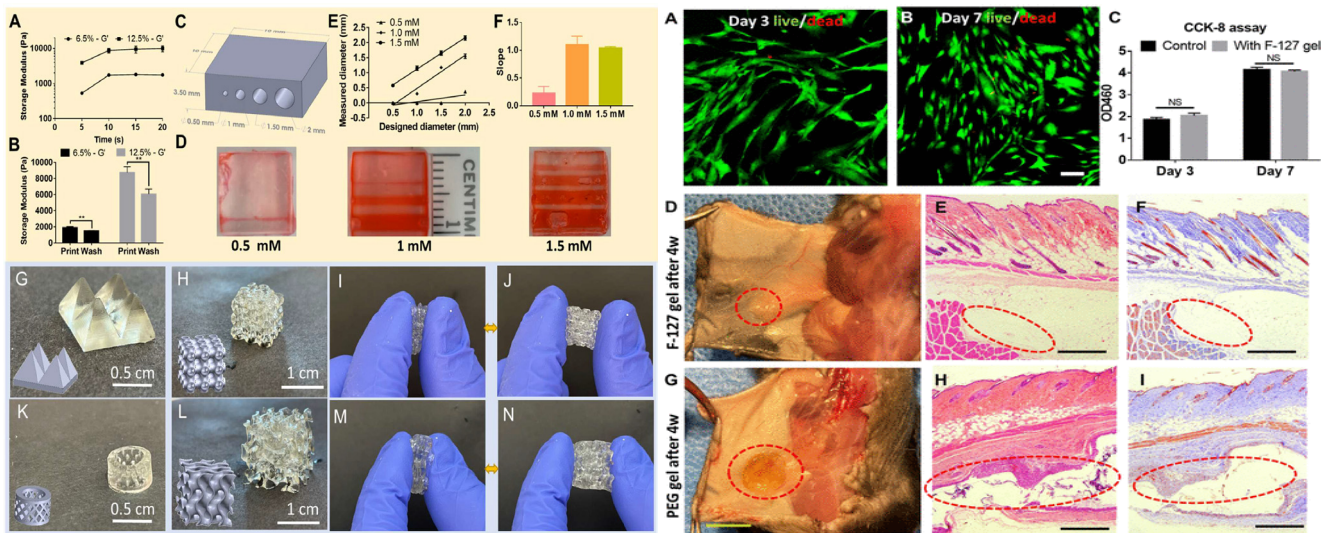


Figure 6. (Left): Evaluation and Optimization of Hydrogel Precursor Formulations, Along with the Resulting Structures Produced Via DLP Printing with Various Shapes. (A) The storage modulus of hydrogels immediately after printing was measured at different curing durations for two precursor concentrations ($n=3$). For some data points, the error bars were too small to be visible, so they are omitted. (B) Comparison of the storage modulus values before and after washing the samples with water ($n=3$). (C) Design of a cuboid with channels of diameters 0.5, 1, 1.5, and 2 mm, used to optimize the concentration of the photoabsorber (tartrazine). (D) Images of the printed cuboids with channels of 0.5, 1, and 1.5 mm tartrazine, filled with red food coloring to visualize the channels. (E) The measured diameters of the printed channels were compared to their designed dimensions across three replicates ($n=3$). (F) The slope of the line fitting the data for each tartrazine concentration group, indicating the accuracy of channel fabrication ($n=3$). (G) An array of four pyramids (each 5 mm per side) printed and connected at their bases. (H) A lattice cube measuring 10 mm per side, featuring circular channels in all directions. (I) The lattice cube manually compressed to demonstrate flexibility. (J) The lattice cube returning to its original shape after compression. (K) A printed tube with an outer diameter of 6 mm, a wall thickness of 1 mm, and diamond-shaped cutouts measuring 0.5 mm by 1 mm. (L) A gyroid cube measuring 15 mm per side, with its design adapted from an open-source model (<https://www.thingiverse.com/thing:757884>). (M) The gyroid cube manually compressed. (N) The cube restoring to its initial shape after deformation. **(Right): In vitro and in vivo biocompatibility assessments of DLP-printed poloxamer hydrogels.** Live/dead cell imaging of ADMSCs cultured with the printed hydrogel on day 3 (A) and day 7 (B). (C) Analysis of ADMSC proliferation with and without hydrogel coculture on days 3 and 7. (D) Photograph of the poloxamer hydrogel following a 4-week subcutaneous implantation. (E, F) Histological examination of skin tissue near the implanted poloxamer hydrogel, including Hematoxylin and eosin (H&E) staining and Masson's trichrome staining. (G) Image showing the PEG hydrogel after 4 weeks of subcutaneous implantation. (H, I) Corresponding H&E and Masson's trichrome stained images of skin tissue adjacent to the PEG hydrogel. Scale bars: 100 μ m (white), 500 μ m (black), 8 mm (yellow)^[358].

gelatin served as both a bioactive component and co-initiator in the crosslinking process, enabling its successful integration into the network. Modulating the PEGDA:gelatin ratio influenced the physical properties: higher PEGDA content increased stiffness (from 5 to 28 kPa), reduced water absorption, and shortened crosslinking time. The inclusion of PEDOT:PSS enhanced electrical conductivity and significantly decreased photopolymerization time (from 60 to 10 seconds). In vitro tests with human cardiac fibroblasts confirmed cytocompatibility, with the 1.5:1 ratio promoting optimal cell adhesion. These findings suggest that PEGDA-gelatin/PEDOT:PSS hydrogels have promising potential for cardiac tissue engineering owing to their customizable physical and biological properties^[357].

Shi et al.^[358] addressed the significant limitations in employing DLP 3D printing for wearable sensor applications by developing a photoreactive poloxamer derivative, Pluronic F-127 diacrylate. This material overcomes the lack of suitable biocompatible and DLP-compatible photopolymers, enabling the fabrication of high-resolution, complex micelle-based hydrogels with shape-memory properties. The dehydrated hydrogels exhibit a shape-memory effect and conformally attach to detection geometries upon rehydration, illustrating

the 4D printing capability that is advantageous for device storage and application^[358]. Furthermore, these hydrogels demonstrate excellent cytocompatibility and in vivo biocompatibility, supporting their potential use in multifunctional wearable systems. Post-processing with lithium chloride (LiCl) solution yields conductive ionic hydrogels with antifreezing, antismelling properties, good transparency, and water retention. As capacitive flexible sensors, the DLP-printed hydrogels show outstanding sensitivity, durability, and stability in detecting multimodal deformations, even at -20°C . Additionally, the authors successfully applied DLP-printed conductive hydrogels as real-time human motion and tactile sensors, highlighting their robust sensing performance in low-temperature environments. In contrast, DLP-printed PEGDA constructs, after freeze-drying, exhibited significant morphological alterations and structural delamination upon rehydration, with infused dye diffusing throughout the structure rather than remaining confined within channels, indicating structural disruption^[358].

Chen et al.^[359] designed a sophisticated, biomimicking scaffold to tackle uterine infertility. Using innovative techniques like 3D bioprinting and layer-by-layer assembly, they crafted a hierarchical, shape-shifting

structure that mimics the uterus's natural form and function. The core, made from a flexible blend of poly(l-lactide-co-trimethylene carbonate) (PLATMC) and PLGA, simulates the myometrium's stretchiness. A surface coating of polydopamine, estradiol, and hyaluronic acid creates an intelligent delivery system for sustained hormone release, boosting biological compatibility.

Adding the finishing touch, stem cell-laden GelMA/Gel hydrogel was 3D printed onto the scaffold, allowing cells to thrive and migrate as the structure biodegrades. Remarkably, the scaffold transforms from flat to tubular in body-like conditions, perfectly suited for uterine tissue growth. This innovative design offers a promising path toward regenerating functional uterine tissue, blending flexibility, biomimicry, and controlled hormone delivery^[359]. Miksch et al.^[361] introduced a cutting-edge approach to tissue engineering using granular synthetic hydrogels as versatile bioinks. These stimuli-responsive microgels, created via submerged electrospray and UV photopolymerization, vary in degradability and size, allowing precise control. They assembled these microgels into porous scaffolds through particle jamming and extrusion printing, with the ability to fine-tune pore sizes using chemical cues in a logic-based manner. The resulting scaffolds are highly cellularizable, enabling easy cell incorporation after printing and even direct annealing of cell-laden microgels. This innovative method allows for large-scale 3D cultures within a customizable, macroporous environment, offering unprecedented control over scaffold properties in both space and time. Such advances pave the way for more effective tissue regeneration and complex tissue models^[361].

6.2 PGS

(PGS was first created by Robert Langer's team in 2002 to fill the need for a durable, biodegradable, and compatible elastomer capable of functioning within dynamic tissue environments^[335]. This copolymer combines glycerol and sebacic acid, both naturally occurring substances already approved for use in FDA-regulated medical devices, highlighting its biocompatibility^[363,364]. Since its development, PGS has demonstrated extensive versatility across numerous biomedical fields, including cardiac tissue engineering^[365-370], vascular grafts^[371,372], retinal repairs^[373], skin regeneration^[374], neural repair^[375-377], vocal fold treatment^[378], cartilage repair^[379-381], and bone and dental applications^[382-385].

The synthesis of PGS involves a polycondensation reaction followed by thermal cross-linking. However, this process can be challenging, often requiring lengthy reaction times under strict conditions such as high temperatures and vacuum, which complicates consistent production and limits scalability^[386,387]. To address these issues, researchers, including Langer's group, introduced

a photocurable version of PGS in 2007 by functionalizing it with acrylate groups to produce poly(glycerol-co-sebacate) acrylate (PGSA)^[363]. This modification allows for rapid photo-cross-linking using UV or visible light within approximately 10 minutes at room temperature, simplifying processing. Due to its biomimetic qualities and ease of fabrication, PGSA has become popular in applications like cell encapsulation, surgical adhesives, and 3D printing^[363,388]. Further, PGS has been modified with various functional groups, such as methacrylate, norbornene, fumarate, and cinnamates, to expand its manufacturing options and applications.

The mechanical properties of these materials can be tailored by adjusting variables like molecular weight or cross-linking density. For example, PGS prepolymers synthesized at different temperatures yield different stiffness levels, with higher temperatures producing stiffer materials. Similarly, altering the molar ratio of glycerol to sebacic acid influences the elasticity. PGSA's mechanical behavior can also be customized by modifying the precursor's molecular weight, degree of acrylation, and curing parameters. Higher degrees of acrylation generally increase tensile strength and Young's modulus, enabling the fabrication of both stiff, less elastic structures suitable for hard tissues and softer, more stretchable forms for soft tissue engineering.

In terms of biodegradability, PGS and PGSA degrade primarily through surface erosion^[365,366,371,373,377,385,387-392], which involves breaking ester bonds at the material's surface, an advantageous process for tissue engineering and controlled drug delivery^[393,394]. In general, PGS tends to degrade more slowly under in vitro conditions compared to in vivo environments. For instance, Wang et al.^[395] observed that only about 17% of the dry weight of PGS was degraded after 60 days of incubation in PBS at 37°C in vitro. In contrast, PGS implants in seven-week-old female Sprague-Dawley rats completely degraded within the same period. This accelerated degradation in vivo is believed to be due to the activity of enzymes and macrophages present at the implantation site, which facilitate breakdown. Supporting this, in vitro enzymatic and hydrolytic degradation studies showed that PGS could lose 60% of its mass within 48 hours and be fully degraded in just 6 hours under enzymatic conditions. Additionally, research by Chen et al.^[396] demonstrated that the degradation behavior of PGS could be modulated by adjusting synthesis parameters. For example, PGS produced at 130°C exhibited minimal degradation in PBS or cell culture media, whereas PGS synthesized at 120°C degraded faster, and those at 110°C degraded even more slowly, indicating synthesis conditions influence degradation rates. Similarly, PGSA exhibits comparable degradation characteristics to PGS, with its degradation rate being adjustable through the degree of acrylation. Higher degrees of acrylation tend to slow

down degradation, offering a means to tailor its lifespan for specific applications^[396].

The biocompatibility of both PGS and PGSA has been extensively evaluated through in vitro and in vivo studies, supporting their broad biomedical utility^[365-398]. Wang et al.^[395] cultured NIH/3T3 fibroblast cells on PGS-coated Petri dishes, using poly(lactic-co-glycolic acid) (PLGA)-coated dishes as a control due to PLGA's widespread use. Results showed that PGS supported greater cell adhesion and exhibited improved cell morphology after six days compared to PLGA. In vivo comparisons of PGS and PLGA scaffolds via subcutaneous implantation in Sprague–Dawley rats revealed that PGS elicited a similar inflammatory response but resulted in significantly less fibrous capsule formation over a 35-day period.

Qu et al.^[234] demonstrate the use of 4D printing technology to fabricate inferior vena cava filters from a copolymer of poly(glycerol sebacate) acrylate-co-hydroxyethyl methacrylate (PGSA-co-HEMA). The 4D printing process enables precise control over the device's shape and properties, allowing the filter to undergo a shape transformation at near body temperature (37.8°C) for minimally invasive deployment. The study highlights that the 4D printed filters possess excellent biocompatibility, biodegradability, and mechanical stability, making them suitable for clinical use. Simulated deployment and thrombus interception tests further confirm the effectiveness and feasibility of this 4D printed approach.

One notable study by Lin et al.^[66] a patient-specific, absorbable left atrial appendage occluder (LAAO) was developed using 4D printing, aiming to better match the mechanical behavior of native tissue and reduce complications like wear and perforation. They employed bioinspired network designs, optimized to replicate the stress–strain properties of the LAA tissue, ensuring improved conformity and biocompatibility. Degradation tests confirmed the device's gradual breakdown without compromising mechanical strength, while long-term implantation studies showed excellent biocompatibility over 48 weeks. The device also demonstrated outstanding durability in compression tests. A notable innovation was its magnetic field-triggered, remote-controlled transformation, allowing precise, minimally invasive deployment. Initial trials in swine hearts confirmed the device's potential for transcatheter applications.

In another investigation, Apsite et al.^[399] developed bilayer scaffolds composed of aligned polycaprolactone-poly(glycerol sebacate) fibers and randomly arranged methacrylated HA-MA fibers, produced through electrospinning. These scaffolds served as a culture platform for PC-12 neuronal cells. A key feature of this approach is the rapid formation of tubular structures upon

immersion in an aqueous buffer. The diameter of these tubes could be precisely tuned by adjusting parameters such as layer thickness, overall scaffold dimensions, and medium ion concentration. The resulting scaffolds exhibited a stable, self-folded scroll-like configuration that maintained integrity over four weeks of degradation. In summary, PGS and PGSA are promising, customizable biomaterials with tunable mechanical and degradation properties, making them highly adaptable for diverse tissue engineering and regenerative medicine applications.

6.2.1 PGS and PGSA

3D printing offers a powerful approach for creating intricate geometries, broadening the potential uses of PGS and PGSA in biomedical fields. For extrusion-based 3D printing, the viscosity of the bioink is crucial in ensuring the stability of the printed structure and enabling continuous extrusion. To this end, Yeh et al.^[397] formulated printable PGSA bioinks with viscosities between 3.18 and 8.78 Pa s by adjusting the molecular weights of PGSA, which was achieved by modifying the polycondensation time of the PGS prepolymer before acrylation. Notably, optimal viscosity was obtained by blending 10% low molecular weight PGSA (Mn=5.78kDa) with 90% high molecular weight PGSA (Mn=6.32kDa), supplemented with 0.5 wt % of the photoinitiator DMPA. This mixture could be rapidly cured under UV light within one minute after extrusion, enabling the fabrication of complex structures such as a knee's lateral meniscus and ear cartilage. Given PGSA's excellent printability, high resolution, capacity to form macroscale features, and superior mechanical properties, this material shows significant promise for tissue engineering and in vivo applications.

In parallel research, Yeh et al.^[400] also developed a photocurable derivative of PGS called norbornene-functionalized PGS (Nor-PGS). These macromers undergo cross-linking via thiol–ene click chemistry facilitated by a four-arm thiolated cross-linker in the presence of a photoinitiator and UV light. Using extrusion-based 3D printing, they fabricated various structures, including porous open-lattice cubes as well as nose and ear shapes. The mechanical properties and degradation rates of the cured Nor-PGS could be tuned by adjusting the cross-linker concentration^[401]. Similar to PGSA, higher cross-linking densities resulted in increased modulus and strength but reduced stretchability and slower degradation. Cell viability assays confirmed that NIH/3T3 fibroblasts thrived on the 3D-printed Nor-PGS scaffolds, demonstrating its biocompatibility and potential for tissue engineering applications.

6.2.2 PGSM

Advancing the quest for truly dynamic and adaptive implantable nerve guidance conduits, Singh et al. introduced an innovative PGS derivative called PGSM,

which possesses the remarkable ability to rapidly undergo photo-cross-linking when exposed to light in the presence of a photoinitiator^[401]. This material was utilized in a pioneering 3D printing process, where a DLP system equipped with a 405nm wavelength light source fabricated hollow, cylindrical PGSM conduits tailored for nerve repair applications. The resulting conduits exhibited an average modulus of approximately 3.2MPa, aligning closely with the mechanical stiffness of native nerve tissue, which ranges from 0.45 to 3.0MPa^[402]. This contrasts sharply with traditional materials like polycaprolactone, poly(3-hydroxybutyrate), and poly-L-lactide, which are typically over 100 times stiffer, underscoring PGSM's superior biomimicry^[403,404].

Looking toward the future, integrating this material into the emerging realm of 4D printing could revolutionize nerve regeneration strategies. By designing PGSM scaffolds that respond to physiological stimuli such as temperature, pH, or enzymatic activity, it becomes possible to create adaptive structures that can change shape, stiffness, or porosity over time^[250]. For instance, a 4D printed PGSM conduit could initially provide a flexible, conformable environment for axonal growth, then gradually stiffen or reshape to support maturation and functional integration as healing progresses. In vivo studies have demonstrated the potential of PGSM conduits to facilitate axonal regeneration, with observable nerve growth extending through the scaffold and into the distal stump after 21 days^[400-404]. By harnessing the dynamic capabilities of 4D printing, future nerve guidance conduits could not only mimic the mechanical properties of native tissue more closely but also adapt in real-time to the evolving needs of regenerating nerves, ultimately enhancing repair outcomes and restoring nerve function with unprecedented precision and functionality.

6.3 Polyurethanes

Polyurethanes (PUs) constitute a versatile class of polymers characterized by the presence of urethane (–NHCOO–) groups within their backbone structure^[405]. These materials are primarily synthesized through condensation reactions involving diisocyanates and electrophilic agents like alcohols and amines, often in the presence of chain extenders, catalysts, and other additives. The underlying reaction mechanisms can be classified into two main types: a one-stage polymerization, where diisocyanates, oligodiol, and chain extenders react simultaneously, or a two-stage process, in which the remaining components are reacted separately, and chain extenders are added subsequently^[406]. Both aromatic and aliphatic isocyanates are employed in PU synthesis, with aromatic variants such as diphenylmethane diisocyanates and toluene diisocyanates being more prevalent in industrial applications due to their higher reactivity and the superior mechanical properties they impart to the final

polymers.

The choice of oligodiol further influences PU characteristics, with categories including polyether, polyester, and specialized polyols like polycarbonate, polycaprolactone, and polybutadienes. Polyether-based PUs, typically derived from PEG or poly(tetramethylene-ether) glycol, are known for their high flexibility and resistance to hydrolysis. However, they are vulnerable to oxidative and thermal stress, limiting their use in high-temperature sterilization processes such as autoclaving. To enhance performance at elevated temperatures, polyester-based PUs were developed; these are synthesized from diols like poly(ethylene adipate)diol or poly(butylene adipate)diol, which introduce ester bonds that are more thermally stable than ethers. Nonetheless, ester bonds are susceptible to hydrolytic degradation, restricting their application in aqueous environments^[407].

To overcome these limitations, polycarbonate-based PUs have been engineered for superior thermal stability, mechanical strength, and durability in aqueous conditions. The synthesis typically involves diols such as poly(ethylene adipate)diol or poly(butylene adipate)diol, with chain extenders like ethylene glycol, 1,4-butanediol, or cyclohexane dimethanol, which introduce cross-linking and hydrogen bonding to reinforce the polymer network. Based on their reaction mechanisms and structural features, PUs are broadly classified as either thermoplastic (TpPU) or thermosetting (TsPU).

Thermoplastic PUs are linear block copolymers formed from difunctional reagents without cross-linkers, resulting in materials with low melting points and limited mechanical strength at high temperatures. Their solubility in polar solvents allows ease of processing via techniques such as solvent casting and fiber spinning. Importantly, their processability and tunable properties have made them highly suitable for additive manufacturing methods, including 3D printing. Conversely, thermoset PUs are synthesized using multifunctional reagents like trimethylolpropane or glycerol, often in conjunction with excess isocyanates, forming cross-linked networks. These networks confer high thermal stability, mechanical robustness, and resistance to deformation at elevated temperatures. Additionally, PUs can form interpenetrating polymer networks (IPNs) with other polymers such as epoxy and acrylates, combining advantageous properties, PU/epoxy IPNs, for instance, exhibit a balance of flexibility and toughness.

A defining feature of PUs' mechanical behavior lies in their microphase separation, driven by the distinct hard and soft segments within their structure. Hard segments, often containing aromatic groups like benzenes, act as physical cross-linking points, providing structural integrity, while soft segments, such as esters, allow chain mobility and energy dissipation. Under external forces, the hard

segments maintain the overall framework, whereas the soft segments absorb and dissipate energy as heat. Recent advancements aim to enhance biostability and flexibility by optimizing hydrogen bonding in the hard segments and fine-tuning microphase separation. This tunability extends to their physical, chemical, and biological properties, opening new avenues for biomedical applications^[407,408].

Coupled with the rapid progress in 3D printing technologies, the potential to exploit PUs in innovative ways has expanded significantly. The ability to precisely control their microstructure and properties makes PUs highly adaptable for fabricating complex, application-specific biomedical devices. Looking ahead, integrating PUs into 4D printing, where printed structures can change shape or properties over time in response to stimuli, offers exciting possibilities. For example, smart PU-based scaffolds could be designed to respond to physiological cues, morphing shape or stiffness during healing processes, thus providing dynamic support tailored to tissue regeneration. Such stimuli-responsive PUs could facilitate minimally invasive procedures, enable on-demand drug delivery, or adapt their mechanical properties in situ, vastly improving patient outcomes. As research continues to deepen our understanding of their structure-property relationships and processing capabilities, PUs are poised to become a cornerstone in the next generation of adaptive, multifunctional biomedical implants enabled by 3D and 4D printing technologies^[409].

Cheung et al.^[410] explored the potential of 4D printing for creating shape-memory textiles capable of time-dependent transformations. Their research focused on polymer-textile composites printed onto textile substrates, addressing the challenge of bonding smart polymers to fabrics, a limitation in previous studies restricted to single-driven or non-reversible polymers. They examined TPU and thermoplastic elastomers with Shore hardness values of 70 A, 82 A, and 40D, aiming to improve interfacial adhesion and assess effects on peel resistance, mechanical properties, and shape recovery.

Results showed that TPU with a Shore hardness of 70A significantly increased peel strength, up to 1600% compared to other variants, indicating better bonding. Mechanical testing revealed that the 82A specimens had higher tensile strengths (around 652–666 N) and greater resistance to deformation, leading to superior shape recovery (94.72%). However, these specimens had slightly lower shape fixity compared to the 70A/40D variants, which offered better shape fixity but less recovery^[410].

Jung et al.^[411] developed bio-based thermoplastic polyurethanes (SMTPIs) with fast shape memory response. Made from renewable components like corn

oil-derived polyester polyol and bio-based diols, these materials were characterized by spectroscopy and microscopy, revealing phase separation and morphology details. The optimized SMTPIs showed high tensile strength (24–27MPa), large elongation (358–552%), and hardness (84–92 Shore A). They also exhibited 100% shape recovery, demonstrating their potential as eco-friendly, temperature-responsive shape memory materials.

Hu et al.^[412] developed TPU/CNTs composites with enhanced mechanical and shape memory properties. Using melt blending, they incorporated up to 0.6wt% CNTs, finding that 0.4 wt% offered optimal performance with improved melt strength and tensile strength of 26.7MPa. The composites showed excellent shape fixation (>99%) and recovery (93.27%) within 30 seconds, thanks to CNTs' strong light absorption and photothermal conversion, especially in the visible and NIR ranges. Low thermal conductivity and CNT alignment during 3D printing further boosted shape memory effects.

Rahmatabadi et al.^[413] first 4D printed bilayer-encapsulated PCL-TPU shape memory composite structures using dual-material extrusion. The encapsulation of PCL by TPU addressed bonding issues and improved SME performance, including fixity, shape and stress recovery, and stress relaxation under bending and compression. PCL served as the switching phase, TPU as the net point, and PCL's melting temperature as the transition temperature. The composites showed stable stress recovery over time, outperforming previous extrusion-based SMPs that suffered from stress relaxation due to weak crystallinity and molecular disentanglement.

Liu et al.^[414] compared polyester- and polyether-type TPU blended with PLA at 10, 30, and 50wt% for 4D printing. Polyester TPU showed stronger interfacial bonding, higher thermal stability, greater tensile strength, and smoother surfaces. Polyether TPU exhibited higher tensile strain and faster, more responsive shape recovery. Increasing TPU content slowed recovery in polyester systems but accelerated it in polyether ones.

Jiang et al.^[415] developed a 3D-printable resin containing two polyurethane-based oligomers, poly(pentadecalactone diacrylate (PPDLA) and polycaprolactone diacrylate (PCLDA), with distinct transition temperatures, to fabricate single-network two-way SMPs (2W-SMPs) via digital light projection. These materials exhibit high shape fixity (>97%) and recovery (>89%), with properties easily tunable through composition adjustments. Although primarily demonstrated through 3D printing, the stimuli-responsive, reversible shape-changing characteristics of these SMPs position them as promising candidates for 4D

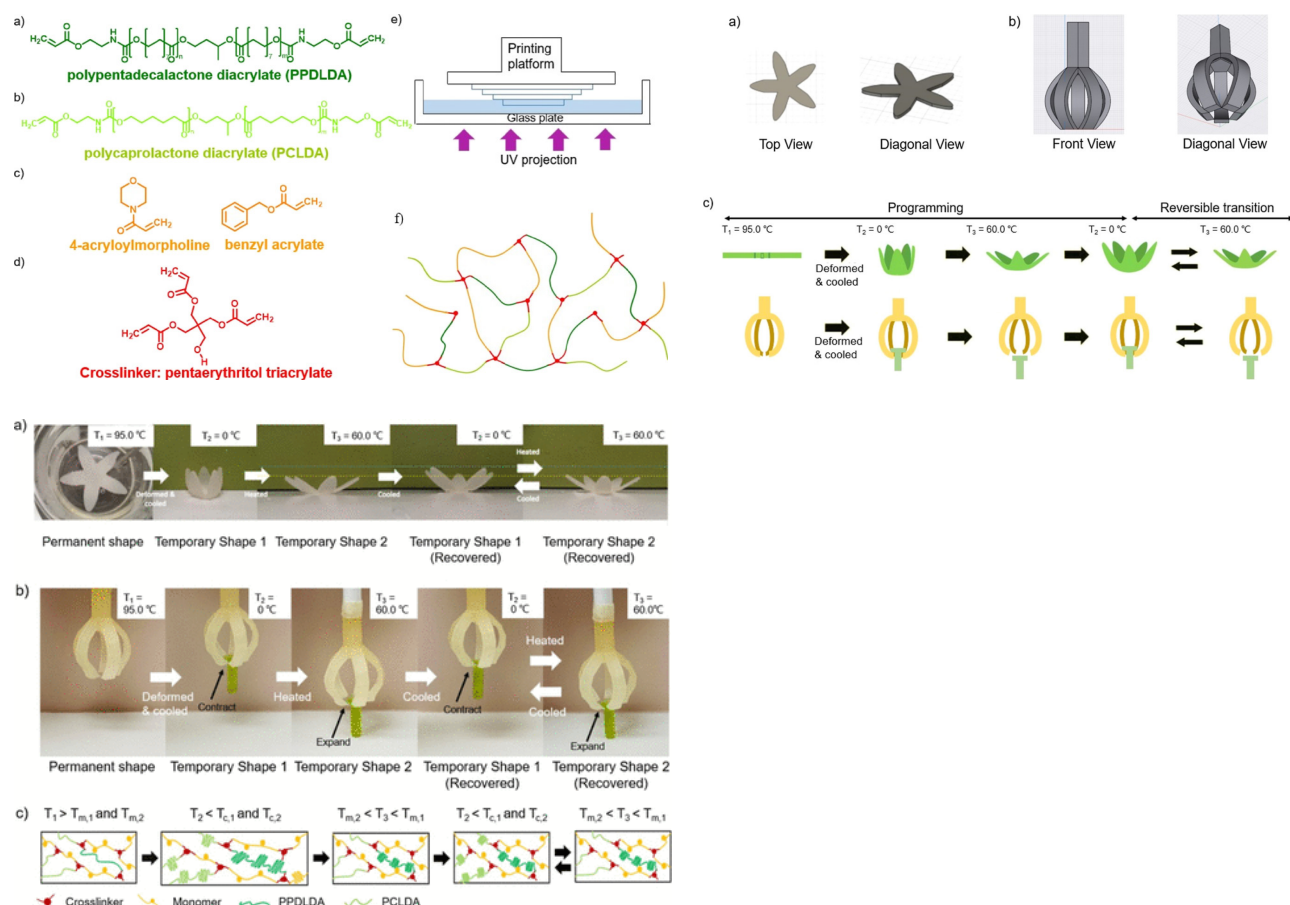


Figure 7. (Top-Left): Composition and characteristics of the monomers and oligomers used in the study. (A) PPDLDA; (B) PCLDA; (C) various monomer structures; and (D) the crosslinking agent. (e) Illustration illustrating the process of DLP 3D printing. (F) Diagram showing the formation of a crosslinked shape memory polymer (SMP) network via the additive manufacturing method. **(Top-Right): Fabrication of polyurethane-based resin structures through 3D printing.** (A) Computer-aided design (CAD) model of a floral shape. (B) CAD model of a claw-shaped object. (C) Illustration of the shape memory programming process and the ability of the printed structures to undergo reversible shape changes. **(Bottom): Demonstration of dual-directional actuation in 3D-printed devices and the underlying shape memory mechanism.** (A) A printed flower with petals that open and close. (B) A printed claw that can grasp and release objects. (C) The microstructural basis underlying the single-network two-way shape memory effect Reprinted with permission from Ref.^[415].

printing applications, enabling the creation of dynamic, reconfigurable structures for uses in soft robotics, medicine, and beyond (Figure 7).

6.3.1 Application of Polyurethanes in 4D Soft Robotics Applications

Soft robotics represent an innovative frontier in automation, utilizing intrinsically soft materials such as fluids, gels, and elastomers to create machines capable of flexible, adaptive movements^[416]. Traditionally, these robots are fabricated through casting processes of soft materials like PUs, followed by assembling various components. However, direct additive manufacturing via 3D printing offers a transformative approach, significantly reducing fabrication time and costs while enabling complex, customized designs. For example, Patel et al.^[417] pioneered the use of highly stretchable aliphatic urethane diacrylate-based PUs as cross-linkers for 3D printing robotic hands. Some of their printed structures achieved a remarkable failure strain of up to 1100%, demonstrating exceptional elasticity. These materials facilitated the direct fabrication of pneumatically actuated grippers

capable of picking up objects, showcasing the potential for rapid prototyping and functional device creation. In other advancements, Gul et al.^[418] utilized a multi-headed extrusion 3D printer with light-assisted curing techniques to construct a three-legged soft robot from epoxy and polyurethane structural components. They embedded shape memory alloy (SMA) wires as actuators within the structure, enabling locomotion that mimicked a spider's gait. This integration of active materials within 3D printed soft robots exemplifies the potential for complex, biomimetic movements. Similarly, Yang et al.^[419] employed fused deposition modeling (FDM) to fabricate a polyurethane-based SMP and conductive thermoplastic TPU. Their design included a pneumatically driven gripper with variable stiffness and active position feedback. When electrical current heats the TPU, it softens the SMP, inducing a controlled shape change for grasping objects. By monitoring the piezoresistive behavior of the TPU components, they achieved precise control and sensing capabilities.

These advanced components exemplify the versatility of 3D printing in creating soft robotic systems with integrated actuation, sensing, and adaptive features.

Extending this concept into biomedical applications, such as surgical catheters or minimally invasive devices, could revolutionize surgical procedures. For instance, soft, shape-shifting robotic tools could navigate complex anatomical pathways, adapt their stiffness in response to tissue environments, or perform delicate manipulations, all enabled by 3D printed, multifunctional polyurethane-based materials. The convergence of soft robotics and additive manufacturing thus holds immense promise for developing intelligent, adaptable biomedical devices that enhance patient care and surgical precision.

6.3.2 Application of Polyurethanes in 4D Tissue Engineering

PU are highly regarded in tissue engineering and regenerative medicine due to their excellent biocompatibility, customizable biodegradability, and diverse mechanical properties^[420]. For instance, Whatley et al.^[421] employed biodegradable and elastic PU to create intervertebral disc scaffolds using FDM 3D printing. The resulting structures accurately replicated the lamellae architecture of injury sites at both micro- and macro levels. Neural cells seeded onto these scaffolds aligned along the concentric lamellae, guided by the topographical features of the printed design, indicating potential for neural tissue repair. Similarly, Xu et al.^[422] fabricated vascular stents from biodegradable PUs via liquid-frozen deposition manufacturing (LFDM) 3D printing. In vivo experiments demonstrated early-stage vascularization along the stents. They further enhanced this approach by incorporating heparin into the resin, which promoted angiogenesis, showcasing the suitability of PUs for vascular applications due to their elasticity, anticoagulant properties, and biodegradability. Additionally, embedding proteins within PU matrices suggests opportunities in drug delivery systems and functional tissue scaffolds.

Water-based PUs have also been leveraged in cell encapsulation techniques. Hung et al.^[423] developed PU nanoparticle composites that were printed using LFDM to produce scaffolds aimed at cartilage regeneration. Compared to similarly fabricated PLGA scaffolds, the PU-based structures exhibited superior elasticity and supported increased chondrocyte proliferation. In another study, Hsieh et al. utilized water-based PU to print neural conduits, which were implanted into adult zebrafish with traumatic brain injuries. After four weeks, the treated groups showed marked improvements in mobility and survival rates relative to untreated controls^[424]. Building on this, Huang et al.^[425] introduced water-dispersible graphene and graphene oxide into the PU scaffolds to boost electrical conductivity, resulting in improved oxygen metabolism and neural differentiation.

6.3.3 Application of Polyurethanes in 4D Surgical Guides and Dental Applications

The advent of rapid prototyping with 3D printing

has enabled the creation of customized surgical guides tailored to individual patients. Traditional guides are mass-produced and often have limited fitting accuracy, which can pose challenges during internal surgeries such as those for coronary artery disease^[426]. Guides must also possess sufficient mechanical strength to withstand surgical stresses without provoking adverse immune reactions. The high precision and durability of 3D-printed PU structures have been exploited to develop personalized surgical tools with excellent fit and resilience. For example, Holzapfel et al. produced a pelvic guide based on a CT scan-derived model for a patient with periacetabular tumor, closely matching the anatomical modifications and withstanding the surgical procedure without complications. Beyond surgical guides, PU-based 3D printing is also prominent in dental applications, such as clear aligners used for orthodontic correction. Invisalign, a commercially successful product introduced in 1999, utilizes custom, computer-generated aligner molds to gradually reposition teeth. Its success underscores the potential for PU materials and 3D printing technologies to revolutionize a broad range of biomedical devices and treatments in the future^[426].

7 COMPARATIVE ANALYSIS: NATURAL VS. SYNTHETIC BIOMATERIALS FOR 4D PRINTING

While Sections 5 and 6 detail the properties and processing of specific natural and synthetic biomaterials for VP-based 4D printing, this section provides a critical comparative analysis of their inherent trade-offs and establishes criteria for material selection tailored to specific application requirements. Understanding these distinctions is paramount for designing effective 4D printed constructs.

7.1 Performance Trade-offs: Key Properties

The choice between natural and synthetic biomaterials for 4D printing is a complex decision grounded in the careful balancing of intrinsic material properties and application-specific demands. This decision-making process involves evaluating a spectrum of critical performance metrics; each acting as a key parameter that influences how effectively a material can meet the functional, biological, and mechanical requirements of the intended construct. These metrics encompass not only the material's inherent ability to interact with biological systems, withstand mechanical stresses, and undergo controlled transformations over time, but also how they behave during the printing process itself, including their processability, stability, and responsiveness to stimuli. Understanding these multifaceted properties is akin to deciphering a material's "biological DNA", its capacity for integration, adaptability, and resilience within complex environments. For instance, natural biomaterials often excel in mimicking the dynamic and multifaceted nature of native tissues, providing biochemical cues that facilitate

cellular functions and tissue integration^[304,306]. Conversely, synthetic biomaterials offer a high degree of tunability, allowing precise control over mechanical strength, degradation kinetics, and structural integrity, which is vital for engineering devices that need to endure mechanical loads or operate reliably over extended periods.

This comprehensive insight empowers researchers and engineers to tailor their material choices to the nuanced demands of diverse applications, be it regenerating delicate tissues that require bioactive scaffolds, designing soft robotic components with programmable shape-shifting capabilities, or fabricating aerospace structures where long-term stability and robustness are paramount (Table 2). Ultimately, the strategic selection of natural versus synthetic biomaterials in 4D printing is a sophisticated balancing act, one that integrates scientific principles with creative innovation to unlock new frontiers in programmable, functional materials.

7.1.1 Bioactivity & Cellular Interaction

Natural biomaterials such as GelMA, collagen, dECM), HA, and alginate inherently contain biochemical cues that facilitate cellular interactions. These materials naturally possess cell-adhesive motifs, such as the RGD (Arg-Gly-Asp) peptide sequences present in GelMA and collagen, which are recognized by cell surface receptors, promoting adhesion, proliferation, and differentiation. Additionally, they contain enzymatically degradable sites that mimic natural tissue remodeling processes, supporting tissue integration and regeneration. Their biological origin allows them to emulate native extracellular matrices closely, making them highly suitable for applications like tissue engineering scaffolds or implantable devices where integration with host tissue is critical^[270,281,282,309,311].

In contrast, synthetic biomaterials such as PEGDA, PU, and PGSM are typically bioinert. They do not inherently contain cell-recognition sites or biochemical cues; therefore, they generally exhibit lower bioactivity. To promote cellular attachment and biological responses, these materials often require surface functionalization with bioactive molecules (e.g., conjugating RGD peptides) or incorporation of bioactive fillers. While this adds steps to the fabrication process, it allows precise control over the biofunctionalization, enabling customization to specific cellular behaviors or tissue responses^[357,358,423-425].

7.1.2 Mechanical Properties & Structural Integrity

Synthetic biomaterials offer remarkable versatility in mechanical tuning. Their chemical structures are designed to allow precise control over properties such as stiffness, toughness, and elasticity. For example, PEGDA and PU formulations can be engineered to exhibit elastic moduli spanning from a few kilopascals (kPa) to gigapascals (GPa), accommodating a broad spectrum of

applications; from soft tissue scaffolds to load-bearing implants or aerospace components. These materials also maintain their shape and structural integrity over time, even under sustained mechanical loads, making them ideal for devices requiring high durability and stability^[357,352,358].

Natural biomaterials, however, are generally softer and less mechanically robust. GelMA, HA, dECM, and alginate hydrogels typically exhibit low to moderate stiffness (in the kPa to low MPa range), which can limit their use in load-bearing applications unless reinforced or combined with other materials. They are more prone to swelling, creep, or degradation under mechanical stress, especially in aqueous environments. To address these limitations, reinforcement strategies are often employed, such as embedding them within supportive frameworks (e.g., PCL scaffolds) or creating hybrid formulations that combine natural and synthetic components, thereby achieving the desired shape fidelity and mechanical performance necessary for complex 4D transformations^[250,393-397,404].

7.1.3 Degradation Kinetics & Predictability

Synthetic biomaterials generally feature predictable and controllable degradation profiles. Their degradation is primarily hydrolytic, facilitated by labile chemical bonds such as esters or urethanes incorporated into their backbone. By adjusting parameters like molecular weight, crosslinking density, and chemical composition, researchers can finely tune degradation rates to match tissue regeneration timelines or device lifespan, enabling precise temporal control over functionality, such as temporary stents or drug delivery systems^[66,399,401,407].

In contrast, natural biomaterials predominantly degrade enzymatically through biological pathways. For instance, collagen and GelMA are degraded by matrix metalloproteinases, while hyaluronic acid is broken down by hyaluronidases. This enzymatic degradation closely mimics natural tissue remodeling but introduces variability, as the rate depends heavily on the local cellular environment, enzyme concentrations, and inflammatory responses^[287-289]. Consequently, degradation rates are less predictable and harder to regulate independently from bioactivity and mechanical properties, posing challenges for applications where precise timing of structural changes is essential.

7.1.4 Printability & Processing Complexity

Applications requiring rapid, high-fidelity printing (e.g., complex microfluidic devices) often favor synthetic resins due to their predictable viscosity and rapid curing kinetics. Natural hydrogels, while biocompatible, may present challenges like slower curing or lower resolution. Synthetic biomaterials are often engineered with well-defined chemical modifications, such as (meth)acrylation, which enable rapid and efficient photocrosslinking under

Table 2. Key Features, Trade-off and Applications of Natural and Synthetic Biomaterials in 4D Printing

Feature	Natural Biomaterials (e.g., GelMA, Alginate, HA)	Synthetic Biomaterials (e.g., PEGDA, PUs, PCL-MA)
Biocompatibility	Typically high (inherent bioactivity) ^[359,361]	Variable (often requires modification; risk of cytotoxic residues) ^[357,358]
Degradation	Enzymatic/hydrolytic; often tunable but batch-dependent ^[270]	Primarily Hydrolytic; Highly tunable & predictable ^[396,407]
Mechanical properties	Generally softer, weaker; limited tunability ^[350-358]	Wider range (soft to rigid); Highly tunable & reproducible ^[399,415]
Printability/resolution	Can be challenging (viscosity, slow cure)	Generally excellent; high resolution achievable
Stimulus responsiveness	High intrinsic response to bio-stimuli (pH, enzymes) ^[365]	Requires functionalization; excellent for external triggers (light, mag) ^[390-411]
Batch consistency	Lower (source variability) ^[362]	High (Precise chemical synthesis) ^[402-405]
Cost	Variable (can be high for purified forms) ^[361]	Variable (often lower at scale) ^[400-403]
Key advantages	Superior cell interaction, bioactivity, inherent bio-stimuli ^[279]	Tunable mechanics/degradation, high print fidelity, consistency ^[393-397]
Key disadvantages	Variability, weaker mechanics, printability challenges ^[267,269]	Potential cytotoxicity, lack of inherent bioactivity ^[390-394]
Ideal applications	Tissue scaffolds, drug delivery (bio-responsive), cell-laden constructs ^[260-270]	High-resolution structures, load-bearing implants, actuators, devices requiring precise mechanics ^[396-399]

controlled conditions. Their predictable chemistry allows for high-resolution, oxygen-tolerant stereolithography and DLP, leading to precise spatial control and complex architectures. Furthermore, their viscosity can be readily modulated to optimize flow during printing, facilitating process standardization and scalability^[275,286,308,397].

Natural biomaterials, however, present more complex processing challenges. Many require chemical modifications, such as methacrylation of GelMA, functionalization of HA or alginate, to achieve suitable photocrosslinking properties^[283,284]. Unmodified natural polymers like pure collagen may rely on thermal gelation, ionic crosslinking, or support bath techniques (e.g., FRESH) to enable printing, often resulting in lower resolution, slower fabrication speeds, and limited compatibility with high-throughput VP systems^[319,320]. Additionally, natural sources can vary batch-to-batch, affecting reproducibility and consistency in printing quality.

7.1.5 Immunogenicity & Regulatory Pathway

From a regulatory perspective, natural biomaterials often pose additional considerations. When highly purified and properly processed, they typically exhibit low immunogenicity; however, their biological origin can introduce variability and potential contaminants, complicating approval processes. For example, bovine-derived collagen or tissue extracts may carry risks of immunogenic responses or pathogen transmission, whereas recombinant or highly purified sources mitigate this concern.

Synthetic biomaterials, being chemically defined, usually offer lower inherent immunogenicity, with well-characterized compositions that simplify regulatory approval pathways. They also tend to have fewer batch-

to-batch variations and impurities, which is advantageous for clinical translation. Nevertheless, both natural and synthetic biomaterials must be carefully evaluated for residual leachables such as photoinitiators, unreacted monomers, or degradation byproducts, which can induce immune responses or toxicity^[291].

7.2 Hybrid Strategies: Combining Strengths for Optimized 4D Materials

Understanding that no single biomaterial can perfectly fulfill all the demanding criteria for diverse 4D applications, a compelling and innovative approach is the development of hybrid material systems. These systems strategically integrate natural and synthetic components to synergistically harness their respective advantages, transcending the limitations inherent to each material class. Such hybrid strategies unlock new realms of functionality, enabling the design of complex, multi-functional, and highly tailored constructs.

7.2.1 Natural-Synthetic Hybrid Networks

One of the most promising avenues involves constructing integrated network systems where natural polymers, such as GelMA, HA, or dECM, are chemically or physically intertwined with synthetic polymers like PEGDA or PGSM. This integration results in a cooperative scaffold that exhibits enhanced mechanical robustness, structural stability, and predictable degradation kinetics, while maintaining the biological cues essential for cell attachment, proliferation, and differentiation. For instance, Skardel et al.^[308] developed a liver dECM bioink reinforced with thiolated gelatin, HA, and PEG acrylate, creating a bioactive yet mechanically resilient matrix suitable for hepatic tissue engineering. Similarly, Kirillova et al. engineered a methacrylated alginate/HA composite, leveraging the tunable crosslinking chemistry to control

stiffness and degradation^[325]. These hybrid networks serve as dynamic platforms that can be finely tuned to emulate the complex biomechanical and biochemical milieu of native tissues, facilitating more accurate tissue regeneration and functional integration.

7.2.2 Composite Materials: Bioactive Fillers and Reinforcements

Another versatile strategy involves embedding natural polymers as bioactive fillers or modifiers within synthetic matrices, or reinforcing natural hydrogels with synthetic micro- or nano-fibers and particles^[281,288,399]. This approach enhances the biofunctionality of synthetic supports, imparting cell recognition sites, enzymatic degradability, or growth factor delivery, while simultaneously improving mechanical strength and durability. For example, incorporating nanocellulose fibers into natural hydrogels can significantly improve their tensile strength and elasticity, enabling applications in load-bearing tissue scaffolds or soft robotics. Conversely, embedding bioactive molecules or nanoparticles within synthetic matrices can direct cellular responses, promote angiogenesis, or enable stimuli-responsive behaviors—creating multifunctional composites tailored for specific regenerative or actuation tasks.

7.2.3 Multi-Material 3D & 4D Printing: Spatially Controlled Design

The advent of multi-material VAM provides a transformative platform to fabricate constructs with spatially segregated regions of distinct materials, each optimized for a specific function, within a single, integrated device. This localized optimization allows the combination of rigid, synthetic frameworks for structural support with soft, natural, bioactive regions for cell interaction^[201-209]. For instance, a hybrid construct could feature a synthetic, high-strength backbone that endures mechanical loads, coupled with natural hydrogel zones rich in bioactive cues to promote cellular infiltration and tissue integration^[204]. Alternatively, integrating synthetic actuators with natural hydrogel sensors could produce sophisticated, responsive devices capable of complex movements and environmental feedback^[202,205].

7.2.4 The Power of Hybrid Strategies

These hybrid approaches represent a paradigm shift in biomaterials design — moving away from the constraints of monolithic materials towards a modular, systems-level engineering mindset. By combining the biological richness of natural biomaterials with the tunable, durable properties of synthetics, researchers can create next-generation 4D printed devices that are more adaptable, functional, and capable of meeting the multifaceted demands of advanced biomedical, robotic, and aerospace applications. This integrative methodology not only broadens the design space but also paves the

way for customizable, patient-specific solutions, where each component can be engineered to fulfill precise roles within a cohesive, dynamic system.

8 EMERGING APPLICATIONS OF 4D PRINTING

The advent of 4D printing introduces a new era of smart materials capable of autonomous transformation, surpassing the constraints of traditional 3D printing substances. These dynamic materials, such as SMPs, can adapt their form in response to external stimuli, unlocking innovative design possibilities across diverse industries. For example, advancements in VP technology have enabled the rapid fabrication of highly detailed, precise, and smooth structures from SMPs, making complex, functional devices more attainable than ever before. The synergy of these cutting-edge techniques paves the way for breakthroughs in areas like biomedical devices, aerospace components, responsive sensors, actuation systems, and cybersecurity measures. This section delves into the expanding role of VP-printed SMPs, showcasing successful applications and exploring the transformative potential of these high-performance materials in shaping future technological landscapes.

8.1 Biomedical Applications

Current 3D printing methods often face challenges when fabricating complex, curved biological structures within the human body, limiting their widespread biomedical application. In contrast, VP-based additive manufacturing combined with SMPs offers a promising alternative, as these materials can undergo reversible shape changes in response to stimuli, enabling the creation of dynamic, adaptable implants. As research progresses, more VP-printed SMPs are being developed for potential medical uses. However, before these materials can be employed as implants or devices, they require comprehensive evaluation of biocompatibility, sterilization, and biodegradability^[427]. Major concerns include residual unreacted monomers, photoinitiator remnants, and degradation by-products, which risk leaching into tissues and causing toxicity or inflammation, impacting long-term safety. To mitigate these issues, strategies such as enhancing polymerization efficiency, using less toxic or biodegradable initiators, and designing controlled degradation pathways are being explored.

Zhao et al.^[428] emphasized that reducing biotoxicity associated with residual monomers, photoinitiators, and degradation products in photocurable resins requires a multifaceted approach. This includes increasing crosslinking density, selecting low-toxicity or biodegradable photoinitiators like macromolecular variants, designing molecular frameworks with safe degradation pathways, and surface modifications with bioactive agents. Implementing these measures can significantly improve the safety profile of photocurable

resins for biomedical applications. Mahjoubnia et al.^[178] introduced a bioresorbable shape memory elastomer suitable for 4D printing, capable of high elasticity around physiological temperatures. Made via DLP by copolymerizing glycerol dodecanoate acrylate with acrylic acid, it forms a tunable, crosslinked network. The material exhibits excellent shape programming at body temperature, mimicking soft tissue mechanics, and supports cell growth in vitro, with promising vascular grafting potential and biodegradability demonstrated in vivo. A patient-specific heart device was successfully printed, illustrating its potential for personalized medicine.

Similarly, Zhang et al.^[429] developed poly(glycerol dodecanoate) acrylate (PGDA), a shape memory polymer with a transition temperature between 20°C and 37°C. This allows shape programming at room temperature and deployment within the body. PGDA enabled creation of intricate structures like stars and cages, with shape fixation and recovery near-perfect and repeatable. Its Young's modulus decreased during phase transition, aligning with biological tissues. In vitro and in vivo tests confirmed its adaptability for vascular grafts and tissue scaffolds, highlighting its promise for personalized medical devices.

Another study by Zhang et al.^[430] evaluated a magneto-responsive hydrogel scaffold with a "fried egg" structure, incorporating chitosan-coated Fe₃O₄ nanoparticles via 4D printing for auricular cartilage regeneration. The magnetic activation improved cartilage repair, with mechanical properties akin to natural cartilage. The chitosan coating provided anti-inflammatory and antibacterial effects, promoting macrophage M2 polarization and reducing inflammation. Transcriptomic analysis indicated modulation of macrophage immunity via the JAK2/STAT3 pathway, enhancing regeneration and biocompatibility. Doostmohammadi et al.^[431] introduced a 4D printed biocompatible PLA/PMMA blend optimized via Artificial Neural Networks (ANN) and Response Surface Methodology (RSM). The melt-blended materials, printed with a pellet-based 3D printer, showed excellent shape recovery (100%) and tensile strength (65.2 MPa). The resulting bio-screw demonstrated mechanical robustness and shape memory, suitable for orthopedic and dental implants, offering an innovative method for high-performance, biocompatible 4D printing. Lin et al.^[65] developed shape memory vascular stents with negative Poisson's ratio structures through 4D printing, optimized via genetic algorithms. Mechanical tests confirmed their ability to expand rapidly within blood vessels, making them promising for treating vascular stenosis. Their shape memory behavior was excellent, and in vitro feasibility demonstrated their potential for minimally invasive vascular repair.

The mismatch in mechanical properties between

implants and tissues often leads to wear or perforation. Commercial Nitinol-based occlusion devices' limited biocompatibility and non-degradability can cause complications like allergies or corrosion. Lin et al.^[66] addressed this by developing a 4D printed, patient-specific, absorbable LAAO that matched tissue deformation, reducing complications. Designed based on bioinspired stress-strain curves, the device showed good degradation behavior, long-term stability, and remote-controlled transformation triggered by magnetic fields. Its deployability in swine hearts demonstrated promising transcatheter application potential, illustrating the broad applicability of bioinspired design concepts to reduce device-related issues.

Mohol et al.^[432] created a triple-shape memory polymer by blending PLA with polypropylene carbonate (PPC), 3D printed via extrusion. The blend exhibited phase-segregated morphology with two distinct glass transition temperatures, enabling triple-shape memory effects (triple-SME). The optimal composition (PLA50/PPC50) achieved high shape fixity (95.63%) and recovery (96.26%), suitable for minimally invasive surgery. In vitro degradation showed only 7.5% mass loss over 56 days, and cytotoxicity tests confirmed biocompatibility, indicating its potential as a tissue engineering implant.

A novel approach for gastric cancer treatment by Mahmoud et al.^[433] involved 4D printed, magnetically steerable patches designed for localized drug delivery. Made from agarose modified with chitosan and superparamagnetic iron oxide nanoparticles (SPIONs), these patches could be swallowed, rehydrate, and expand within the stomach, releasing drugs directly at the tumor site. Magnetic guidance allowed precise placement, and the system showed promise for improving gastric cancer therapy through targeted, controlled drug release.

Zhou et al.^[434] developed a shape-memory peripheral stent supporting long-term drug release, synthesized from star polymer s-PCL via ring-opening polymerization initiated by β -cyclodextrin (β CD). The crosslinked c-PCL demonstrated suitable mechanical properties, elasticity, and burst pressure comparable to natural tissue. Incorporating β CD improved biocompatibility, while sustained paclitaxel release highlighted its potential for long-term vascular support and drug delivery, addressing critical needs for small-diameter scaffolds in limb ischemia treatment.

To expand 4D printing beyond simple shape change, Zhang et al.^[435] used plant protein (zein) gel inspired by amyloid fibril formation. Printed within a layered-Carbopol supporting bath with varying water content, the constructs exhibited functional heterogeneity—such as drug loading, release, and degradation—based on the bath composition. This approach enabled the fabrication

of nerve conduits and drug-eluting urethral stents, demonstrating that 4D printing can incorporate multiple functionalities alongside shape transformation, thus broadening its biomedical potential.

The biocompatibility of PGS and PGSA has been extensively studied. Wang et al.^[395] found that NIH/3T3 fibroblasts cultured on PGS-coated substrates showed better attachment and organization than on PLGA. In vivo, PGS scaffolds elicited similar inflammation levels but induced less fibrous capsule formation over 35 days, indicating improved tissue response. Similarly, Yeh et al.^[397] confirmed that PGSA scaffolds supported cell proliferation and growth, further endorsing their suitability for tissue engineering.

Integrating additive manufacturing with shape-morphing materials offers significant potential for personalized medical devices. 4D printing enables structures to transform shape after fabrication. In tissue engineering, VP-printed SMPs mainly serve as stents and scaffolds—stents to keep blood vessels or airways open, and scaffolds to support cell growth and tissue regeneration. PCL is frequently used due to its favorable mechanical properties and tunable thermal response. Using a methacrylated polycaprolactone precursor and UV-LED stereolithography based on medical imaging data, shape memory endoluminal devices like tracheal stents can be fabricated. This aligns with trends in personalized medicine and could broaden the use of shape memory biomedical devices. Building on Zarek et al.^[436], who developed a 4D-printed tracheal stent addressing migration and deployment issues through a tailored arch design and shape memory, this study further explores material optimization. While high recovery and fixing ratios were achieved, questions about PCL's biocompatibility and hydrophilicity remain, requiring further research before clinical use.

Fer et al.^[88] created biodegradable, shape-memory poly(propylene fumarate) scaffolds via DLP, including DP10, DP40, and DP200 structures. Their T_g ranged from about 26.6°C to 49.1°C, near body temperature. T_g increased with post-curing time but decreased with larger scaffold size due to reduced UV penetration and crosslinking. The star-shaped DP40 and DP200 scaffolds could have their mechanical properties tuned by adjusting post-curing, allowing customization for specific applications. Biodegradable scaffolds with transition temperatures near body temperature are promising for minimally invasive implantation and tissue integration. For instance, oligomeric poly(propylene fumarate) supports cell infiltration and vascularization during soft tissue repair. Additionally, piezoelectric ceramic-SMP composites are being studied for bone healing, mimicking the bioelectric signals of natural bone to promote regeneration. Li et al.^[437] developed 3D-printed acrylate

epoxidized soybean oil (AESO)-based piezoelectric scaffolds doped with Ag-3-(trimethoxysilyl) propyl methacrylate (TMSPM)-coated Barium titanate (pBT) nanoparticles, which improved piezoelectric properties with a d₃₃ of 0.9pC/N and an output current of 146.4 nA, comparable to natural bone. These scaffolds exhibited rapid shape recovery under NIR light, successfully supporting bone cell differentiation and healing, showing promise for bone tissue engineering.

Further innovations include remotely activated nanocomposite scaffolds, such as gold nanorod-infused SMPs responding to near-infrared light, enabling on-demand shape recovery and targeted therapy. pH-sensitive and humidity-responsive SMP scaffolds are also under investigation for precise responses within physiological environments. Yu et al.^[438] developed 3D-printed protein-based nanocomposites containing gold nanorods (AuNRs) with a plasmon resonance around 795 nm, embedded in BSA/PEGDA and methacrylate bovine serum albumin/PEGDA matrices. These bioplastics respond to near-infrared (NIR) light by undergoing shape recovery without water, through mechanical unfolding and refolding of BSA proteins. They achieved 99% shape recovery within one minute under NIR light, demonstrating the potential for remote-controlled shape memory scaffolds, although such effects may not suit all applications.

Li et al.^[439] designed a dual-responsive 4D-printed scaffold for complex bone defect repair, incorporating Fe₃O₄@SiO₂ nanoparticles within bioceramic and biopolymer inks. This allows minimally invasive implantation, with shape recovery triggered by NIR and magnetic stimulation. In vivo, the scaffold promoted bone regeneration, vascularization, and activation of osteogenic pathways, effectively fitting irregular defects. Hwangbo et al.^[440] developed a collagen/hydroxyapatite scaffold with microchannels via 3D and 4D printing, aimed at spinal fusion. It supported osteogenesis and vascularization, with enhanced bone formation and blood vessel growth in vivo, indicating its potential as an effective bone graft substitute.

Pfarr et al.^[441] introduced a 4D bioprinting technique to create human-scale, small-diameter vascular grafts using sodium alginate and collagen peptide bio-ink. These grafts, seeded with endothelial progenitor cells or human umbilical vein endothelial cells (HUVECs), showed organized matrices with viable, functional cells and biomechanical properties similar to human saphenous veins. They had low thrombogenicity and successfully implanted in a perfused cadaver model, indicating strong clinical potential. Chiesa et al.^[442] used 4D printing to develop self-deploying, bio-based scaffolds for minimally invasive gastrointestinal tissue repair. Starting from a tubular shape, the scaffold unfolds

into a flat sheet upon hydration, driven by a silk/gelatin material with differential swelling, modeled via finite element analysis. Biological tests on colorectal cell lines showed it supported cell growth, highlighting its promise for tissue regeneration. Challenges remain in optimizing degradation rates, mechanical strength, and long-term biocompatibility for in vivo applications.

Micro-scale devices like microrobots hold great promise for minimally invasive therapies. Magnetic field-driven, biodegradable SMP microrobots can be remotely navigated to deliver drugs or perform hyperthermia, with shape memory enabling controlled deployment. For example, drug-loaded helical structures can be directed to target sites and triggered to release therapeutics via magnetic or thermal stimuli, achieving high precision^[435]. Personalized, drug-releasing stents made with VP techniques exemplify advances in this area. Through in situ welding and coating strategies, researchers can fine-tune drug release profiles over extended periods, reducing infection risks and enhancing treatment efficacy. Microneedle arrays with embedded nanoparticles are also being designed for painless, controlled drug administration, with shape memory functionality allowing on-demand release triggered by environmental cues such as temperature or pH.

Hu et al.^[443] developed a hybrid nanocomposite hydrogel using NIPAM, Laponite, and Neodymium Iron Boron (NdFeB) particles, enabling 4D-printed soft millirobots with dual temperature and magnetic responsiveness. These robots demonstrate excellent mechanical properties and biocompatibility, allowing precise control and autonomous movement. Various structures, such as magnetic catheters and bio-inspired devices, were fabricated capable of navigating complex environments and transporting cargo. This work highlights the potential of stimuli-responsive hydrogels for advanced soft robotics in biomedicine. Maher et al.^[444] proposed multimaterial microrobots for microscale pH sensing. These feature a hard polymer backbone for optical trapping and 4D-printed hydrogel sensing elements that swell with pH changes. They provided visual pH readout via microscopy, with swelling observed between pH 2.3 and 8.8, especially from pH 5 to 7. The sensors exhibited stability over multiple cycles and two months of storage. Moving at around 14µm/s in phosphate-buffered saline, these microrobots show promise for microfluidic pH measurement.

Li et al.^[445] introduced SPROUT, a novel single-layer 4D printing method that uses focused light to encode anisotropic density gradients within microscale materials. This overcomes the limitations of traditional bilayer methods, enabling the creation of structures with high curvature. These shape-morphing structures can reversibly fold and unfold in response to stimuli, such

as different chemical environments. The high curvature achievable with SPROUT allowed the fabrication of untethered microrobotic grippers, which exhibited reliable, repeatable motion, making it suitable for soft robotic applications and smart actuators. This technique offers a rapid, versatile approach to microscale 4D printing with complex geometries.

Liu et al.^[446] developed a morphology-reconfigurable millirobot capable of switching locomotion modes via in-situ magnetization reprogramming in response to different magnetic field patterns. This adaptive feature enables seamless transition between rigid, high-velocity movement and soft, adhesive actuation, allowing navigation through confined, complex environments such as small lumens or irregular surfaces. The robot demonstrated multimodal locomotion, including rolling, flipping, rotation, and gliding, effectively maneuvering through diverse terrains. It also showed potential for targeted drug delivery within oviduct-mimicking phantoms and ex vivo tissues. Magnetization reprogramming during navigation offers a versatile strategy for self-adaptive robots capable of complex biomedical tasks.

Xin et al.^[447] created environmentally adaptive shape-morphing microrobots (SMMRs) that utilize programmed differences in expansion rates within pH-responsive hydrogels to enable dynamic shape changes for micro-/nanocargo manipulation. Incorporating magnetic propulsion, they designed a microcrab (SMMC) capable of precise delivery through an "opening-closing" claw mechanism. They also developed a microfish (SMMF) that encapsulates doxorubicin (DOX), closing its mouth in neutral pH and releasing the drug in acidic conditions, allowing controlled, environment-triggered drug delivery. The SMMF demonstrated localized treatment of HeLa cells within an artificial vascular network. These programmable microrobots show great potential for complex cargo operations and on-demand drug delivery, with ongoing improvements expected to expand their biomedical applications.

Park et al.^[448] developed a biodegradable microbot for thermal therapy and controlled drug delivery, powered by magnetic fields. Constructed with PEGDA, PETA, Fe₃O₄ nanoparticles, and the anticancer drug 5-fluorouracil (5-FU), the microbot's polymer backbone provides structural integrity, while magnetic nanoparticles enable remote manipulation. When exposed to an alternating magnetic field, it can be precisely directed to targeted locations for thermal treatment and drug release.

Despite promising developments, SMP-based drug systems face challenges in biocompatibility, degradation control, and stimulus responsiveness, limiting their clinical translation. Future efforts focus on developing

multifunctional resins that combine mechanical actuation, biodegradability, and controlled drug release to advance VP-printed biomedical devices.

8.2 Soft Robotics and Actuators

VP-printed SMPs have become increasingly prominent in the development of flexible sensor systems. The inherent ability of SMPs to respond to various external stimuli, including electrical, thermal, optical, and chemical signals, renders them highly suitable for sensing applications across multiple domains. Compared to conventional shape memory alloys, SMPs offer notable benefits such as reduced production costs, lighter weight, and simpler fabrication processes. These features make SMPs more adaptable and cost-effective options for manufacturing flexible sensors. Moreover, by integrating SMPs with other functional materials, it is possible to engineer advanced sensors that combine excellent thermal, mechanical, and shape-memory characteristics. These composite films can be designed to exhibit high conductivity and flexibility, enabling their use in wearable electronic devices and other flexible sensing platforms^[449].

The pioneering application of VP-printed SMPs in flexible electronics can be traced back to 2015, when researchers like Zarek et al.^[450] introduced a shape-memory thermoset based on PCL, which could be processed via SLA. By incorporating conductive materials into SMP matrices, they showcased potential uses in responsive electronic components. For instance, as depicted in their work, silver nanoparticle inks were used to print electrical contacts. When triggered by temperature, the SMP's shape-memory effect facilitated the reconnection of a broken circuit, causing an LED to illuminate. Heating the SMP with an applied voltage of 50V prompted electrothermal recovery, restoring its original shape and electrical conductivity, thus illustrating its utility in smart sensing and wearable electronic applications. Zhang et al.^[451] presented a groundbreaking approach to multifunctional sensing using 4D printing technology. They developed an adaptive strain sensor (AMSS) based on the shape memory properties of polylactic acid (PLA), combined with a bioslit structural sensing unit and a bi-directional bilayer design. By utilizing PLA's phase transition and slit architecture, they achieved precise macro-microstructure tuning, resulting in a sensor highly sensitive to strain, temperature, and mechanical stimuli. The macro-deformation allowed the AMSS to conform to human joints and recognize full-range motion. Additionally, the close relationship between shape transformation and strain sensing enabled position and self-sensing capabilities. The sensor could distinguish temperature from mechanical signals through resistive signal separation, and its wireless module improved portability^[451,452]. Ren et al.^[453] developed 4D-printed conductive composites for soft actuators with tunable stiffness and self-sensing capabilities. The materials can adjust stiffness over three orders of magnitude and

provide real-time feedback on stiffness, deformation, and pressure through resistance signals analysed with machine learning. They demonstrated applications including cardiac-mimicking actuators and pressure-sensing therapeutic insoles that can detect plantar pressure and release pressure to reduce pain. Ren et al.^[454] used 4D printing to develop versatile tactile sensors with adjustable sensitivity, measuring range, and shape adaptation for unstructured surfaces. They fabricated interdigital electrodes from nanocarbon black/polylactic acid and shape memory polyurethane, enabling the sensors to change detection parameters through heat-induced deformation of the shape memory polymer. By fine-tuning printing parameters, the sensors could conform to curved surfaces like spheres and saddles. These shape-changing tactile sensors offer great potential for environment self-adaptation and self-adjusting sensing in human-robot interaction.

Further advancements include the development of complex conductive structures through DLP techniques, such as the work by Mu et al.^[455] who dispersed multi-walled carbon nanotubes (MWCNTs) within photopolymerizable resins. They identified that a 0.3wt% loading of MWCNTs yielded optimal electrical conductivity in structures with a layer thickness of approximately 19 micrometers. This enabled fabrication of capacitive sensors capable of detecting pressure or deformation by monitoring changes in capacitance caused by mechanical deformation. In addition, innovative 4D printing approaches have been employed to create SMP-based smart patches for biomedical monitoring. Alam et al.^[456] formulated SMP lattices infused with liquid crystal (RM257) and coated with nanosilver to serve as flexible, skin-adherent sensors. These patches could detect joint movements by measuring resistance variations as the SMP deformed during flexion and extension, thus serving as motion sensors.

Another notable development involved the creation of 2W-SMPs that are both recyclable and responsive to environmental stimuli, such as temperature changes. Mu et al.^[457] engineered a polybutadiene-based SMP with rapid, reversible actuation properties, capable of responding within 0.2 seconds. Such materials hold promises for safety applications like fire alarms, where swift response and reusability are critical. To address the need for multi-stimuli responsiveness, Wu et al.^[458] introduced multilayer SMP composites driven by magnetic fields and Joule heating, enabling rapid shape recovery under magnetic induction. These multilayer structures, fabricated via magnetic field-assisted DLP (MF-DLP), demonstrated accelerated recovery speeds due to uniform magnetic particle distribution, with T_g values reaching 120°C, broadening their applicability in sensing and actuation.

However, a significant challenge remains in developing

VP-compatible materials that support multi-excitation responses^[459-461]. The scarcity of suitable photopolymerizable resins restricts the creation of multifunctional sensors. Many high-performance polymers like polycaprolactone or polyurethane lack inherent light-reactive groups, necessitating complex chemical modifications that increase production costs and may compromise material properties. Additionally, incorporating nanofillers or high-molecular-weight components often raises resin viscosity, impairing processability and curing efficiency. Most VP-printed SMP sensors to date are single-stimulus, primarily responding to thermal triggers^[462]. To expand their functional scope, future research must focus on designing dual- or multi-stimuli responsive SMPs, possibly through advanced chemistries such as dynamic covalent networks like vitrimers, which combine robustness with recyclability. Such materials could operate effectively in complex environments, enabling more versatile sensing capabilities^[463]. Finally, innovations in multi-material VP printing, like grayscale, multi-resin, and centrifugal multi-material techniques, are vital for producing heterogeneous structures with spatially controlled functionalities^[464]. Coupled with integrated real-time monitoring tools, these advancements can significantly accelerate the development of reliable, high-performance flexible sensors, paving the way for breakthroughs in soft robotics, wearable electronics, and biomedical sensing systems.

8.3 Data Security (Encryption) and Anti-Counterfeiting

SMPs demonstrate distinctive deformation capabilities and ease of processing under external stimuli, making them promising for innovative 3D encryption techniques^[172,465-470]. However, simple shape changes are vulnerable to tampering and decryption, falling short of the security standards required for high-level encryption^[466]. To address this, Liu et al.^[467] designed a robust, flexible, and self-healing thermoplastic shape memory polyurethane (HEOMC-PU) that responds to light and heat, enabling secure information hiding and retrieval. When exposed to specific UV wavelengths (365nm and 254nm), coumarin groups within the material exhibit reversible fluorescence, allowing for encrypted data that can be decrypted through UV irradiation and thermal recovery. Their process involves multiple stages: initially, segments are self-healed into a star shape, then secure information is patterned onto the surface using a photomask, creating a fluorescence-based encryption visible only under UV light. This encrypted data can be erased with 254nm UV light and rewritten using 365nm UV, facilitating a recyclable encryption process. The second layer of protection employs the shape memory effect combined with origami techniques, ensuring the shape remains intact under sunlight and UV exposure. Although effective, the reliance on UV light and complex origami structures to prevent unauthorized access pose limitations, particularly for outdoor applications with

restricted UV exposure and in scenarios demanding rapid, efficient encryption/decryption.

Building on this, Liu et al.^[468] integrated g-DLP technology with hydrophilic UV-curable SMPs (HU-SMPs) to create a dual encryption system capable of reversible, recyclable data display. Using grayscale imaging, they modulated crosslinking density within the material, where regions with lower crosslinking scatter light differently when submerged in water, revealing encrypted information. This method allows for programmable encryption by controlling grayscale and 3D shape, with reversible decryption triggered by temperature and humidity changes. Post-decryption, the information can be permanently stored or erased via UV irradiation. As demonstrated, the HU-SMP films initially curl and then recover shape above their T_g . When immersed in water, the scattering effects of incompletely crosslinked regions reveal the encrypted data, which can be permanently fixed or erased depending on subsequent UV treatment. Variations in folding methods during shape recovery further enable dual decryption pathways, though reliance on water immersion limits some practical applications.

Additionally, Chen et al.^[172] developed a thermochromic SMP system that changes color with temperature, adding a layer of security for 4D-printed structures. By embedding thermochromic microcapsules, the material can reversibly shift from white to other colors such as red, blue, or yellow upon heating and cooling, enhancing data security. They demonstrated dual encryption using folding SMPs: heating a QR code to 80°C causes it to reshape and change color, while cooling it to 40°C restores the original appearance, enabling secure decoding. Building on this, Ge et al.^[470] introduced photochemical microcapsules into thermochromic, shape-changing polymers, resulting in a dual-mode system that combines shape deformation and multicolor changes under temperature variations and UV light. This allows printed structures to undergo simultaneous shape shifts and color transformations, making them suitable for multifunctional information hiding and anti-counterfeiting applications.

8.4 Aerospace Innovations

Within the realm of aerospace engineering, the development of sophisticated and intricate structures, ranging from aircraft and satellites to rockets and space station, demands advanced manufacturing techniques capable of delivering high-precision, complex components. Additive manufacturing, especially 3D printing, has revolutionized the production of small-batch, high-value parts essential for aerospace applications. By enabling the fabrication of monolithic components with seamless integrity, 3D printing eliminates the necessity of assembling multiple parts into hinges or joints, thus significantly enhancing the overall strength and reliability of aerospace elements

operating under extreme conditions^[471]. Major industry players like General Electric have harnessed this technology to produce parts such as fuel nozzles with intricate internal cooling channels, achieving notable improvements in durability while reducing weight, crucial factors for flight efficiency^[472]. Nevertheless, when dealing with components of irregular shapes and sizes, manufacturing complexity and costs escalate. This challenge has propelled the adoption of 4D printing, which offers a cost-effective pathway to produce complex, adaptive parts with superior performance characteristics. The ability of 4D printing to fabricate components of arbitrary geometry at a lower cost is fueling its growing adoption within aerospace sectors.

In pioneering research, Wu and colleagues^[473] demonstrated the potential of 4D metal printing to repair damaged sections of space stations, presenting a compelling proof-of-concept. Their approach involved transforming flat, 2D metallic precursors into three-dimensional curved structures tailored to fill gaps in space station frameworks. Precision laser stimulation was employed to induce localized thermal stresses, enabling the printed metal strips to bend and reshape dynamically according to operational needs. By controlling laser parameters such as scanning frequency and position, these strips could be reshaped on demand into various configurations, exemplifying the transformative potential of 4D metal printing in space repair missions.

A transformative application of 4D technology in aerospace is the development of morphing wings, dynamic structures capable of altering their shape during flight to optimize aerodynamics and efficiency^[474]. These adaptive wings can modify parameters like span, camber, or twist, offering enhanced aerodynamic performance and maneuverability across diverse aircraft types, including military fighters, unmanned aerial vehicles, and future commercial planes^[475]. The significance of morphing wings lies in their promise to reduce fuel consumption, extend flight ranges, and promote sustainable aviation practices. Conventional manufacturing techniques often struggle to produce the complex internal architectures necessary for such adaptable wings. However, 4D printing provides an innovative and cost-efficient solution, enabling the creation of intricate, hinge-free structures that can achieve extensive deformation. For instance, Fasel et al.^[476] showcased the FDM-based 4D printing of continuous fiber composites for a 2-meter wingspan drone, which demonstrated exceptional maneuverability solely through shape morphing, generating controlled moments along all axes^[476]. Similarly, Hoa et al.^[477] explored the fabrication of responsive, compliant wings with a sandwich structure, comprising flat upper and lower skins with a corrugated, carbon/epoxy core. Under load, these wings exhibited both vertical and horizontal deflection, successfully morphing up to 20°, capable of supporting substantial forces, making them suitable for small UAVs^[477].

Beyond structural adaptation, 4D printing addresses critical challenges in deploying aerospace devices such as satellites and space station components. Self-deploying structures have become a focus, with 4D printing enabling the fabrication of components that activate and transform autonomously. Zhang et al.^[478] developed deployable solar panels with shape-memory polymer hinges, which can unfold via Joule heating, facilitating deployment in space^[478]. Similarly, Testoni et al.^[479] engineered active, reconfigurable satellite appendages using 4D-printed SMP and SMA hinges, capable of bending to predetermined angles, maintaining positions without continuous energy input, and undergoing multiple reorientation cycles, streamlining energy collection and reducing mechanical complexity in small satellite systems^[479].

In an inventive leap, Li and colleagues applied multimaterial 4D printing to design biomimetic explosive catapults inspired by *Viola verecunda* seed dispersal mechanisms. These devices leverage localized heat stimuli to trigger rapid ejection velocities reaching 3.6m/s and launch distances up to 112 times the projectile length. Such robust ejection capabilities were demonstrated in launching various objects, including satellites, nets, and projectiles, from a single aerospace platform, showcasing the potential for satellite deployment, debris clearance, and space station operations^[480]. Through these groundbreaking advances, 4D printing is establishing itself as an indispensable tool for next-generation aerospace manufacturing, enabling the creation of adaptive, lightweight, and multifunctional structures tailored for the demanding environment of space exploration and aviation.

8.5 Breakthroughs in Electronics and Photonics through 4D Printing

Electronics and photonics, fields centered around the control and manipulation of electrons and photons, have historically driven technological progress across countless industries^[481]. However, the environmental impact and high energy demands of mass-producing conventional devices have sparked a quest for innovative manufacturing strategies. Enter 4D printing: a revolutionary approach that introduces dynamic, shape-shifting capabilities to electronic and photonic components, fostering a new era of adaptable, efficient, and sustainable devices.

One of the pioneering feats in this domain was achieved by Sundaram et al.^[482] who demonstrated the self-assembling nature of 4D-printed electronic structures. Using multicomponent inkjet techniques, they created layered constructs capable of folding into complex three-dimensional shapes autonomously once detached from their initial surface, an advancement that broadens the horizon for fabricating intricate geometries unattainable through traditional methods^[482].

Another notable innovation involved the use of shape-memory polymers derived via SLA printing, coated with conductive silver nanoparticles, to produce flexible, shape-recovering electronic sensors. These devices could detect temperature changes and complete circuits by returning to their original form, showcasing the potential for resilient, foldable electronics^[483].

The landscape of 4D electronics is expanding with versatile approaches to circuit design. Researchers have employed solvent-activated polymers like SU-8^[484], electroactive composites^[485], and acrylate-based resins^[486] to print functional electrical pathways and sensors. For example, a fully printed, stretchable stress sensor was developed by Mu et al.^[487] incorporating a silver wire embedded within layered substrates. When stretched, resistance increased proportionally, providing a sensitive measure of deformation, ideal for wearable health monitors or soft robotics. Similarly, Bodkhe and colleagues^[488] engineered piezoelectric shape-memory polymers capable of sensing mechanical stimuli while actively deforming, paving the way for truly integrated responsive systems. Weber's team^[489] also explored shape-memory alloys such as nitinol, demonstrating their utility in pre-stressed circuits that can be activated or deactivated through thermal triggers, adding reconfigurability to electronic systems. In the realm of photonics, 4D micro- and nanofabrication techniques have unlocked unprecedented control over light-matter interactions^[490,491]. Zhang and colleagues^[492] produced nanoscale SMP structures capable of altering their shape and, consequently, their optical properties in response to temperature. These nanostructured patches could dynamically modulate light transmission, either blocking or allowing light passage, by mechanically collapsing or expanding^[492]. To overcome issues like nanostructure sticking caused by van der Waals forces, subsequent research incorporated surface treatments with hydrophobic coatings, creating high-resolution, reconfigurable nanostructures with vibrant, tunable colors^[491].

The miniaturization of kirigami and origami principles has also revolutionized nanophotonics, enabling the creation of reconfigurable optical components with tailored properties. Xu et al.^[493] designed nano-kirigami sheets made from stiff nanocomposites that could steer light beams across a broad angular spectrum, opening new avenues for dynamic beam shaping^[493]. Meanwhile, Wang and colleagues^[494] manipulated the folding angles of origami-inspired structures to produce chiral metamaterials with switchable optical activity. These adaptive systems could be toggled between different chiral states, allowing for customizable electromagnetic responses with potential uses in lightweight sensors and communication devices^[494]. Liu's team^[495] further advanced this field by demonstrating reconfigurable metasurfaces capable of generating Fano resonances with adjustable circular dichroism, enhancing the control over

polarized light at the nanoscale. On the integration front, Chen et al.^[496] pioneered an on-chip nanokirigami platform capable of large-scale, electromechanical reconfiguration. By applying electrostatic forces, they achieved dynamic optical modulation across visible and near-infrared wavelengths, facilitating versatile, miniaturized optical systems. Similarly, Jiang et al.^[497] developed stretchable split-ring resonator arrays that could switch between non-chiral and chiral configurations, enabling reprogrammable circular polarizers with broad or narrow spectral responses, thus advancing the development of flexible, multifunctional optical devices.

These strides underscore 4D printing's transformative potential in crafting adaptive, multifunctional electronic and photonic systems. By enabling structures that can morph, reconfigure, and respond to external stimuli, this technology unlocks new frontiers in device design, miniaturization, and sustainability. Nonetheless, the current material palette remains limited compared to traditional additive manufacturing, emphasizing the need for continued development of innovative, nano-compatible materials^[498]. As the field matures, the cross-pollination of 4D printing with electronics and photonics promises to inspire breakthroughs in areas such as biomedical devices, optical computing, and beyond, heralding a future where devices are not only functional but also capable of evolving in real-time.

9 PROGRESS AND FUTURE PERSPECTIVES IN PHOTOPOLYMERIZATION-BASED 4D PRINTING

Despite significant advances, critical barriers persist in material design, process scalability, and functional complexity. Below, we propose concrete research directions to address these challenges, leveraging emerging opportunities in chemistry, materials science, and engineering. The section on biocompatible photocurable materials highlights the current limitations posed by commercially available (meth)acrylates, which often generate toxic leachables, and the lack of biospecificity in photoinitiators. To address these challenges, the proposed research pathway includes developing enzyme-cleavable crosslinkers, such as peptide-acrylate conjugates, that degrade into non-acidic metabolites, thereby enhancing biocompatibility. Additionally, innovation in photoinitiators is necessary; designing biomolecule-photoinitiator hybrids that can be activated by visible light, specifically within the 450–550nm range, could potentially eliminate the cytotoxic effects associated with UV exposure. Furthermore, engineering immunomodulatory bioinks that incorporate immobilized cytokines like TGF- β may help to direct stem cell differentiation in situ, creating a more favorable environment for cellular interaction.

In the area of living 3D constructs, there is a significant

gap arising from the slow kinetics of RAFT polymerization, which limits architectural complexity, alongside oxygen inhibition that disrupts control during printing. The proposed strategy focuses on optimizing catalysts, specifically by creating heterogeneous photocatalysts, such as graphitic carbon nitride nanosheets, which are capable of facilitating oxygen-tolerant, high-fidelity printing. This could enable the integration of multi-material systems, allowing for the fabrication of core-shell structures with spatially resolved mechanical gradients, ideal for applications such as vascular grafts. Additionally, leveraging photoinduced electron/energy transfer could lead to advancements in 4D reprogramming, enabling the triggering of post-print network reconfiguration through light-guided shape-memory resetting.

The section addressing mechanical property modulation notes the brittleness of highly cross-linked networks and the stress concentrations caused by inhomogeneous curing as current gaps. Research pathways suggest implementing dual-cure systems that combine rapid acrylate polymerization with slower thiol-ene click chemistry to facilitate delayed stress relaxation^[499,500]. Another innovative approach involves using magnetic field-aligned cellulose nanofibers during printing to create anisotropic toughness, resulting in more than 200% enhancement in fracture strain. To further assist in the development of adaptive architectures, computational models predicting stimulus-driven property changes, such as temperature-dependent modulus shifts, are essential for informing resin formulations^[501].

On the topic of long-wavelength activation, the limitations imposed by UV and visible light, which restrict penetration depth to less than 5 mm, and the inefficiency of near-infrared initiators, create substantial barriers to clinical translation. Proposed pathways include synthesizing heavy-atom-free photosensitizers with triplet-triplet annihilation capabilities, particularly BODIPY derivatives, which could allow activation in the 780-850 nm range with quantum yields exceeding 50%. Device integration is also essential, particularly the combination of CLIP technology with upconverting nanoparticles to facilitate deep-tissue printing, such as transdermal bone implants. Moreover, designing multifunctional initiators that incorporate MRI contrast agents, like Gd³⁺-chelated porphyrins, could enable real-time monitoring of the curing process, further bridging the gap toward clinical applications^[502].

In concluding remarks, it is emphasized that VP-based 4D printing is at a pivotal moment; while significant advancements in stimuli-responsive resins and high-resolution techniques have enabled remarkable functionality, the next step must focus on material innovation to propel the field forward^[503]. Key priorities include the transition to sustainable feedstocks, replacing petroleum-derived resins with circular-economy alternatives such as terpene-based photopolymers.

Closed-loop control can be achieved by integrating in situ sensors like Raman spectroscopy with machine learning algorithms for real-time optimization of curing processes. Additionally, the pursuit of multi-functional systems through the co-printing of structural, conductive, and responsive materials via multi-wavelength vat systems is crucial. Establishing standardized protocols, such as those from ISO and ASTM, for quantifying factors like shape-memory cyclability, biocompatibility, and recyclability will also play an important role in this evolution. The convergence of these strategies will facilitate the transition of 4D printing from laboratory prototypes to solutions that are both clinically viable and industrially scalable (Table 3). Despite significant advances, critical barriers persist in material design, process scalability, and functional complexity. Below, we propose concrete research directions to address these challenges, leveraging emerging opportunities in chemistry, materials science, and engineering.

9.1 Developing Biocompatible Photocurable Materials

Bioprinting involves the precise fabrication of three-dimensional structures containing living cells and biologically active components. This process requires materials with high biocompatibility, transparency, and suitable mechanical properties. Many commercially available photocurable resins, particularly those based on (meth)acrylate chemistry, pose biocompatibility challenges due to residual monomers, oligomers, and degradation products that can leach out and cause cytotoxic effects. For instance, uncured (meth)acrylate monomers can generate irritating or toxic compounds, while their hydrolytic degradation produces acids that may disrupt local pH and impair cell viability. Furthermore, the limited water solubility and biocompatibility of many photoinitiators restrict their use in biological environments. Therefore, the development of specialized bioinks, comprising polymers with favorable rheological, biological, and mechanical properties, is essential for clinical translation. Among FDA-approved polymers, PEG derivatives are prominent due to their hydrophilicity, low immunogenicity, and ease of functionalization^[363,364]. These materials have been successfully utilized in SLA and DLP to produce drug delivery platforms and tissue scaffolds with controlled release profiles. Similarly, gelatin-based derivatives, such as GelMA, support cell adhesion and proliferation, making them suitable for bioprinting complex tissue models^[279-283]. Nevertheless, the limited diversity of fully biocompatible and printable formulations underscores the need for continued innovation and optimization in this area.

9.2 Toward Truly Living 3D Constructs with Controlled Radical Photopolymerization

While 4D printing enables time-dependent shape and property changes, traditional free radical polymerization produces networks that are inherently non-living and

Table 3. Key Challenges and Corresponding Research Pathways

Challenge	Targeted Research Pathway
Petroleum-based SMPs	Develop bio-derived resins (e.g., lignin-epoxy acrylates, soybean-oil oligomers) with dynamic covalent bonds (vitrimers) for recyclability.
High viscosity of nanocomposites	Engineer surface-functionalized nanoparticles (e.g., SiO ₂ -PEG, cellulose nanocrystals) to reduce agglomeration and enable >20 wt% loading without viscosity penalties.
Irreversible acrylic SMPs	Design photocurable cycloaddition-based resins (e.g., Diels-Alder, anthracene dimerization) enabling reversible network reconfiguration.
Light blockage in composites	Optimize wavelength-selective photoinitiators (e.g., NIR-upconverting nanoparticles) for deep curing in opaque composites.
Slow living polymerization	Integrate flow photoreactors with vat printing to enhance RAFT kinetics via rapid reagent mixing.

irreversibly formed. To realize dynamic, adaptable structures that can be reprogrammed or functionalized after fabrication, controlled "living" radical polymerization techniques are essential. Such methods enable the incorporation of new monomers or functionalities in a reversible, on-demand manner under light activation^[504,505].

Experimental strategies include UV-triggered incorporation of monomers into existing networks via chain transfer agents such as trithiocarbonates (TTCs). For example, monomers like N-isopropylacrylamide have been integrated into TTC-containing networks, demonstrating controlled growth^[327,354]. However, surface and gel systems often exhibit uncontrolled polymerization due to limited light penetration and unstable radical intermediates. An alternative approach employs photoredox catalysis, using visible light-activated catalysts, to mediate controlled RAFT polymerization within 3D constructs. Johnson et al. demonstrated that photocatalytic activation of TTC-based networks can enable sequential monomer addition, producing multi-material structures with tailored properties. Although promising, challenges such as slower reaction kinetics and the need for precise control over polymerization protocols must be addressed before practical implementation^[506].

9.3 Modulating Mechanical and Physical Properties of 3D Printed Structures

Photopolymerization techniques allow the fabrication of complex, multifunctional architectures with tunable properties. Nonetheless, highly cross-linked networks tend to be brittle and exhibit poor impact resistance due to inhomogeneous polymerization. To enhance toughness and flexibility, strategies such as employing alternative polymerization mechanisms, e.g., thiol-ene chemistry, step-growth polymerization, or dual curing, have been explored. Incorporating flexible oligomers, such as siloxanes, into resin formulations can significantly improve elasticity, reduce surface energy, and modify thermal stability^[507]. For instance, blending siloxane-based monomers with acrylates produces materials with decreased glass transition temperatures and increased ductility, suitable for applications demanding high deformability^[508,509]. Additionally, reinforcing the polymer matrix with nanomaterials like cellulose nanocrystals

can improve mechanical strength and chemical stability. For soft robotics and stretchable electronics, the development of highly elastic, UV-curable elastomers, such as formulations with epoxy acrylates and urethane diacrylates, has yielded structures with elongations exceeding 1000%, rivaling silicone rubbers. These materials facilitate the production of complex, durable, and highly deformable devices for biomedical and wearable applications^[36,510].

9.4 Extending Activation Wavelengths to Longer Spectra

Early photopolymerization systems relied on photoinitiators with high absorption in the UV range, which, while effective, present limitations including shallow penetration depth, slow curing rates for large structures, and potential cellular damage^[511-513]. To overcome these issues, the development of photoinitiators and photocatalysts that absorb in the visible or NIR spectrum has become a primary focus. Visible-light-sensitive systems enable safer, deeper, and faster polymerization, expanding the scope of biomedical applications.

Examples of such chromophores include oil blue N, pheophorbide a, bacteriochlorophyll a, and aluminum phthalocyanine, each with absorption peaks suitable for activation with specific wavelengths. These dyes facilitate deeper light penetration, reduce phototoxicity, and improve print resolution^[514,515]. Future research aims to design new photoinitiators with tailored absorption properties, higher quantum efficiencies, and compatibility with biological environments, thus enabling more effective, safe, and versatile photopolymerization-based 3D printing systems.

10 LIMITATIONS AND STRATEGIES FOR IMPROVEMENT

This comprehensive review explores recent breakthroughs in the realm of VP 3D printing of SMPs, emphasizing advancements in printing techniques, material innovations, and promising application avenues. Since the advent of 4D printing in 2013, this technology has profoundly transformed additive manufacturing by incorporating the dimension of time, enabling the creation of smart, stimuli-responsive structures. SMPs, owing to their unique shape memory effects, are central to this

progress. The high precision and versatility offered by VP methods have been instrumental in addressing the complex demands of fabricating dynamic, functional materials.

The discussion begins with an overview of various VP technologies, including DLP, SLA, LCD, PμSL, and TPP, each capable of finely tuning exposure parameters such as intensity and wavelength to achieve precise material processing. Recent advances include novel photopolymers, overcoming challenges associated with UV-initiation by employing photosensitive initiators with red-shifted absorption. Progress in controlled living radical polymerization methods, such as RAFT, further enables post-print modifications and the development of materials with living features. Performance of photocurable SMPs hinges on molecular architecture, photopolymerization kinetics, influencing shape fidelity, recovery, and cyclic stability. Concerning materials, the resins suitable for 4D printing predominantly include acrylate-based, polycaprolactone-based, polyurethane-based, and epoxy-based formulations. Acrylate-based resins are favored for their rapid curing and adjustable thermal properties, allowing customization of mechanical and shape memory characteristics through compositional and network modifications. Epoxy resins, known for their superior mechanical strength and thermal stability, are widely employed but tend to be brittle; recent strategies like incorporating toughening agents or designing interpenetrating polymer networks (IPNs) have successfully improved their toughness and shape memory performance.

One of the key challenges in developing high-performance SMPs is their inherent brittleness, primarily caused by high crosslink densities. To mitigate this, the inclusion of low concentrations of chain transfer agents or flexible co-monomers can enhance toughness and elongation at break. While combining different monomers or creating hybrid systems increases formulation complexity, such approaches enable fine-tuning of critical properties, including shape fixation, recovery efficiency, and environmental stability. In addition, the chemical mechanisms underlying photopolymerization, mainly radical initiation, thiol-ene/yne, and cationic pathways, play a fundamental role in defining resin performance. Each mechanism presents unique benefits and limitations, influencing factors such as reaction speed, network uniformity, oxygen tolerance, and mechanical robustness. Continued innovation in photoinitiator chemistry and network design is expanding the capabilities of photocurable resins, fostering the development of materials suitable for advanced applications like biomedicine, electronics, and soft robotics.

The integration of multi-material VP printing with multi-stimuli responsive SMP resins remains a significant frontier. Achieving this synergy promises to substantially enhance the functionality and complexity of 4D-printed structures. Concurrently, the incorporation of real-time monitoring

and in situ characterization, such as optical, spectroscopic, and thermal sensors, offers a high-impact pathway for accelerating resin development and ensuring the reliability of printed parts. Embedding these sensors enables feedback-controlled processes, optimizing exposure, curing, and post-processing conditions, which reduces residual monomers, improves dimensional accuracy, and enhances interlayer adhesion. Utilizing data-driven models to interpret sensor data further accelerates formulation and process optimization, although challenges such as sensor integration, standardization, and cross-chemistry compatibility persist.

Ultimately, the future of VP 4D printing of SMPs hinges on balancing material performance with environmental sustainability. Developing recyclable, eco-friendly formulations, possibly through the use of biodegradable monomers or greener chemistries, and expanding wavelength ranges for photoinitiation are critical goals. As photopolymerization techniques evolve, leveraging diverse chemical pathways, including radical, thiol-ene/yne, and cationic mechanisms, will enable the creation of high-performance, stimuli-responsive materials that meet the demanding requirements of next-generation applications, from personalized medicine to adaptive soft robotics.

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Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

Author Contribution

Kashi PA contributed to writing—original draft, methodology, investigation, funding acquisition, and conceptualization; Didari M contributed to writing—original draft, validation, and formal analysis; Shahbaz M contributed to writing—original draft, software, resources, and methodology.

Abbreviation List

ADSCs, Adipose-derived stem cells
AFCT, Addition-fragmentation chain transfer
ALG, Alginate
AMSS, Adaptive multifunctional strain sensor
ANN, Artificial neural networks
βCD, β-cyclodextrin
Bis-GMA, Bisphenol A-glycidyl methacrylate
CLIP, Continuous liquid interface production
CMA, Collagen methacrylamide

dECM, Decellularized extracellular matrix
 DLP, Digital light processing
 DMA, Dynamic mechanical analysis
 ECHs, Electroconductive hydrogels
 FDM, Fused deposition modeling
 FOT, Fiber-optic taper
 FRESH, Freeform reversible embedding of suspended hydrogels
 GAGs, Glycosaminoglycans
 g-DLP, Grayscale digital light processing
 GelMA, Gelatin methacryloyl
 GelNB, Gelatin norbornene
 GM-HA, Glycidyl methacrylate-modified HA
 HA, Hyaluronic acid
 HBC-MA, Hydroxybutyl methacrylated chitosan
 IPNs, Interpenetrating polymer networks
 LAAO, Left atrial appendage occluder
 LAP, Lithium phenyl-2,4,6-trimethylbenzoylphosphinate
 LCD-DLP, Liquid crystal display-based masking projection
 LFDm, Liquid-frozen deposition manufacturing
 MF-DLP, Magnetic field-assisted DLP
 MTF, Modulation transfer function
 Nor-PGS, Norbornene-functionalized PGS
 PCL, Polycaprolactone
 PEDOT:PSS, Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
 PEG, Polyethylene glycol
 PEGDA, Polyethylene glycol diacrylate
 PGS, Poly(glycerol-co-sebacate)
 PGSA, Poly(glycerol sebacate) acrylate
 PGSM, Poly(glycerol-co-sebacate methacrylate)
 PLATMC, Poly(L-lactide-co-trimethylene carbonate)
 PNIPAAm, Poly(N-isopropylacrylamide)
 PUs, Polyurethanes
 PμSL, Projection micro-stereolithography
 RAFT, Reversible addition-fragmentation chain transfer
 RSM, Response surface methodology
 SLA, Stereolithography
 SMPs, Shape memory polymers
 SMTPUs, Shape memory thermoplastic polyurethanes
 SPIONs, Superparamagnetic iron oxide nanoparticles
 TEGDMA, Triethylene glycol dimethacrylate
 Tg, Glass transition temperature
 Tm, Melting point
 TPP, Two-photon polymerization
 TpPU, Thermoplastic polyurethane
 TsPU, Thermosetting polyurethane
 UDMA, Urethane dimethacrylate
 VAM, Volumetric additive manufacturing
 VP, Vat photopolymerization

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