science, engineering and health studies

Invited Review

Science, Engineering and Health Studies
https://lio1.tci-thaijo.org/index.php/sehs
ISSN (Online): 2630-0087

A comprehensive review of polymeric bioinks for vat photopolymerization 3D bioprinting: Theories, current advances, progress, and pharmaceutic applications

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***Received**: 19 January 2025*
***Revised**: 11 March 2025*
***Accepted**: 1 April 2025*
***Published**: 3 December 2025*

***Citation**:*
Suriyaamporn, P., Ngawhirunpat, T., Panomsuk, S., Chantasart, D., & Opanasopit, P. (2025). A comprehensive review of polymeric bioinks for vat photopolymerization 3D bioprinting: Theories, current advances, progress, and pharmaceutic applications. Science, Engineering and Health Studies, 19, 25010002.

ABSTRACT

Polymeric bioinks utilized in vat photopolymerization 3D bioprinting represent a novel technology in pharmaceutical applications, enabling the precise creation of complex drug delivery systems and groundbreaking approaches to personalized medicine. Vat photopolymerization methods regulate the polymerization of photosensitive bioinks by sequentially creating precise layers through light exposure. These polymeric bioinks are formulated from biocompatible materials comprising polymers, photoinitiators, photoabsorbers, plasticizers, and additives. Frequently utilized biocompatible polymers comprise gelatin methacryloyl, poly(ethylene glycol) diacrylate, and hyaluronic acid methacrylate. Critical parameters for these bioinks and the printing process include viscosity, temperature, printability, and fidelity, as well as mechanical properties, light intensity, exposure time, layer thickness, and post-processing. In pharmaceuticals, vat photopolymerization, a significant breakthrough in personalized medicine, is used to construct drug delivery devices for drug discovery and screening. Due to the high precision of this technology, it is possible to manufacture dosage forms with the desired release profile tailored to the patient, thereby increasing the effectiveness of the drug and patient compliance. Polymeric bioinks thus offer a novel approach to the production of pharmaceuticals through vat photopolymerization 3D bioprinting. Additional research has been directed toward the optimization of bioink characteristics to improve clinical outcomes and the customization of healthcare, revolutionizing the medical and pharmaceutical landscape through synergistic 3D bioprinting.

Keywords: polymeric bioink; vat photopolymerization 3D bioprinting; pharmaceutical applications; personalized medicine; pharmaceutical innovation

1. INTRODUCTION

A transformative era in biomedical engineering and pharmaceutical products has emerged with the development of three-dimensional (3D) bioprinting technologies that facilitate the production of intricate structures with precision, accuracy, and efficacy (Mendoza-Cerezo et al., 2023). Vat photopolymerization is distinguished from other techniques used due to its high resolution and capacity to create complex structures. Stereolithography (SLA), digital light processing (DLP), masked stereo-lithography (MSLA), and continuous liquid interface production (CLIP) are among the most prevalent vat photopolymerization 3D bioprinting techniques (Zhang et al., 2021). Polymeric bioinks are essential for the successful manufacture of biomedical and pharmaceutical 3D printing products serving as their fundamental components. These bioinks must be biocompatible as well as exhibit the requisite rheological properties and responsiveness to light-based curing mechanisms (Jose et al., 2024).

Vat photopolymerization 3D bioprinting is a technique that involves the layer-by-layer construction of structures by controlling the polymerization of photosensitive polymers through patterned light exposure (Ware et al., 2023). The utilization of polymeric bioinks is essential in biomedical engineering because of their ability to accurately model the physical and biological characteristics of the natural extracellular matrix. This capability supports cellular functions and facilitates tissue maturation post-printing (Patrocinio et al., 2023). Furthermore, these bioinks facilitate the development of tissue engineering scaffolds, personalized medicine, disease models for drug screening, and patient-specific drug delivery systems in pharmaceutical applications (Parihar et al., 2024). Developing bioinks that exhibit biocompatibility and functional integrity post-cure while also possessing the requisite rheological and biochemical properties for printing is challenging.

The selection of suitable polymeric bioinks involves an understanding of polymer chemistry, photochemistry, and biocompatibility. Photopolymerizable bioinks frequently contain macromolecules with acrylate or methacrylate groups, which can produce crosslinked networks when exposed to light. The most commonly used polymers are gelatin methacrylate (GelMA), polyethylene glycol diacrylate (PEGDA), methacrylated hyaluronic acid (HAMA), methacrylated chitosan (ChMA), polyethylene glycol dimethacrylate (PEGDMA), acrylated epoxy resins, N-vinylpyrrolidone-based polymers (NVP), alginate methacrylate, methacrylated cellulose, fibrin-based polymers, sulfobetaine methacrylate (SBMA), polycaprolactone triacrylate (PCLTA), polypropylene fumarate (PPF), poly(2-hydroxyethyl methacrylate) (pHEMA). These materials are chosen for their adjustable properties, including mechanical strength, viscosity, rheology, and degradation rate are all adjustable, and these materials are chosen accordingly. The dynamics of photoinitiation and the kinetics of crosslinking reactions are also considered in the development of these bioinks (Yu et al., 2020). Incorporating photoinitiators that facilitate quick polymerization without producing harmful byproducts is crucial for high-resolution printing (Bagheri & Jin, 2019). Manipulating the crosslinking density affects not only the mechanical properties of bioprinted constructs but also their biological characteristics, such as cell adhesion, nutrient transport, and matrix remodeling (Fang et al., 2023).

Vat photopolymerization 3D bioprinting represents a promising direction for the pharmaceutical sector, particularly in the areas of precision medicine, toxicity assessment, and drug discovery. By employing innovative 3D printing techniques to generate tissue models that resemble biological tissues, it is possible to assess therapeutic efficacy and safety with greater precision, thereby reducing the need for animal research (Hu et al., 2025). These models have the potential to replicate disease states and the responses of individual patients to treatments, thereby providing a reliable tool for personalized medicine. Vat photopolymerization offers a promising method for the production of medicinal products due to its scalability and accuracy (Lam et al., 2023).

The integration of polymeric bioinks with vat photopolymerization processes is revolutionizing pharmaceutical manufacturing by enabling the creation of complex, scalable, and highly customized medical products. This advanced approach combines the precision of vat photopolymerization with the adaptability of bioinks, facilitating the production of tailored drug delivery systems, tissue scaffolds, and other biomedical applications. Such innovations hold the potential to transform patient care, offering personalized solutions for diverse medical needs. This review delves into the scientific and technological foundations of this integration, exploring the mechanisms by which bioinks and photopolymerization processes interact to achieve optimal performance. By leveraging advancements in materials science and additive manufacturing, the pharmaceutical industry can overcome traditional limitations in scalability, precision, and biocompatibility. The applications of vat photopolymerization in pharmaceutical manufacturing are vast. It enables high-resolution 3D printing of intricate structures with precise control over material properties, making it particularly valuable in regenerative medicine and therapeutic drug development. However, challenges remain, including optimizing bioink formulations, ensuring cellular viability during the printing process, and addressing the environmental impacts of photopolymerization materials. Moreover, interdisciplinary research involving materials science, biomedicine, and engineering will be critical to unlocking the full potential of this technology. Such collaboration will drive innovation, refine processes, and expand the capabilities of vat photopolymerization, shaping the future of pharmaceutical manufacturing and personalized medicine (Xu et al., 2021).

2. VAT PHOTOPOLYMERIZATION 3D BIOPRINTING

Vat photopolymerization 3D bioprinting uses light to polymerize photosensitive materials, enabling the precise fabrication of complex shapes. In the pharmaceutical sector, this technology holds significant promise and has emerged as a revolutionary technique, providing innovative methodologies for the formulation and development of advanced drug delivery systems (Xu et al., 2021). The accuracy and adaptability of this technique enable the design of dosage forms with precise release profiles, geometries, and mechanical characteristics, essential for targeted drug administration and sustained release formulations. The capacity to integrate multiple materials and active compounds in a single print operation facilitates the development of multi-drug delivery systems, potentially streamlining treatment

protocols for complex disorders. This technology is essential for personalized medicine (Milliken et al., 2024).

This method utilizes photopolymerization principles, in which light-induced reactions facilitate the transformation of liquid monomers into solid polymers, creating accurate, layer-by-layer structures that can replicate the intricate architecture of biological tissues. Each of the most notable vat photopolymerization techniques, including SLA, MSLA, DLP, and CLIP, offers unique advantages in terms of material adaptability, speed, and resolution (Pagac et al., 2021). The fundamentals of various vat photopolymerization 3D bioprinting methods are illustrated in Figure 1, which also includes standard inkjet and extrusion bioprinting techniques.

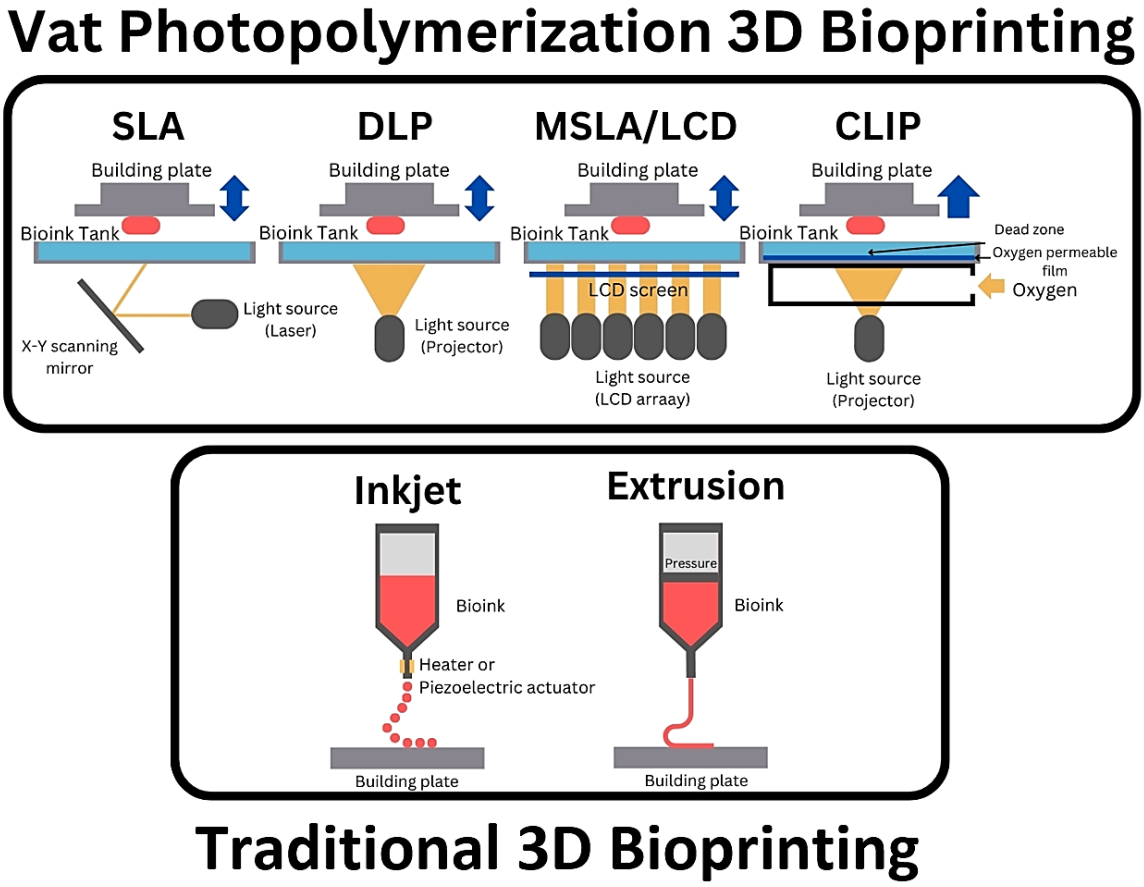


Figure 1. The principles of vat photopolymerization, inkjet, and extrusion 3D bioprinting

2.1 Stereolithography (SLA)

SLA is a vat photopolymerization 3D printing method essential for rapid prototyping in additive manufacturing (Wu et al., 2020). SLA uses a laser to selectively cure and consolidate photosensitive polymer resin in successive layers based on the principle of vat photopolymerization. The initial layer on the surface of liquid resin is delineated by a laser beam, solidifying it precisely at the focus point. The build platform is lowered after each layer is finished, allowing a new layer of resin to coat the previous one. This process is repeated until the entire product has been solidified and formed. This method is particularly well-suited for the production of complex designs with high accuracy, smooth surfaces, and tight tolerances (Murphy et al., 2022; Pagac et al., 2021).

2.2 Masked stereolithography (MSLA) or liquid-crystal display (LCD)

MSLA is a variation of SLA, that employs an LCD as a mask to project light onto the surface of a photosensitive resin. This method differs from conventional SLA by using a UV LED light source to project onto the LCD screen rather than utilizing a laser to trace each layer. Each pixel functions as a micromask, either allowing or preventing light from passing through. This approach has significantly expedited the printing process by enabling the simultaneous curing of an entire layer. A key advantage over conventional SLA is that the exposure time per layer remains consistent regardless of the part's complexity. This allows for the simultaneous and efficient printing of multiple or larger objects. Homogeneous exposure ensures high-resolution details and a smooth surface finish, which is essential for applications requiring precise dimensional accuracy. This technology is widely recognized for producing durable components cost-effectively and efficiently, making it a critical asset for rapid prototyping and small-batch production in the pharmaceutical sector (Junk & Bär, 2023).

2.3 Digital light processing (DLP)

DLP utilizes UV light to polymerize a photopolymer resin, using a digital projector to display an image of each layer onto the resin surface. This image projection enables the rapid curing of entire layers, enhancing the efficiency of the printing process. DLP technology employs micromirrors on a semi-

conductor chip called a digital micromirror device (DMD). Each micromirror represents a unique pixel in the projected image. By directing UV light onto mirrors that can tilt toward or away from the light source, DLP can accurately project these images onto the resin. This ability to control light exposure with such granularity allows DLP printers to achieve excellent resolution and accuracy. DLP facilitates the production of precise components with smooth surfaces and complex details. Due to its rapid and economical production, DLP is a preferred method for prototyping and manufacturing across diverse industrial sectors (Murphy et al., 2022; Pagac et al., 2021).

2.4 Continuous liquid interface production (CLIP)

CLIP is an advanced 3D printing technology developed by Carbon3D company. CLIP accelerates the printing process by forming a product continuously from a resin pool, eliminating the layer-by-layer pauses that limit other 3D printing methods. The core innovation in CLIP is a special UV-transparent, oxygen-permeable window at the bottom of the resin pool. This window creates a "dead zone" of uncured resin between the window and the printed object. Oxygen inhibits the photopolymerization process, preventing the resin from curing against the window and allowing the object to be drawn out of the resin pool continuously. A projector under the resin pool uses digital light projection to cure the resin above the dead zone. By eliminating the mechanical separation steps required between layers in conventional SLA, MSLA, or DLP, CLIP substantially accelerates the overall process and enables much higher print speeds. CLIP is particularly advantageous for producing components with complex geometries, smooth vertical surfaces, and exceptional mechanical properties. It is also effective for manufacturing on a commercial scale, offering significant advantages in terms of speed and material properties (Murphy et al., 2022; Pagac et al., 2021).

The efficiencies of each vat photopolymerization 3D bioprinting method are presented in Table 1 (Chekkaramkodi et al., 2024). Vat photopolymerization 3D bioprinting offers distinct advantages over traditional inkjet and extrusion 3D printing, especially regarding precision, accuracy, and resolution. These properties are essential for constructing intricate biomedical structures with nanoscale precision. A smooth surface finish improves the biological efficacy of printed materials. Additionally, the use of various photosensitive polymers facilitates the customization of mechanical, chemical, and biological properties to closely resemble tissues. Moreover, this method is highly efficient in the production of intricate designs without the need for support materials, thereby streamlining the manufacturing process and reducing waste by circumventing the nozzle clogging and material waste prevalent in other 3D printing techniques (Chekkaramkodi et al., 2024; Xu et al., 2023).

Table 1. The different efficiencies of each type of vat photopolymerization 3D bioprinting

Properties	SLA	MSLA	DLP	CLIP
Technology	Laser moves across resin tank	LEDs expose light through LCD screen	Mask shapes UV light for printing	Continuous printing via UV-permeable oxygen membrane
Resolution	*** (25–50 µm)	**** (40–50 µm)	***** (10–50 µm)	**** (30–50 µm)
Accuracy& Precision	****	***	**	*****
Speed	** (8 to 16 mm/h)	*** (15 to 50 mm/h)	**** (30 to 60 mm/h)	***** (100 to 500 mm/h)
Cost	***	**	****	*****

*, **, ***, ****, ***** indicated lowest, low, moderate, high, and highest, respectively

3. FUNDAMENTALS OF PHOTOPOLYMERIZATION

Photopolymerization, a crucial reaction mechanism in polymer chemistry, entails the conversion of monomers into intricate polymeric structures via light energy. it is an essential category of polymerization distinguished by its rapid processing and precision (Husár et al., 2014). Photopolymerization offers a unique advantage that is especially beneficial for precision applications, including the production of biomedical devices and pharmaceuticals (Al Rashid et al., 2021).

3.1 Process of photo-crosslinking reactions

Generally, photopolymerization involves three phases: initiation, propagation, and termination. The mechanistic phases of photopolymerization are regulated by specific molecular dynamics, as illustrated in Figure 2 (Elkhoury et al., 2023; Yu et al., 2022).

Initiation: During the initial stage of photopolymerization, a photoinitiator absorbs light and generates reactive species, such as free radicals. The chain reaction polymerization process commences with the interaction of these reactive species with monomer molecules. The selection of a photoinitiator is essential, as its absorption spectrum must match the wavelength of the light source being used to guarantee effective initiation (Elkhoury et al., 2023; Yu et al., 2022).

Propagation: The interaction between active monomer species and other monomers causes the rapid extension of polymer chains. This phase is influenced by reaction parameters and the characteristics of the monomers. By neutralizing radicals, oxygen can impede or prevent the reaction (Elkhoury et al., 2023; Yu et al., 2022).

Termination: The elongation of polymer chains is frequently terminated by mechanisms such as chain combination or disproportionation. The polymer is stabilized when the light source is terminated, disrupting

the formation of new reactive species. Inhibitors can be used to intentionally halt or modify the reaction at specific stages (Elkhoury et al., 2023; Yu et al., 2022).

3.2 Photopolymerization mechanism types

Free-radical chain polymerization: Free-radical chain polymerization is a frequently employed method in the synthesis of polymeric materials due to its efficiency and simplicity. The process commences with the formation of free radicals, which are typically generated by the decomposition of a photoinitiator in response to light exposure. The chain reaction is perpetuated by the generation of new radicals as a result of the reaction between these radicals and unsaturated monomers. This technique is indispensable for the creation of bioinks or bioresins, as it enables the rapid polymerization of intricate structures in 3D bio-printing under controlled conditions. This method is highly adaptable and suitable for a wide range of biological applications due to its ability to precisely modify molecular weight distribution and polymerization rates (Elkhoury et al., 2023; Yilmaz & Yagci, 2020).

Radical-mediated Thiol–ene photocrosslinking: Radical-mediated thiol–ene photocrosslinking is a distinct form of photopolymerization that occurs when thiol and alkene groups interact under UV light and a radical initiator. This approach is remarkable for its superior control over network formation, yielding polymers with consistent characteristics and less stress. The thiol–ene reaction is often selected for bioink formulations because it generates consistent crosslinked networks, which are crucial for the effective integration and functionality of bioprinted tissues and devices. Additionally, these networks also exhibit exceptional mechanical properties and dimensional stability. Additionally, the use of thiol–ene photocrosslinking can mitigate oxygen inhibition, a common obstacle in free-radical polymerization, thereby improving the overall efficiency of the curing process (Cramer et al., 2003; Elkhoury et al., 2023).

Photomediated redox reactions: In the presence of light, photomediated redox reactions involve the transfer of electrons, which can be used to initiate polymerization in bioink and resin formulations. This reaction is especially advantageous when dealing with delicate biological components as it frequently operates under benign conditions and is less likely to inflict harm to the cells or proteins embedded in the bioink. This method facilitates the development of intricate structures with precise internal architectures by utilizing redox pairs that are responsive to light, thereby allowing for temporal control over the polymerization process. In addition, potential UV-induced cellular damage can be mitigated by customizing photomediated redox reactions to operate under visible light, expanding the applicability of these materials in clinical and in vivo contexts (Elkhoury et al., 2023; Lu et al., 2024).

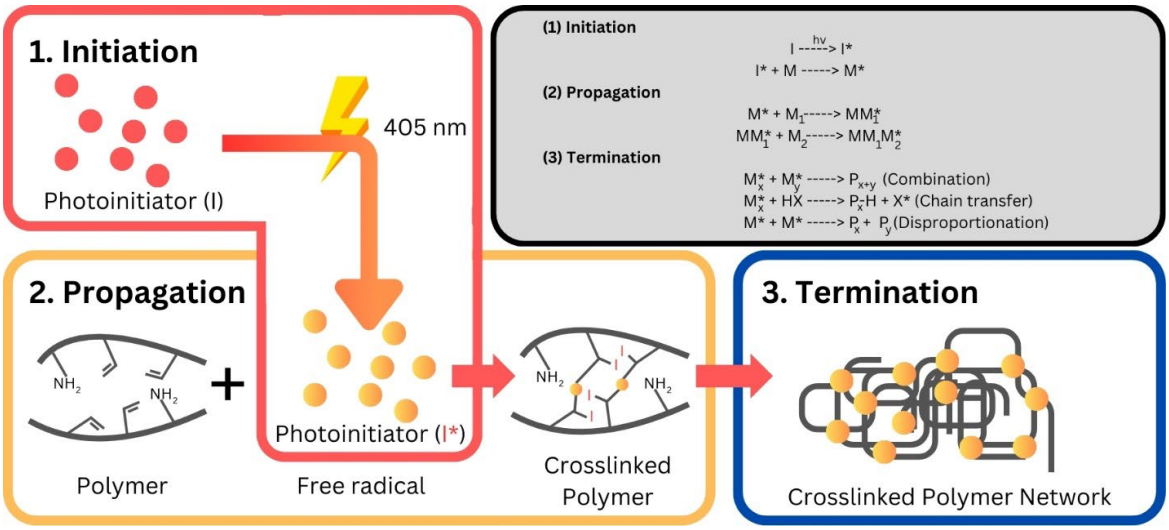


Figure 2. Schematic of the three stages of a photo-crosslinking reaction: initiation, propagation, and termination

4. COMPONENTS OF POLYMERIC PHOTOPOLYMERIZABLE BIOINKS

Developing specialized bioinks is essential for the successful fabrication of high-fidelity and functional pharmaceutical products or medical devices in the evolving field of 3D bioprinting. Polymeric photopolymerizable bioinks are at the forefront of this technology, providing the requisite precision and adaptability for developing intricate biological structures (Tripathi et al., 2023). These bioinks comprise a precise combination of polymers, photoinitiators, photo absorbers, and various functional additives, each of which plays a critical role in the bioprinting process. The components of polymeric photopolymerizable bioinks are illustrated in Figure 3 (Gugulothu et al., 2023).

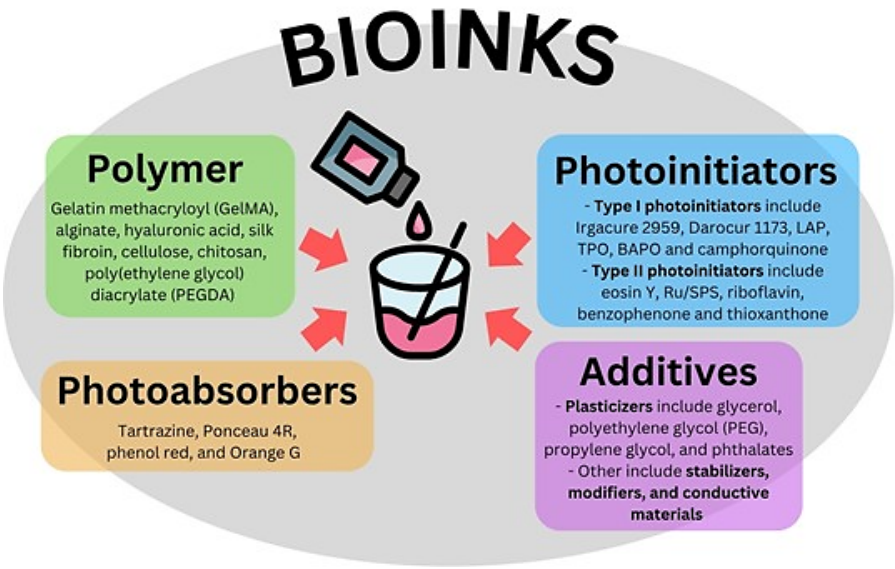


Figure 3. The components of polymeric photopolymerizable bioinks

4.1 Polymers

The fundamental components of photopolymerizable bioinks are polymers, which are macromolecules engineered for fast solidification upon light exposure. Commonly, the polymers mixed in bioinks include natural polymers such as alginate and hyaluronic acid, alongside synthetic polymers including gelatin methacryloyl (GelMA), poly (ethylene glycol) diacrylate (PEGDA) and polyacrylamide, as shown in Table 2. These polymers are chosen based on their biocompatibility, mechanical qualities, and the specific demands of the targeted tissue or organ. Polymer selection is critical for printability and for ensuring subsequent cell adhesion, proliferation, bio-compatibility, and differentiation (Schittecatte et al., 2023).

Gelatin, a collagen derivative, is utilized extensively in bioresins because of its biocompatibility and biodegradability. It generates hydrogels upon crosslinking, which can replicate the natural extracellular matrix, facilitating cell adhesion and proliferation. Gelatin is thermoreversible, allowing it to alternate between sol and gel forms in response to temperature variations, which is advantageous in temperature-controlled printing applications. Gelatin methacryloyl (GelMA) is a modified gelatin that has been functionalized with methacrylate groups, enabling it to undergo crosslinking when exposed to light in the presence of a photoinitiator. This alteration endows GelMA with superior physical qualities compared to conventional gelatin, rendering it exceptionally suitable for application in bioresins (Patrocinio et al., 2023; Tan et al., 2022).

Collagen, a predominant protein in the animal kingdom, is essential for providing structural support in tissues. Collagen is valued in bioresins for its exceptional bio-compatibility and capacity to enhance cellular interactions and tissue regeneration. It is often employed in tissue engineering and regenerative medicine (Patrocinio et al., 2023; Tan et al., 2022).

Silk fibroin is a protein that provides exceptional mechanical strength and elasticity. It is extracted from the silk of Bombyx mori silkworms. It is biocompatible and biodegradable, with controllable degradation rates, and can be processed into a variety of forms, rendering it suitable for scaffold and film applications in biomedical fields (Patrocinio et al., 2023; Tan et al., 2022).

Fibrin is utilized in bioresins owing to its intrinsic role in tissue regeneration and wound repair. Fibrin polymers function as scaffolds in tissue engineering, promoting cell migration and new tissue formation (Patrocinio et al., 2023; Tan et al., 2022).

Alginate, a polysaccharide derived from brown seaweed, can form a hydrogel in the presence of divalent cations, such as calcium ions. It is frequently used as a bioink and in wound dressings due to its mild gelation conditions, facilitating cell encapsulation and viability (Patrocinio et al., 2023).

Cellulose, the most common organic polymer, is biocompatible and exhibits exceptional tensile properties. In bioresins, modified cellulose derivatives, including carboxymethylcellulose, are employed as matrices for drug delivery and tissue engineering due to their hydrogel-forming capabilities and stability (Patrocinio et al., 2023; Tan et al., 2022).

Hyaluronic acid, a naturally occurring polysaccharide, is essential for tissue hydration and elasticity. Hyaluronic acid is utilized in bioresins due to its biocompatibility and capacity to regulate cellular activity, making it suitable for applications related to cartilage and skin tissues (Patrocinio et al., 2023; Tan et al., 2022).

Chitosan, a polysaccharide derived from chitin, found in the exoskeletons of crustaceans, chitosan is notable for its biodegradability and antimicrobial properties. It is employed in bioresins for wound healing applications and as a scaffold material in tissue engineering (Patrocinio et al., 2023; Tan et al., 2022).

Gellan Gum, a water-soluble polysaccharide, creates gels in the presence of cations and is utilized in bioresins due to its adaptability and superior gel-forming characteristics. It is often used in culinary applications and investigated for cell encapsulation in 3D bioprinting owing to its advantageous rheological characteristics (Patrocinio et al., 2023; Tan et al., 2022).

Poly (ethylene glycol) diacrylate (PEGDA) is a synthetic polymer often utilized in bioresins for biomedical and biotechnological applications. A derivative of poly (ethylene glycol) (PEG), PEGDA maintains many of PEG's adaptable characteristics while integrating enhanced functionality via its terminal acrylate groups. The acrylate groups allow PEGDA to be crosslinked into a network, forming a hydrogel with distinctive properties (Patrocinio et al., 2023; Tan et al., 2022).

Table 2. Structures of common polymers used in photopolymerizable bioinks

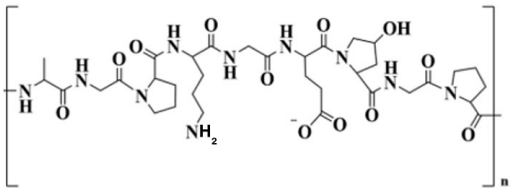
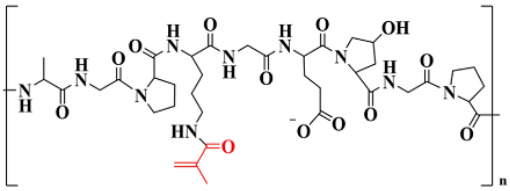
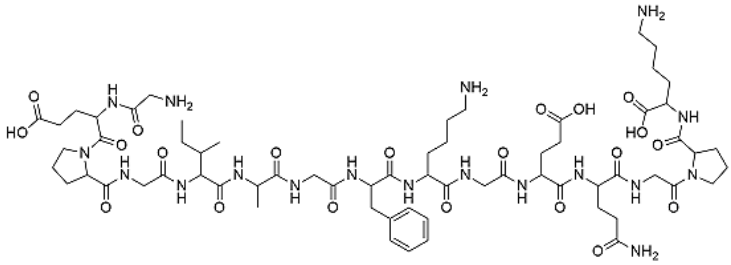
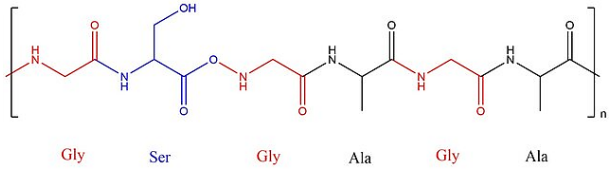
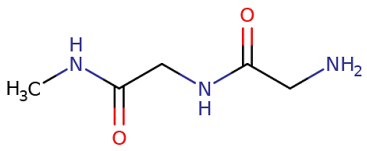
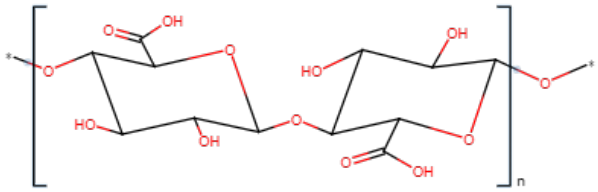
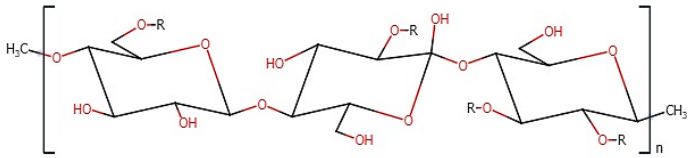
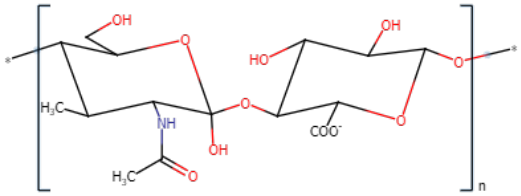
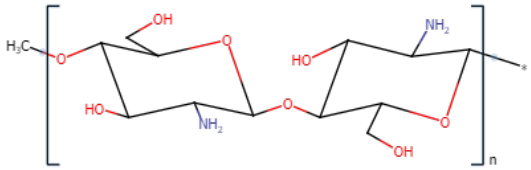
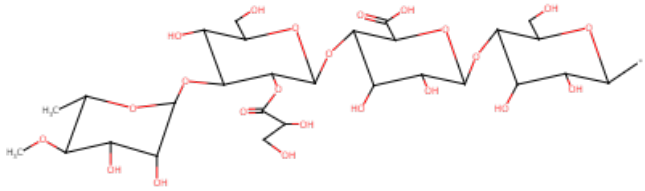
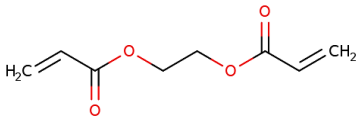
Polymer	Structures	Reference
1. Gelatin		(Ji et al., 2023)
1.1 Gelatin methacryloyl (GelMA)		(Ji et al., 2023)
2. Collagen		(ChemEssen, 2025)
3. Silk fibroin		(King et al., 2023)
4. Fibrin		(Suriyaamporn et al., 2020)
5. Alginate		(Suriyaamporn et al., 2020)

Table 2. The structure of polymers in photopolymerizable bioink (continued)

Polymers	Structures	Reference
6. Cellulose		(Suriyaamporn et al., 2020)
7. Hyaluronic acid		(Suriyaamporn et al., 2020)
8. Chitosan		(Suriyaamporn et al., 2020)
9. Gellan gum		(Suriyaamporn et al., 2020)
10. Poly(ethylene glycol) diacrylate (PEGDA)		(Suriyaamporn et al., 2020)

4.2 Photoinitiators

Photoinitiators are indispensable for initiating the polymerization process, during which monomer units in the bioink interact with photoinitiators that absorb light and produce reactive species, such as free radicals. The 3D printer can build a 3D structure layer-by-layer as the resin solidifies. The efficacy of a photoinitiator is determined by its cytocompatibility, quantum yield of radical generation, and ability to absorb light at specific wavelengths (Zennifer et al., 2022). Photo-curable 3D printing is suitable for fabricating various products, including biomedical devices. The spectral stimulation and mechanisms of action differ for Type I and Type II photoinitiators. Type I photoinitiators are activated by UV light, whereas Type II photoinitiators are responsive to visible light, as shown in Table 3 (Elkhoury et al., 2023; Qin et al., 2014). It is imperative to select a photoinitiator that is appropriate for the bio-printed structure, as it directly affects biocompatibility, curing sensitivity, and mechanical strength.

Type I photoinitiators are substances that undergo photolytic cleavage to generate free radicals directly after UV light absorption. A photoinitiator transforms into reactive radical species when stimulated by UV light. These radicals play a crucial role in initiating the polymerization process by breaking the double bonds in monomers, leading to the formation of polymer chains. Common Type I photoinitiators include Irgacure 2959, Darocur 1173, lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), phenyl bis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO), and camphorquinone. The selection of a photoinitiator for a bioink depends on its effectiveness, the required curing speed, and other specific attributes of the formulation (Elkhoury et al., 2023; Tomal & Ortyl, 2020).

Type II photoinitiators require a co-initiator, often a tertiary amine, which works in conjunction with the photoinitiator to produce free radicals by a bimolecular process. This type involves an excited-state reaction with

the co-initiator upon absorbing visible light, which facilitates the transfer of an electron or hydrogen atom to generate radical species. The polymerization chain reaction is initiated by this process, leading to the formation of polymeric structures. Type II photoinitiators include eosin Y, ruthenium/sodium persulfate (Ru/SPS), riboflavin, benzophenone, and thioxanthone. They are especially advantageous in applications requiring both through- and surface-cure characteristics (Elkhoury et al., 2023; Tomal & Ortyl, 2020).

Table 3. Commonly used photoinitiators for photopolymerization

Photoinitiator	Concentration (%w/v)	Intensity (mW/cm²)	Wavelength (nm)	Exposure time (s)	Reference
Type I photoinitiators					
Irgacure 2959	0.01–1	1.2–3950	250–480	2–1800	Tomal & Ortyl, 2020;
LAP	0.037–1	0.5–2000	365–500	10–300	Elkhoury et al., 2023;
TPO	0.1–2	100–4000	267–380	2–600	Dzwonkowska-Zarzycka &
BAPO	0.1–1	100–2000	250–400	5–600	Sionkowska, 2024
Camphorquinone	0.1–0.5	200–1000	400–500	10–120	
Type II photoinitiators					
Eosin Y	0.001–1	48–203	480–600	120–1200	Tomal & Ortyl, 2020;
Ru/SPS	0.02–1	3–50	400–450	180–900	Elkhoury et al., 2023;
Riboflavin	0.01–0.5	10–200	220–450	120–1200	Dzwonkowska-Zarzycka &
Benzophenone	0.1–2	100–500	250–360	10–120	Sionkowska, 2024
Thioxanthone	0.1–3	100–400	250–400	5–300	

4.3 Photoabsorbers

Photoabsorbers mitigate problems linked to high photoinitiator concentrations, which can lead to rapid and unregulated polymerization and compromise printing quality. To overcome this problem, photoabsorbers are used to absorb excess energy and modulate the curing rate, which naturally decreases as polymerization proceeds. Photoabsorbers remain unaltered and functional, and are often employed as dyes to regulate the penetration of light into the resin. Tartrazine, Ponceau 4R, phenol red, and Orange G serve as photoabsorbers that enhance the printability of constructs by preventing excessive curing (Seo et al., 2022; Yu et al., 2020).

4.4 Plasticizers and additives

Plasticizers and additives are indispensable for regulating the mechanical properties and structural characteristics of bioink tissue polymers. Plasticizers are frequently employed to increase flexibility and decrease the brittleness of printed structures, enabling the development of intricate patterns that closely resemble natural biological architecture. Glycerol, sorbitol, PEG, triethyl citrate, diethyl phthalate, dibutyl phthalate, triacetin, propylene glycol, citric acid esters, adipates, sebacates, phosphate esters, isosorbide derivatives, and lactic acid esters are all examples of plasticizers (Schwab et al., 2020). Furthermore, the use of various additives, including stabilizers such as butylated hydroxytoluene (BHT), Irganox 1010 and Tinuvin; antioxidants such as ascorbic acid, tocopherols (vitamin E), citric acid; fillers such as zinc oxide and calcium carbonate; UV stabilizers like hindered amine light stabilizers (HALS), and other phenolic antioxidants; and conductive materials, enhances the functionality of the bioink. These may include thermal stabilizers that prevent degradation during the printing process and conductivity enhancers that are essential for the development of constructs with electrical capabilities (Bi & Huang, 2022). The plasticizers and additives are used to meet the demands of biomedical applications, including developing organ models, drug delivery systems, and tissue engineering scaffolds.

5. FACTORS INFLUENCING PHOTOPOLYMERIZATION OF POLYMERIC BIOINKS IN 3D PRINTING

In the 3D printing of polymeric bioinks, photopolymerization is a complex process impacted by several parameters that affect the quality, functionality, and reliability of the final printed structures. Understanding these factors is crucial for optimizing printing performance and ensuring that the properties of 3D-printed products are suitable for various applications, particularly in the biomedical field (Gu et al., 2020).

5.1 Rheological properties

Rheological properties, such as viscosity and thixotropy, are important factors for successful printing performance and structural integrity, particularly in vat photopolymerization and extrusion-based 3D printing. A bioink with appropriate rheological properties solidifies easily, maintains its shape after extrusion, and flows through the printing apparatus without obstruction. It is essential to consider viscosity when performing vat polymerization to produce well-defined layers. Low viscosity may result in insufficient resolution and compromise the structural integrity of 3D-printed products, while high viscosity may negatively impact the intended shape and resolution (Habib & Khoda, 2022). Precise control of these factors is essential to ensure that 3D-printed products meet the requirements for biomedical applications and to create high-resolution prints. The primary focus in the development of advanced biomaterials for 3D printing is the modification of rheological characteristics to comply with specific printing processes and desired outcomes. This is essential for the formulation of bioinks.

5.2 Temperature

Effective temperature regulation is critical for the optimal processing and curing of materials. It is essential to maintain the viscosity of bioinks at a level that is conducive to precise extrusion and deposition, as this affects

the overall printability and structural integrity of the final constructs. Therefore, optimal temperature settings are essential. The mechanical properties and dimensional stability of printed products are directly affected by the rate of photopolymerization, which is temperature-dependent. To prevent deformations like warping or shrinkage and to ensure the biocompatibility and functionality of bio-based constructs in biomedical applications, it is essential to maintain controlled temperatures during the printing and post-curing phases (Moon et al., 2024; Schwab et al., 2020).

5.3 Printability and fidelity

In vat photopolymerization, precisely controlling the printing process is essential for success. Printability refers to the ease with which a material can be printed, specifically its capacity to flow through a nozzle and consolidate as intended. Fidelity is the degree of accuracy and detail in the printed object relative to the original digital model. The meticulous calibration of machine parameters, including resolution, layer thickness, and exposure times, is critical for achieving high fidelity. In addition, the optimization of the rheological properties of bioinks, including viscosity and thixotropy, is necessary to ensure the preservation of structural integrity and feature resolution after deposition. The optimization of these aspects ensures that the printed constructs exhibit precise geometry and the requisite functional characteristics for their intended applications, including biomedical scaffolds, electronic components, and consumer products (Ali et al., 2024; Graça et al., 2024).

5.4 Mechanical properties

The mechanical properties of a printed object are influenced by critical parameters such as the printing strategy, the extent of crosslinking, and the polymer matrix characteristics. Proper adjustment of these parameters ensures that the final structure meets the requisite criteria for strength, flexibility, and durability. The rigidity and elasticity of printed materials are directly influenced by the crosslinking density, which is determined by photopolymerization parameters such as light intensity and exposure time (Bonada et al., 2017). Furthermore, the use of polymers and plasticizers can enhance the mechanical properties, such as modulus, elasticity, and tensile strength (Shaukat et al., 2022). The mechanical properties of 3D-printed objects can be customized to closely align with the functional requirements of biomedical devices, pharmaceutical products, and other high-performance applications as a result of these modifications (Shah et al., 2023).

5.5 Light intensity and exposure times

Light intensity and exposure time are important in vat photopolymerization, as they directly influence the material cures and the properties of the final product. The appropriate light intensity can achieve the desired polymerization depth and speed, which enhances the strength and dimensional accuracy of each layer. Careful control of exposure time is also key to avoiding over- or under-curing. Excessive curing can lead to fragile structures, whereas insufficient curing can result in weak layers that impact the overall strength of the object. Consequently, adjusting light intensity and exposure time is essential for attaining the necessary characteristics in printed products, reconciling rapid production with material properties (Billerbeck et al., 2024; Hong et al., 2018).

5.6 Layer thickness and orientation

Layer thickness and orientation significantly affect the resolution, mechanical strength, and overall appearance of the final product. Thinner layers are often associated with improved surface texture and enhanced resolution of details. Conversely, thicker layers expedite the printing process but may compromise surface uniformity and detail. The orientation of each layer significantly affects the anisotropic mechanical properties of the printed product. Aligning the layer structure with known stress regions can enhance the durability and performance of components. The design and implementation of 3D printing projects depend on precisely optimizing layer thickness and orientation to balance print efficiency, structural integrity, and aesthetic quality (Kónya & Ficzere, 2024; Schittecatte et al., 2023).

5.7 Post-processing

Post-processing significantly influences the quality of 3D-printed products. Post-processing methods, including sterilization, washing, and UV curing, are essential for ensuring complete polymer conversion and enhancing mechanical integrity for therapeutic applications. The cleansing stage, typically performed with solvents such as isopropanol or water, is essential for removing uncured residual bioinks that may impact structural and surface properties. Nevertheless, this may also cause swelling and hinder inter-layer adhesion, thereby diminishing the tensile strength and Young's modulus of the material. The UV post-curing process enhances the polymer network by inducing further polymerization, thereby increasing the strength and thermal stability of the material. This procedure is essential for fortifying and stabilizing the structure, although it must be carefully controlled to prevent warping and guarantee dimensional accuracy. Ultimately, post-processing significantly affects the mechanical properties, biocompatibility, and stability of the final bioink construct (Hassanpour et al., 2024; Schittecatte et al., 2023).

6. STRATEGIES TO IMPROVE PRINTING RESOLUTION

The effective production of complex and scalable 3D structures depends significantly on enhancing the printing speed of vat photopolymerization in 3D bioprinting. This technique has the potential to revolutionize tissue engineering and regenerative medicine by enabling the rapid fabrication of intricate and functional biological constructs. However, the balance between printing speed, resolution, and biocompatibility is a critical consideration. The efficacy of photoinitiators in bioresin formulations and the light exposure parameters both affect the rate of photopolymerization. Light exposure is determined by two factors: light intensity and exposure time. A proven strategy to improve printing performance is to reduce the exposure duration for each layer, thereby minimizing the total printing time. However, this approach may lead to diminished printing resolution, as short exposure durations can result in insufficient photopolymerization, compromising the stiffness and structural integrity of the printed construct (Elkhoury et al., 2023).

An alternative strategy involves increasing the intensity of the light. This can enhance the degree of polymerization

and crosslinking density, resulting in stronger and more robust structures. However, it is crucial to recognize that high-intensity light may generate a significant density of radicals, which can hinder their diffusion and lead to heterogeneity within the polymer network. Furthermore, excessive exposure to high-intensity light can result in cellular damage or death. Therefore, achieving an optimal balance between cell viability and printing speed is essential to optimize vat photopolymerization in 3D bioprinting (Li et al., 2023).

Enhancing bioresin formulations or creating novel materials might also augment printing speed and elevate printing resolution, alongside hardware enhancements. The photoinitiator is an essential component of a photopolymerization formulation, since it directly influences the photopolymerization kinetics of the bioresin. By using PIs with substantial absorption overlap with the wavelength of the light source, exposure time can be minimized, facilitating expedited printing. This is accomplished by reducing the time required to solidify each layer. To date, the most effective photoinitiators for one-photon polymerization are activated by UV light and have low solubility in water. Therefore, it is essential to create effective water-soluble visible-light photoinitiators (Li et al., 2023; Zhou et al., 2023).

Furthermore, printing speed may be enhanced by post-treatment, the development of functional hydrogels, and the modification of bioresin solvents. Ge et al. (2023) used deep eutectic solvents (DES) to solubilize N-hydroxyethyl acrylamide (HEAA) and zwitterionic N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (DMAPS). This led to the creation of a mechanically resilient photopolymerized ionogel with outstanding biocompatibility. The resultant structure exhibited remarkable accuracy and excellent resolution, making it suitable for 3D printing. In vat photopolymerization 3D bioprinting, several monomers are often combined to improve the biocompatibility and mechanical characteristics of the resulting hydrogels. However, incorporation of multiple components into the formulation may lead to incompatibility among the elements, thereby diminishing printing quality (Ge et al., 2023). Gong et al. (2020) presented a 3D printing technique termed "shrinking printing," distinguished by a resolution increase induced by complexation. Anionic inks, including methacrylated hyaluronic acid (HAMA), GelMA, and chitosan, were used as bioinks at different concentrations. Following the printing process, the 3D constructs were submerged in a polycationic chitosan solution for post-treatment. The linear dimensions of the hydrogels were diminished to varying extents due to charge complexation and the ejection of water from the hydrogels (Gong et al., 2020).

7. PHARMACEUTICAL APPLICATIONS OF VAT PHOTOPOLYMERIZABLE BIOINKS IN 3D BIOPRINTING

Vat photopolymerization 3D bioprinting, utilizing sophisticated photopolymerizable bioinks, has initiated a novel era of opportunities in the pharmaceutical sector, as seen in Figure 4. The principal pharmaceutical application of vat photopolymerizable bioinks is in high-throughput drug screening and development. This method enables the creation of 3D tissue and organ models that are physiologically realistic, thereby allowing pharmaceutical researchers to monitor and investigate the effects of drugs in more accurate human tissue representations. Compared to conventional 2D cell cultures, 3D bioprinted tissues demonstrate cellular behaviors and drug responses that are more similar to *in vivo* environments. This capability significantly reduces the time and cost associated with drug development by improving the predictability of how drugs will perform in clinical trials, thus decreasing reliance on animal testing and enhancing the translational potential of preclinical studies (Gugulothu et al., 2023; Sun et al., 2024).

Vat photopolymerization facilitates the creation of disease models essential for comprehending the pathophysiology of many illnesses and for evaluating treatment approaches. Bioinks can be designed to include specific cell types, growth factors, and other bioactive substances that might induce or sustain disease conditions in printed tissues. For example, models of cancerous tissues can be created to study tumor growth and metastasis or evaluate the efficacy of chemotherapeutic agents under controlled conditions. Similarly, models of degenerative diseases such as Alzheimer's or osteoarthritis can be constructed to explore the mechanisms of disease and screen potential drugs (Li et al., 2020; Sun et al., 2024).

The application of vat photopolymerizable bioinks in 3D bioprinting is transforming the pharmaceutical sector by facilitating the development of intricate, tailored drug delivery systems, including tablets and transdermal patches. This technique enables unparalleled accuracy in dosage and release kinetics, which enhances efficacy and patient compliance (Awad et al., 2023; Gadi et al., 2024). By aiding in drug formulation development, such as micro-structured transdermal patches and multi-layered tablets, 3D bioprinting provides personalized therapeutics that can be optimized for the unique requirements of each patient (Bom et al., 2021; Tracy et al., 2023). These developments continue to present obstacles, including regulatory compliance, product stability, and consistency. As these issues are resolved and research advances, 3D bioprinting with photopolymerizable bioinks is expected to have a significant impact on pharmaceutical manufacturing, leading to more effective and personalized treatment options (Simon et al., 2024).

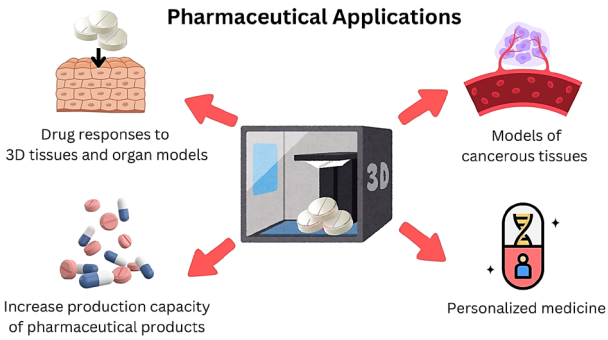


Figure 4. The pharmaceutical applications of vat photopolymerizable bioinks in 3D bioprinting

8. FUTURE DIRECTIONS OF AI IN VAT PHOTOPOLYMERIZATION 3D BIOPRINTING

The pharmaceutical industry is rapidly changing, driven by the combination of AI and vat photopolymerization 3D bioprinting. This technology is already making it easier to create customized medical devices and personalized medicines, improving both efficiency and precision in the manufacturing process. AI tools, such as artificial neural networks and machine learning, are being used for error detection, real-time quality control, and fine-tuning of optimized operations. These advances are especially useful in areas like personalized medicine, where the goal is to tailor treatments to the unique needs of each patient (Jamróz et al., 2018).

Rapid prototyping of intricate pharmaceutical formulations, such as personalized dosage forms and multi-drug delivery systems, is facilitated by the integration of AI with vat photopolymerization 3D bioprinting in drug development. By analyzing patient-specific data, including genetic, metabolic, and clinical profiles, AI facilitates the development of personalized drug release profiles that are custom-fitted to the unique therapeutic requirements of each patient (Hu et al., 2024). This integration aligns with the principles of precision medicine, thereby facilitating the development of more effective and safer therapies for a wide range of patient populations (Kumari et al., 2024). In addition, the physicochemical behavior of printed drug formulations, such as bioavailability, stability, and dissolution rates, is increasingly being simulated using AI-powered predictive modeling. While promoting innovation in pharmaceutical design, these simulations reduce dependence on resource-intensive experimental approaches, thereby expediting the research and development process (Vora et al., 2023). Grof and Štěpánek (2021) provide a notable example of how genetic algorithms were implemented to enhance the internal structure of 3D-printed tablets for personalized medicine. The investigation focused on the inverse problem of designing tablet configurations that satisfy specific drug release profiles, including immediate, delayed, and sequential dissolution. Through the integration of an event-driven erosion algorithm and computational modeling, the methodology effectively determined the optimal spatial arrangements of APIs and excipients. This method precisely regulates drug release kinetics, thereby meeting the therapeutic needs of individual patient. The results emphasize the potential of integrating computational techniques with 3D printing to transform the design of personalized medications and pharmaceutical manufacturing processes (Grof & Štěpánek, 2021).

Significant advancements in the field of decentralized and on-demand pharmaceutical manufacturing are being achieved through the integration of AI and vat photopolymerization 3D bioprinting. AI can analyze regional demands to facilitate the real-time production of medications, thereby assuring timely accessibility in clinical or remote settings and minimizing supply chain disruptions. The pharmaceutical sector has found 3D printing to be a particularly transformative application due to its capacity to enable personalized medication. 3D printing facilitates the development and manufacturing of customized medications by utilizing patient-specific data, including demographic characteristics, physiological requirements, and genomic profiles. These formulations are designed to optimize therapeutic efficacy and reduce adverse effects, thereby signaling a paradigm shift from traditional, one-size-fits-all therapeutic approaches and aligning with the principles of precision medicine (Alzoubi et al., 2023; Kaushik et al., 2023; Parihar et al., 2024). As it evolves, 3D printing is poised to revolutionize pharmaceutical manufacturing by enabling a transition from traditional, centralized, large-scale production to decentralized, on-demand systems. This transformation has the potential to completely redefine the availability, accessibility, and customization of drugs in contemporary healthcare by offering patient-centric solutions that are both flexible and adaptable to the changing requirements of global populations (Suriyaamporn et al., 2024).

In the era of Industry 4.0, the convergence of AI, the Internet of Things (IoT), and advanced manufacturing is revolutionizing the pharmaceutical industry with a focus on developing transformative solutions that directly improve the quality of life rather than merely optimizing production on a small laboratory scale. This revolution in the pharmaceutical industry is particularly advantageous to the healthcare and pharmaceutical sectors. During the manufacturing process, the integration of IoT-enabled smart systems enables the collection of real-time data and feedback. By enabling high precision and quality control, these systems ensure that each product meets its required specifications. AI optimizes production parameters, anticipates potential issues, and reduces waste by analyzing extensive datasets. In addition, these technologies have the potential to enhance the accessibility of healthcare. Decentralized, in-house manufacturing, enabled by 3D printing and smart technologies, has the potential to introduce vital innovations and reduce costs in underserved regions. With the ongoing evolution of these advancements, the emphasis will be redirected toward holistic well-being and individualized care, thereby redefining the way we approach medicine and manufacturing (Suriyaamporn et al., 2024).

9. CONCLUSION AND FUTURE PERSPECTIVES

Polymeric bioinks for vat photopolymerization 3D bioprinting have the potential to transform the pharmaceutical industry by facilitating the development of personalized medical treatments. These technologies enable the advanced development of bioinks that are capable of encapsulating drugs or cells, thereby improving the controlled release of drugs and enhancing the customized efficacy of treatment. Aided by technical improvements, future directions will focus on improving the biocompatibility and mechanical properties of these bioinks to enhance their clinical applicability (Simon et al., 2024; Tracy et al., 2023). The integration of advanced computational modeling to predict the behavior and stability of bioprinted structures in physiological environments will improve the predictability and efficacy of implantable therapeutics and regenerative medicine applications (Bardini & Di Carlo, 2023; Wistner et al., 2023). In addition, the integration of bioprinting with telemedicine and artificial intelligence has the potential to transform the accessibility of emergency medicine and treatment in remote or underserved regions, as well as to enable remote diagnostics and the on-demand fabrication

of medical products at or near the point of care (Kok et al., 2022; Pathak et al., 2023). The development of novel bioinks and sophisticated 3D printing vat photopolymerization methods has revolutionized personalized healthcare and complex drug delivery systems. Future advancements in personalized medicine may concentrate on developing bioink systems that exhibit greater versatility and respond in real time to the unique reactions of individual patients. This 3D printing technology will improve medical and pharmaceutical treatment outcomes by providing customized and patient-specific therapy (Xu et al., 2021). Moreover, the integration of AI in vat photopolymerization is revolutionizing additive manufacturing in the pharmaceutical industry. These technologies enhance precision, speed, and scalability, enabling the production of complex, personalized medical devices and drug delivery systems. AI-driven models optimize printing processes, improve material properties, and ensure consistent quality. However, while challenges such as multi-material complexity and data limitations remain, advancements in hybrid algorithms and bioresin formulations are beginning to resolve these problems. As Industry 4.0 evolves, the synergy of AI, IoT, and advanced manufacturing promises transformative opportunities, redefining production paradigms and enhancing healthcare through tailored, efficient, and accessible solutions (Suriyaamporn et al., 2024).

ACKNOWLEDGMENTS

This research was supported by the National Research Council of Thailand (NRCT: N42A650551). The authors thank the Faculty of Pharmacy, Silpakorn University, Nakhon Pathom, Thailand, for providing facility support.

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