Review: biobased photopolymers for additive manufacturing

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Review: Bio-based photopolymers for additive manufacturing

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Title: “"A review on photopolymers for additive manufacturing: mechanisms, technologies, and the shift towards bio-based precursors"

Authors: Francesca Sacchi, Giovanna Colucci, Federica Bondioli, Marco Sangermano, and Massimo Messori

Dear Editor,

We appreciated your suggestion about the title of our paper. Accordingly, we have changed the title. The new one is “Review: Bio-based photopolymers for additive manufacturing”

A revised manuscript version has been uploaded for submission tracked changes in red. We hope that now the paper can be accepted for publication in Journal of Materials Science. Please let us know if further revision is needed.

Thank you for your time and effort in handling our manuscript.

My best regards,

Giovanna Colucci on behalf of all authors

Editors comment:
Please could you consider changing the title to "Review: Biobased photopolymers for additive manufacturing". We require the format "Review:...." now but are also encouraging authors to shorten titles for their papers. Once this has been done I will be able to accept the paper.

We appreciated the Editor suggestion about the title of our paper. Accordingly, we have changed the title. The new one is “Review: Bio-based photopolymers for additive manufacturing” as reported in the revised version of the paper.

Review: Bio-based photopolymers for additive manufacturing

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Abstract

This review aims to provide a comprehensive overview of photopolymers for Additive Manufacturing (AM) applications, with particular attention to the 3D Printing (3DP) processes for thermosetting polymeric materials, and the main mechanisms and reactions involved during their photopolymerization process.

The introduction highlights the principles and significance of photopolymerization in AM. It is followed by an exploration of free-radical (FRP) and cationic photopolymerization (CP), the two main mechanisms underpinning these processes.

The focus then shifts to the AM technologies suitable for photopolymer processing. Photopolymer-based AM technologies, such as vat photopolymerization (VPP) and ink-jet (IJ) photopolymerization, are examined in detail. VPP has been widely studied for its ability to produce 3D printed components with highly complex geometries and good final resolution by selectively curing liquid resin in a vat through targeted light-activated polymerization reactions. Similarly, IJ, which involves depositing droplets of photocurable resins in a controlled manner and curing them with light, offers precise material deposition, enabling the creation of more detailed and intricate structures.

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in photopolymerization for AM, emphasizing innovations in bio-based precursors and advancements in AM technologies.

Keywords
Photopolymerization; additive manufacturing; vat photopolymerization; ink-jet; bio-based photopolymers.

Abbreviations

Abbreviation	Description
2PP	Two-Photon Polymerization
3DP	Three-Dimensional Printing
ABS	Acrylonitrile butadiene styrene
AESO	Acrylate Epoxidized Soybean Oil
AM	Additive Manufacturing
AP	Anionic Photopolymerization
BAPO	Phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide
BJ	Binder Jetting
CAD	Computer-Aided Design
CIJ	Continuous Ink-jet Printing
CLIP	Continuous Liquid Interface Printing
CNC	Cellulose Nanocrystals
CP	Cationic Photopolymerization
DED	Directed Energy Deposition
DLP	Digital Light Processing
DLS	Digital Light Synthesis
DMD	Digital Mirror Device
DOD	Drop-on-Demand
DPI	Dots per inch
DPP	Daylight Polymer Printing
EAS	Epoxidized Allylsoyate
EMS	Epoxidized Methylsoyate
ESO	Epoxidized Soybean Oil
FDM	Fused Deposition Modeling
FRP	Free-Radical Photopolymerization
FRPCP	Free-Radical Promoted Cationic Photopolymerization
Gel	Gelatine
GelMA	Methacrylate Gelatine
HL	Hot Lithography
IJ	Ink-jet
IPF	International patent family
LCD	Liquid Crystal Display

LED	Light-Emitting Diode
MAESO	Methacrylates Epoxidized Soybean Oil
MCC	Microcrystalline Cellulose
ME	Material Extrusion
MEMS	Micro-Electro-Mechanical System
MJ	Material Jetting
MW	Molecular Weight
NIR	Near-Infrared Light
PA	Polyamide
PBF	Powder Bed Fusion
Ph	Phenyl
PI	Photoinitiator
PIP	Piezoelectric Ink-jet Printhead
PLA	Polylactic Acid
PS	Photosensitiser
ROP	Ring-Opening Photopolymerization
SL	Sheet Lamination
SLA	Stereolithography
SLS	Selective Laser Sintering
STL	Standard Triangulation Language
SDG	Sustainable Development Goal
T_g	Glass Transition Temperature
TIJ	Thermal Ink-Jet Printing
TPO	Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide
UV	Ultraviolet light
VDA	Vanillin Diacrylate
VDM	Vanillin Dimethacrylate
Vis	Visible light
VO	Vegetable Oil
VOC	Volatile Organic Compound
VPP	Vat Photopolymerization

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1. Introduction

Polymeric materials remain essential in modern society due to their remarkable efficiency and cost-effectiveness. Their different properties make them indispensable across a wide range of applications, attracting substantial interest from both the scientific community and industry. Polymers are particularly valuable in the context of additive manufacturing (AM), also known as three-dimensional printing (3DP), that enables the creation of parts with specific properties tailored for various applications.[1]

AM contains a broad spectrum of technologies that fabricate physical objects by adding material layer by layer based on a geometric model. Currently, these technologies are employed in fields such as engineering, medicine, education, architecture, cartography, toys, and entertainment.[1–5]

The ISO/ASTM 52900:2015(E) standard defines AM as *"a process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies".* This definition highlights the fundamental distinction between AM, which constructs objects incrementally from a digital model, and traditional subtractive methods, where the material is removed from a solid block.[3]

AM is recognised as an eco-friendly manufacturing technology and has the potential to decrease the total carbon dioxide emissions by up to 525.5 Mt by 2025. In product development, employing AM can cut development costs by as much as 70% and reduce time to market by up to 90%. These impressive advantages contribute to the projected growth of the global AM market, which is projected to reach between €208 billion and €497 billion by 2025.[2, 5, 6]

The primary markets identified for 3DP include consumer products (estimated at €90 billion to €271 billion), medical components and transportation products (€90 billion to €181 billion), and tool and mould manufacturing (€27 billion to €45 billion). Wohlers Associates research from 2023 indicates that approximately 34.9% of all industrial AM technology systems are installed in North America, with Europe following closely behind at 30.7% and Asia-Pacific accounting for 28.4%. The remaining 6% of systems are distributed across Central and South America, the Middle East, and Africa. Compared to 2019, North America and Asia-Pacific shares have slightly decreased, while Europe and other regions have increased. As AM technology advances and global adoption expands, it will be critical to monitor how these regional trends evolve and how other regions contribute to the AM market growth.[5–8]

A remarkably large portion of AM technology study and use is within academia and research organizations, which is indicative of a real and valid involvement in the AM progress of the industry, which not only enriches the knowledge base but also promotes revolutionary advances in materials, processes and applications in the AM domain and provides a basis for technology start-ups with high growth potential. It serves as a crucial catalyst for digital transformation in manufacturing, connecting the physical and digital realms.[5]

AM of polymers is regarded as one of the most transformative technologies of the modern era, experiencing substantial growth since 2013. Polymers have consistently been the leading material category in AM, with over 8.500 International patent families (IPFs) recorded over time and a notable surge in patent filings from approximately 300 per year in 2013 to nearly 1.100 in 2020. As the largest segment in the AM materials market, polymers—available in forms such as powders, photopolymers, and filaments—offer a diverse and expanding selection. However, their variety remains more limited compared to traditional subtractive manufacturing methods. Notably, in 2021, photopolymers accounted for the second largest share of the global materials market for AM with 25.2%, second only to polymer powders.[5]

Regarding academic research, several scientific articles have been published that explore various aspects of the different technologies that can be used for polymers to date, highlighting the peculiarities of the technological application, and the properties that can be achieved.[9–15]

Limiting this review to thermosetting polymers, it is important to emphasise that AM technologies for these materials present today on the market use photo-crosslinkable resins.[16–21]

Considering this scenario, this review reports the results of a systematic literature review, focusing on relevant studies and scientific publications related to AM and photopolymers. Academic databases such as Google Scholar, PubMed, Scopus, Web of Science, ScienceDirect and SpringerLink were used to collect data. The main keywords used in the searches included photopolymerization, AM, vat (VPP), ink-jet (IJ) photopolymerization, and bio-based photopolymers.

The review is structured as follows: after the introduction on the importance of polymeric materials and AM in the contemporary context, highlighting their efficiency and cost-effectiveness which aroused considerable interest in both the scientific community and industry, Section 2, and its subchapters, explores the concept of photopolymerization and the main reaction mechanisms, with particular emphasis on the advantages and limitations of these methodologies. The main differences between the different types of photopolymerization and how these technologies can be employed in specific applications are widely analysed.

The evolution of manufacturing processes is discussed in Chapter 3, focusing on the importance of AM, especially photopolymerization-based AM, as a key tool for Industry 4.0.

Furthermore, AM is considered green, as it contributes to the reduction of waste and CO_2 emissions, as well as offering the potential to reduce development costs and time to market. Despite progress, challenges remain, such as the need to develop new sustainable materials and improve the properties of the polymers used. However, the growing interest in this technology opens new research opportunities and industrial applications, revolutionizing the manufacturing processes and supply chains.

Chapter 4 and its subchapters deal firstly with VPP, examining the details of this process that uses a liquid resin solidified layer by layer by the action of a UV light source. The advantages, applications, and limitations of this technology are discussed. Then IJ, an emerging technology that allows the deposition of photopolymers in the form of droplets through inkjet printheads, is explored underlining the operation of the process, its advantages in terms of precision and flexibility, as well as its applications.

The last chapter addresses the transition towards the use of bio-based thermoset monomers instead of those derived from fossil sources. The environmental, economic and technological benefits of this transition are discussed, as well as the challenges related to the production and use of more sustainable materials in additive manufacturing.

In the concluding chapter, the main developments described in the paper are summarized with a focus on the future implications of photopolymerization and AM technologies. Open challenges, R&D opportunities and prospects for the adoption of bio-based polymers in AM are also discussed.

2. Photopolymers

Photopolymerization involves the formation of long-chain macromolecules through the ongoing reaction of monomers when exposed to electromagnetic radiation. The principle of a typical photopolymerization process is schematically provided in Figure 1.

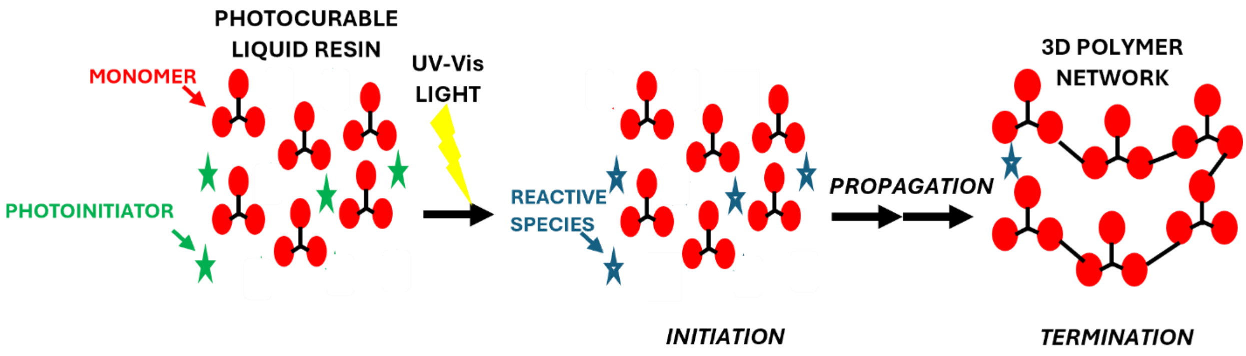

Figure 1. Schematic representation of photopolymerization mechanism.

This process requires the absorption of energy by a photoactive agent, which facilitates the creation of new chemical bonds. These photoactive agents absorb light in the UV-Vis spectral region, generating electronically excited states that either directly crosslink or transform light energy into chemical energy as reactive intermediates.[22]

This exposure initiates a chemical reaction that causes monomers or oligomers to crosslink, resulting in the formation of a solid 3D polymer network. This crosslinking creates a rigid and insoluble network, rendering the material permanently set and resistant to melting or reshaping.[1, 22–25]

Unlike thermal polymerization, which typically requires elevated temperatures, photopolymerization can be conducted at room temperature, without the need for high temperatures, often reducing or eliminating the emission of volatile organic compounds (VOCs), providing a significant advantage for monofunctional monomer polymerization and polymerization applications. Thermosets and photopolymers are intrinsically linked through their shared chemical behaviour, specifically their ability to form cross-linked polymer networks. However, while thermosets harden upon exposure to high temperatures through thermal polymerization, photopolymers undergo polymerization upon exposure to light, typically ultraviolet (UV) or visible (Vis) light. Usually, monomers alone cannot generate the reactive species necessary for photopolymerization upon light exposure.[24, 26–28]

Thus, it is necessary to have in photocurable resin specific photo-reactive molecules, known as photoinitiators (PIs), that can generate reactive species such as free radicals, anions, or cations upon exposure to UV-Vis, or near-infrared (NIR) light, depending on the involved photopolymerization mechanism (FRP and/or CP).[1, 29] Identifying the active species that interact with electromagnetic radiation to form 3D networks with crosslinking points between different polymeric chains is crucial, because they influence both the curing speed and the cost of the process.

Moreover, when selecting a PI, some factors such as commercial availability, solubility in monomers, storage stability, minimal migration, absence of undesirable odour, and ability to prevent yellowing of the cured material, must be considered.[30] The light absorption characteristics of some PIs are illustrated in Figure 2, which highlights the UV-Vis spectra of some well-known radical PIs in Figure 2 (a) and cationic PIs in Figure 2 (b), such as onium salts, including iodonium and sulfonium salts.
Figure 2 (b), which also reported the chemical structures of these PIs, compares the absorption spectra of some cationic PIs with the emission spectra of light sources generally used in 3DP, which are primarily UV (365 nm) or visible (405 nm) LEDs. The characteristics of the light source used in photopolymerization are particularly important and must be carefully defined because they directly influence the choice of materials and the result. The wavelength of the light source mainly determines the selection of the PI, which must be done to ensure the overlap between the emission wavelength of the source and the absorption wavelength of the PI.

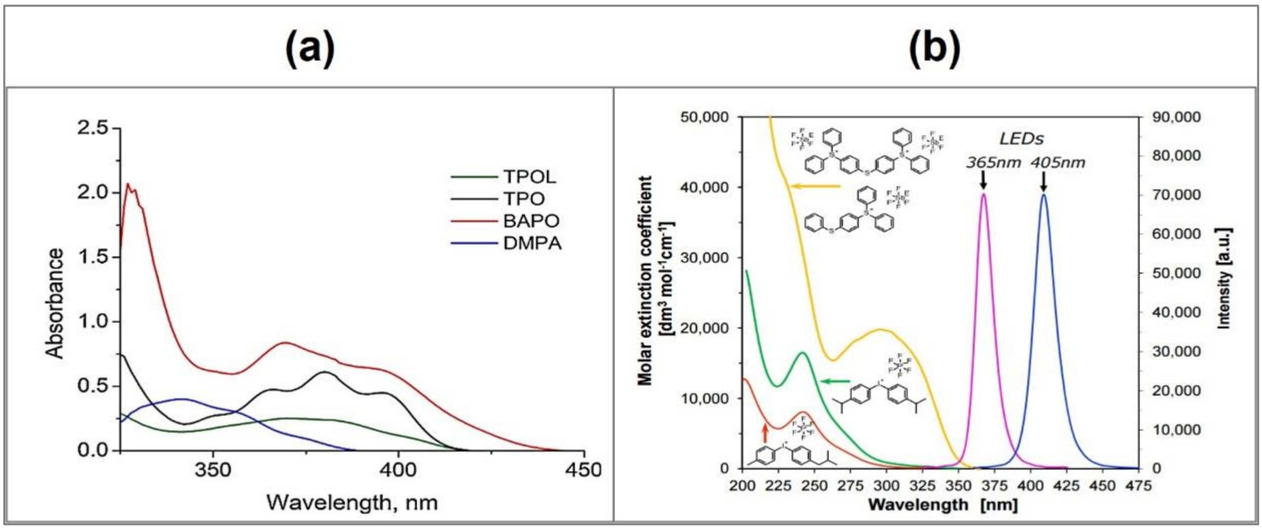

Figure 2. Comparison between UV-Vis spectra of (a) radical PIs (TPOL: ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate; TPO: diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide; BAPO: phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide; DMPA: 2,2-dimethoxy-2-phenyl acetophenone)[31]; (b) iodonium and sulfonium salts cationic PIs.[32]

Moreover, the photopolymerization rate and efficiency are both influenced by the intensity and resolution of the light source employed in the process while the exposure time required for the photopolymerization of the liquid resin plays a crucial role to minimize the amount of unreacted monomer at the end of the process, ideally reducing it to zero or near-zero levels.
Studies have shown that a range of light sources with wavelengths between 200 and 700 nm can be used to polymerise photosensitive liquid resins to be compatible with the absorption spectrum of the chosen PI. Mercury lamps, with their continuous emission spectrum, offer a wide wavelength

coverage but global environmental protection initiatives have supported the transition to the use of light-emitting diodes (LEDs). LEDs emit light at specific, discrete wavelengths, typically around 365, 385, 395 and 405 nm (±5 nm), resembling a monochromatic spectrum, as visible in Figure 2 (b).[28] LEDs provide advantages such as higher energy efficiency, "cold cure" capabilities, and instantaneous start-up. However, their major limitations are the lower light intensity, affecting the complete polymerization depending on layer thickness, and the efficiency of surface and depth polymerization. Nevertheless, LED technology is increasingly used in UV IJ applications.[33] As a result, some PIs, which are effective with mercury lamps, may not be compatible with LED lamps.

To address this issue, photosensitisers (PSs) are employed as reactive species that can extend the activation wavelength of PIs toward the red end of the spectrum.[34] PSs typically have electron-rich chemical structures that exhibit strong absorption characteristics in the near UV-Vis region of the spectrum. They possess high molar extinction coefficients, minimal oxygen inhibition, enhanced reactivity with photolysis of onium salts, which are the PIs used in CP, prolonged excited states, and well-matched absorption properties to the emission spectra of the relevant irradiation devices.

PSs offer additional benefits such as wide availability, good solubility, stability, reduced costs, and low toxicity.[35] This limitation has spurred extensive research into developing PIs that are better suited to the UV-Vis spectrum typical of modern LED sources. For instance, in CP, the absorption peaks of commonly used PIs are often lower than the emission peaks of current LED technologies, as shown in Figure 2(b), necessitating the inclusion of PSs to extend the spectral sensitivity of PIs.[36] Therefore, the selection of PIs, PSs, and sources, depends on the reaction mechanism and the starting monomer used.

In photopolymerization reactions, the absorption of UV energy by the PI initiates a series of energetic processes. Initially, a high-energy singlet state is generated, which can transform into a more stable but less energetic triplet state through intersystem crossing. Most PIs generate radicals from the triplet state, although some can also interact from the excited singlet state, as depicted in the so-called Jablonski diagram (Figure 3).[33]

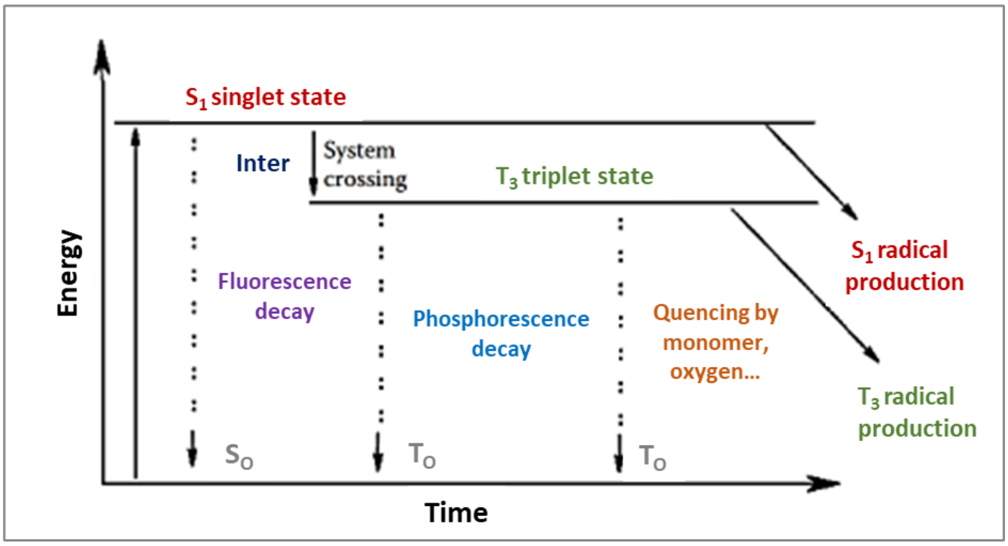

Figure 3. Jablonski diagram showing energy vs. time.

Multiple decay processes can occur from the excited states. The singlet state may revert to the ground state through fluorescence or transition to an excited triplet state via intersystem crossing. The triplet state might decay via phosphorescence, be suppressed by monomers or oxygen, or proceed to generate radicals through various chemical mechanisms. For effective polymerization, a PI must efficiently absorb energy and enter an excited state, ensuring uniform absorption throughout the film layer to achieve complete depth curing.[33]

As previously mentioned, depending on the monomer chosen, a specific reaction mechanism is involved: acrylate/methacrylate and thiol-based monomers typically follow the FRP mechanism, while epoxy resins are the most reactive for CP.[37–39] FRP resins cure quickly but often result in high volumetric shrinkage and are susceptible to inhibition by oxygen, which can prevent complete polymerization.[22, 26] In contrast, CP mechanisms are not hindered by oxygen and generally offer better mechanical and physical properties with reduced shrinkage, although these processes are slower, moisture-sensitive, and require higher radiation power.[39]

Photopolymers are commonly employed in VPP and IJ AM technologies, as noted by Crivello and Reichmanis in the past, the significance of photopolymer technology is profound, influencing nearly every aspect of modern life. [40–42]

2.1 Free-Radical Photopolymerization

Radicals are charged species containing an unpaired electron, forming the fundamental component of any photocurable FRP system through light absorption by the PI. These active radicals subsequently engage with the monomer, initiating a chain growth polymerization process that ultimately terminates. Oxygen inhibition poses a significant challenge in FRP curing, with two primary issues arising. Firstly, oxygen tends to quench the lowest excited triplet state of many aromatic rings. Secondly, the initiation process can be hindered as free radicals may also be quenched, resulting in inefficient polymerization initiation.[22]

Measures to exclude oxygen include the application of inert gases, such as nitrogen, the use of transparent sheets, or paraffin waxes, the choice of PIs insensitive to oxygen, or the use of new technologies still available on the market, instruments that will be described in the following chapters.[43]

Achieving adequate photo-crosslinking both on the surface and through the layer in the air is, therefore, a critical issue, especially for thick samples, as the greater the thickness, the more difficult it is to obtain homogeneous photo-crosslinking in the sample. In general, as the sample thickness increases, the ability to achieve high monomer-to-polymer conversions decreases.

The FRP mechanism involves several steps, with the first being initiation, subdivided into dissociation (1) and association (2).

In dissociation, the PI molecule is cleaved upon light exposure, generating radicals with active sites.[22]

$$\mathbf{PI} \rightarrow \mathbf{2R^{\bullet}} \quad (\mathbf{1})$$

Where remember that $\mathbf{PI}$ is the photoinitiator and $\mathbf{R^{\bullet}}$ is radical with the active site.

This reaction is driven by light, in the case of photopolymerization, to break the chemical bonds and to produce the radical species.

Thus, the radical is transferred to the monomer by addition mechanism:

$$\mathbf{R^{\bullet}} + \mathbf{M} \rightarrow \mathbf{RM^{\bullet}} \quad (\mathbf{2})$$

The propagation of the chain (3-4) continues until there is a monomer available.

$$\mathbf{M_1^{\bullet}} + \mathbf{M} \rightarrow \mathbf{M_2^{\bullet}} \quad (\mathbf{3})$$

$$\mathbf{M_i^{\bullet}} + \mathbf{M} \rightarrow \mathbf{M_{i+1}^{\bullet}} \quad (\mathbf{4})$$

where $\mathbf{M}$ is a monomer and after the joint with the radical group $\mathbf{R}$ it became $\mathbf{RM^{\bullet}}$, a polymer chain that can be defined $\mathbf{M_1^{\bullet}}$ that is still able to continue to react and for this reason is called active polymeric chain.

In general, this process occurs when an active polymer chain, denoted as $\mathbf{M_i^{\bullet}}$, reacts with another monomer unit, $\mathbf{M}$, resulting in the continuous of the polymeric active chain of length "**i+1**," termed as $\mathbf{M_{i+1}^{\bullet}}$.

The final stage of this reaction, known as termination, involves the transfer of the radical away from the active polymer chain, resulting in the formation of inactive polymer structures. Termination can occur through two mechanisms, one of which typically prevails depending on the specific polymer and reaction conditions. Terminal radicals with easily transferable hydrogen atoms are more likely to undergo disproportion, while more stable or less sterically hindered radicals tend to terminate through combination. This termination process influences the polymer chain length and end-group structure. Research by Nakamura *et al.* demonstrated that in macromolecular systems, viscosity plays a critical role in determining the preference between disproportion and combination, with disproportion becoming increasingly favoured as viscosity increases.[44]

The first termination mechanism, disproportion (5), requires each molecule involved to transfer its radical to form an inactive chain. For instance, if two active chains are present in a reacting system, after termination, two resulting inactive polymeric chains will remain in the system:

$$\mathbf{M_i^{\bullet} + M_j^{\bullet} \rightarrow P_i + P_j \ (5)}$$

In contrast, in the other mechanism, combination (6), a pair of active polymer chains merge to form a single inactive polymeric chain with a length equal to the sum of their lengths, thereby losing their radicals:

$$\mathbf{M_i^{\bullet} + M_j^{\bullet} \rightarrow P_{i+j} \ (6)}$$

where $\mathbf{M_i^{\bullet}}$ and $\mathbf{M_j^{\bullet}}$ respectively represent two generic active polymer chains with lengths or polymerization degree of "**i**" and "**j**", $\mathbf{P_i}$ and $\mathbf{P_j}$ respectively denote the inactive chains with lengths of "**i**" and " **j**" formed from $\mathbf{M_i^{\bullet}}$ and $\mathbf{M_j^{\bullet}}$, instead $\mathbf{P_{i+j}}$ signifies the inactive chain obtained from the combination of the two active chains with a length of "**i+j**".[22]

PIs are essential for initiating photopolymerization, and they can be classified into two main types: Type I and Type II. The primary difference between them lies in their cleavage and activation mechanisms. Type I PIs undergo a direct photolysis process when exposed to UV or visible light. Upon absorbing light energy, they dissociate into free radicals, which immediately initiate the polymerization process. This mechanism is highly efficient since it does not require any co-initiators.

As a result, Type I PIs are often used in applications where rapid polymerization is required. Examples include benzoin and its derivatives and substituted acetophenones.

Among Type I PIs, those that undergo α- or β-cleavage upon interaction with electromagnetic radiation are notable, such as phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) and diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO), whose chemical structural formulas are shown in Figure 4. BAPO is known for its superior efficiency, especially with modern 3DP technologies that use LED light sources with a maximum emission wavelength of 405 nm. It exhibits a broader absorption spectrum, extending to approximately 450 nm, compared to TPO, which terminates just beyond 400 nm. BAPO also produces more free radicals than TPO, enhancing its performance in polymerization.[45]

Type II photoinitiators require the presence of a co-initiator, such as an amine or hydrogen donor, to generate free radicals. Upon exposure to light, Type II PIs absorb energy and enter an excited state, where they transfer energy to the co-initiator. This energy transfer or electron transfer process enables the co-initiator to produce the free radicals that drive polymerization. As a result, Type II PIs are generally slower and less efficient than Type I PIs but can be tuned for specific applications where this characteristic is desirable.

Typical examples of Type II PIs include benzophenone, xanthones, camphorquinone, anthraquinone, and fluorenones, with some examples of chemical structures shown in Figure 5. In summary, the main distinction is that Type I photoinitiators directly produce free radicals via homolytic cleavage, leading to faster and more efficient polymerization. In contrast, Type II photoinitiators require a co-initiator to produce free radicals, making them less efficient but more adaptable for particular use cases.[28, 46–48]

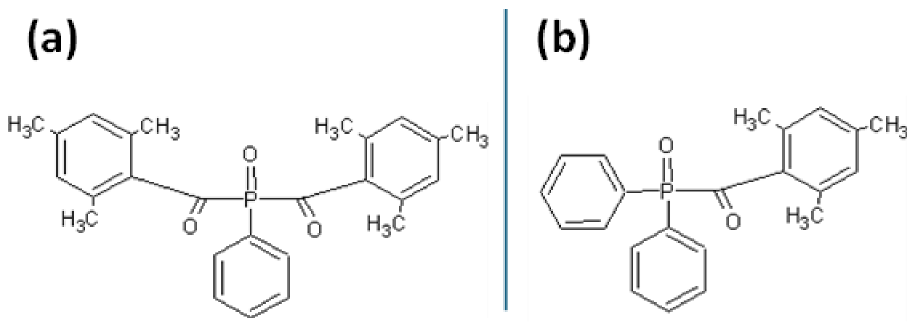

Figure 4 Structural chemical formula of phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) (a), and of diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) (b).

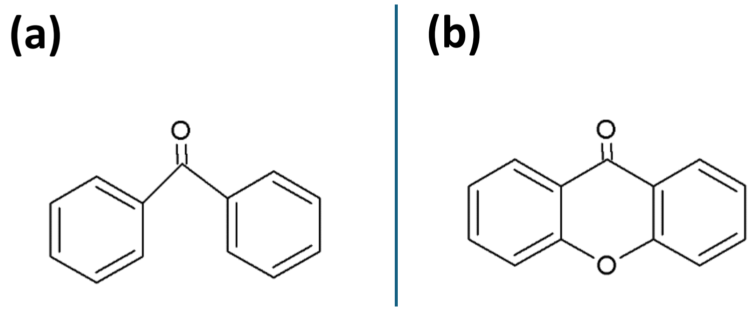

Figure 5 Structural chemical formula of Structural chemical formula of benzophenone (a), and xanthones (b).

2.2 Cationic Photopolymerization

The primary benefit of this photopolymerization mechanism is that it is not sensitive to oxygen, allowing photopolymerization in the presence of air without the need for an inert atmosphere. Cationic PIs are commonly used in the ring-opening photopolymerization (ROP) mechanism, and they have been designed and developed for polymerising epoxy-based monomers and prepolymers.[30, 34, 35, 49, 50] Furthermore, more stable PIs have been discovered, including various onium salts like sulfonium, iodonium, pyridinium, phosphonium, bismuthium, anilinium, and pyrylium salts. Figure 6 presents some representative examples of these compounds.[49, 51]
Among these onium salts, specifically iodonium in Figure 6 (a) and sulfonium in Figure 6 (b) salts, represent the most widely used classes of cationic PIs. The ability of onium salts to promote CP under UV radiation was first highlighted by Crivello in the 1970s.[49]

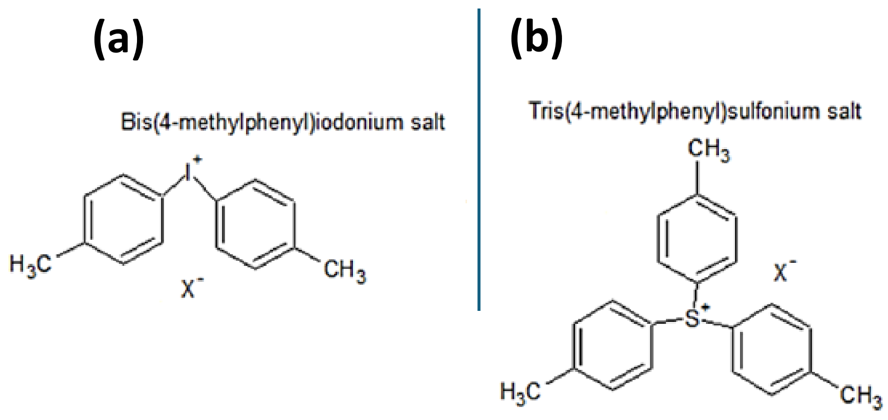

Figure 6. Chemical structure of iodonium or sulfonium salts used as cationic PIs.

Onium salts consist of two components: a cationic centre, typically a heteroatom, and an inorganic counter anion (BF_4^-, PF_6^-, AsF_6^-, or SbF_6^-).[50, 52] The cationic part is responsible for absorbing light, and it is the site of photochemical reactions. Consequently, the structure of the cation influences the UV absorption characteristics, photosensitivity, quantum yield, potential for photosensitization, and thermal stability of the formulation. The anionic component of salt, instead, determines the strength of the acid generated during photolysis and its initiation efficiency.[53] The nucleophilicity and strength of the generated protons increase with the size of the counter anion. Additionally, the nature of the anion affects the characteristics of the propagating ion pair, influencing the polymerization kinetics and termination rate. Thus, these salts act as photoacid generators.[30, 34, 35, 49]

Research by Crivello and Watt demonstrated that the optimal curing speed of cationic active species under UV radiation is achieved with 2-3 wt.% of aromatic onium salts, which act as PIs for the reaction. At concentrations below 1 wt.%, the reaction kinetics are inhibited, and at concentrations above 3 wt.%, there is no additional increase in the reaction rate.[51, 53]

In the case of onium salts, the introduction of electron-donor groups, like methoxy, methylthio, or dimethylamino in the *para* position relative to the halogen group on the aromatic ring causes a slight red shift in the absorption band. Villotte *et al.* explored substituting one benzene ring of an iodonium salt with coumarin (shifting absorption to 350 nm), naphthalimide (shifting absorption to 395 nm), or anthracene (shifting absorption to 410 nm), which effectively dissociates onium salts under various irradiation conditions.[52]

Chemical modifications of onium salts, such as adding chromophore groups to the aromatic rings, can alter the activation wavelength.[30, 35, 54, 55]

Another class of PIs includes dialkylphenacylsulfonium salts, which can undergo reversible photolysis. Upon irradiation, they yield strong Brønsted acids, but the reversible nature leads to rapid termination in the absence of UV light. Conversely, alkoxy pyridinium salts exhibit excellent thermal stability and high solubility, although their synthesis and purification are complex and costly, often failing to achieve the desired absorption characteristics.[52, 56]

Many researchers consider cationic PIs superior to free radical ones because they are not affected by oxygen quenching, can be easily sensitized by dyes in the visible spectrum, and can be thermally post-cured.[34]

The CP mechanism involves several steps.[57] The initiation step (7) involves the formation of a strong acid cation (H^+ or Ph^+):

$$\mathbf{PI}\ (\mathbf{Ph_2I^+}) \rightarrow\ \mathbf{PI}^* \rightarrow\rightarrow\rightarrow\ \mathbf{Ph^+}\ (\mathbf{7})$$

In this context, $\mathbf{PI}$ refers to the photoinitiator, while $\mathbf{PI}^*$ represents the excited state of $\mathbf{PI}$ ($\mathbf{Ph_2I^+}$), indicated by an asterisk (*), which signals a temporarily unstable electronic configuration, and $\mathbf{Ph_2I^+}$ represents the cationic moiety of the iodonium salt and $\mathbf{Ph}$ stands for a phenyl group (C_6H_5). Specifically, the molecule comprises two phenyl groups ($\mathbf{Ph_2}$), which are benzene rings (as illustrated in Figure 6). These phenyl groups are attached to a central ion, iodonium ($\mathbf{I}$) in this case.

In this example, the $\mathbf{Ph_2I^+}$ species carries a positive charge, as it corresponds to a diaryliodonium cation, namely diphenyl iodonium. This cation is paired with an anion, such as SbF_6^-, PF_6^-, or other anions, forming a salt. The general formula for an iodonium salt is typically expressed as $\mathbf{Ph_2I^+PF_6{}^-}$.[30]

Upon irradiation, the $\mathbf{Ph_2I^+}$ cation undergoes decomposition, producing a reactive species (e.g. $\mathbf{Ph^+}$), which acts as a strong acid. The use of onium salts facilitates the photopolymerization of various monomers that are sensitive to cationic initiators. In summary, $\mathbf{Ph_2I^+}$ represents the diaryliodonium ion, which is the central cation responsible for initiating the CP process.

Its decomposition, which can proceed via homolytic or heterolytic mechanisms (Figure 7), is followed by hydrogen transfer reactions, ultimately leading to proton formation.

Photosensitized decomposition may occur through energy transfer (8) or electron transfer (9) between the PI and PS.[30]

$$\mathbf{PS} \rightarrow \mathbf{PS}^* \rightarrow \mathbf{PI}^* \rightarrow\rightarrow\rightarrow \mathbf{Ph^+} \quad (\mathbf{8})$$

$$\mathbf{PS} \rightarrow \mathbf{PS}^* \rightarrow \mathbf{PS^{\bullet+}} + \mathbf{PI^{\bullet+}} (\mathbf{9})$$

In this context, $\mathbf{PS}$ refers to the photosensitiser, while $\mathbf{PS}^*$ represents the excited state of $\mathbf{PS}$, and $\mathbf{PS^{\bullet+}}$ is the radical cation of $\mathbf{PS}$, generated through an electron or energy transfer from the molecule in the excited state ($\mathbf{PS}^*$). Finally, $\mathbf{PI^{\bullet+}}$ is the radical cation of the $\mathbf{PI}$ molecule, produced by the reaction between $\mathbf{PS}$ to $\mathbf{PI}$.

Propagation of the chain (10) follows:

$$\mathbf{Ph^+} \ (\mathbf{or\ PS^{\bullet+}}) + \mathbf{cationic\ monomer} \rightarrow \mathbf{polymer} \quad (\mathbf{10})$$

Thus, the activation of onium salts and the possible mechanisms for this process are essential for efficient cationic polymerization. The potential mechanisms are:

- direct method, which involves a two-step process from photolysis to the initiation of polymerization, as shown in Figure 7.

- indirect method (Figures 8-9) uses PS in multi-component systems to enhance initiation performance. It also involves an onium salt (cationic initiator), a hydrogen donor, and a PS.

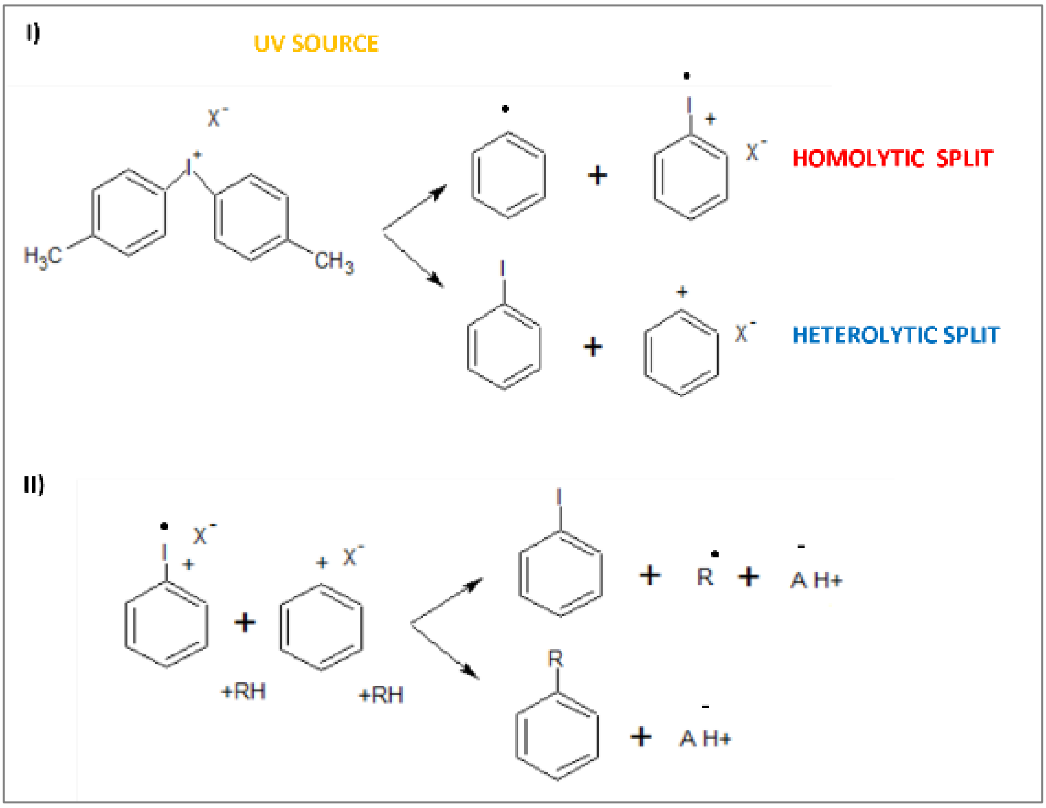

Figure 7. Direct activation mechanism of diaryliodonium salts for cationic ROP by photolysis (I), and Brønsted acid formation (II).

The literature reports three primary mechanisms of indirect activation: the first two are energy transfer and electron transfer, as sketched in Figures 8 and 9, respectively. Energy transfer requires high energy and is not commonly used.

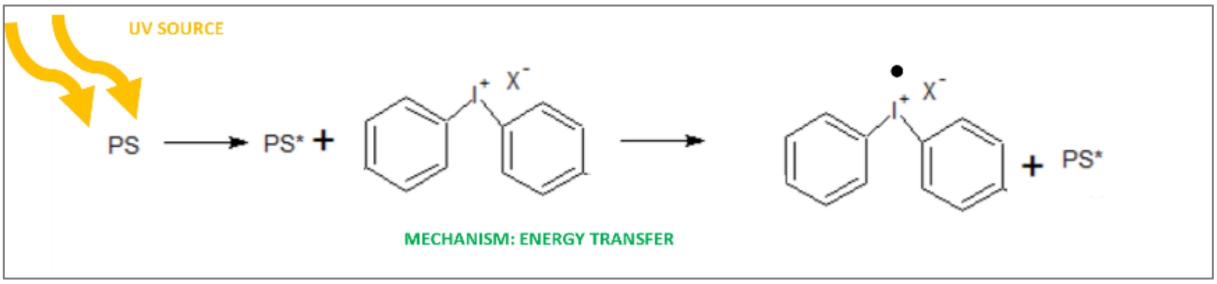

Figure 8. Indirect activation of diaryliodonium salts with energy transfer.

On the contrary, electron transfer is the most favoured process when using PSs due to its higher efficiency.[54]

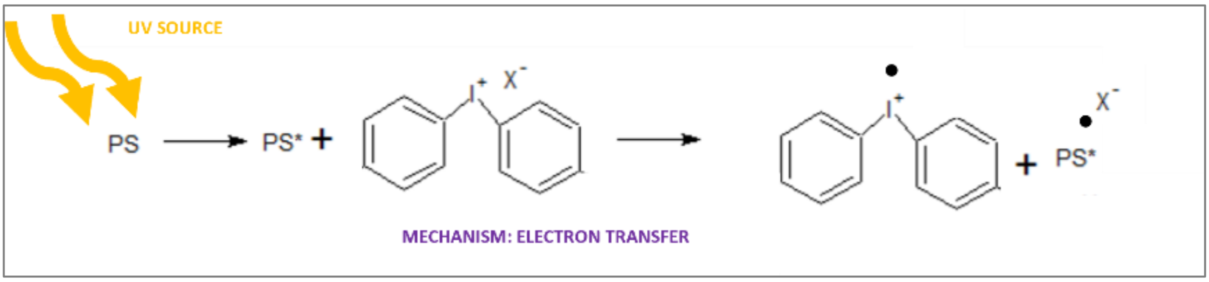

Figure 9. Indirect activation of diaryliodonium salts with electron transfer, photosensitization mechanism.

The third method is the free-radical-promoted cationic polymerization (FRPCP). It is an alternative designed to address the high energy demands of onium salt photolysis. This method uses radical PIs to generate radicals that react with onium salts. Due to its versatility, FRPCP is one of the most promising methods for CP under exposure to wavelengths higher than 350 nm.[23] In FRPCP, a radical $\mathbf{R}^{\bullet}$ is produced from a radical source (which can be a PI or a PS) and then oxidized by $\mathbf{Ph_2I^+}$ to form $\mathbf{Ph_2I^{\bullet}}$ and a cation $\mathbf{R^+}$, suitable for ROP of epoxides. $\mathbf{Ph_2I^{\bullet}}$ Then decomposes into $\mathbf{PhI}$ and $\mathbf{Ph^{\bullet}}$. This mechanism is shown in the reaction schemes 11-13 below:[57, 58]

$$\mathbf{PI \rightarrow PI^{*} \rightarrow R^{\bullet}} \quad \mathbf{(11)}$$

$$\mathbf{R^{\bullet} + Ph_2I^+ \rightarrow R^+ + Ph_2I^{\bullet}} \quad \mathbf{(12)}$$

$$\mathbf{R^+ + Ph_2I + Ph^{\bullet} + monomer \rightarrow polymer} \quad \mathbf{(13)}$$

FRPCP involves complex interactions between a PS, a cationic PI (such as onium salts), and a radical PI (such as BAPO). This process allows the photodecomposition of a cationic PI at higher wavelengths through free radical oxidation.[34]

Recently, new dyes based on phenylenediamine, polystilbene, and polyazine have been studied as PSs for the ROP of epoxides, enabling polyether synthesis under mild irradiation (halogen lamps, LED lamps, etc.).[58]

Monomers commonly used in CP mechanisms, such as epoxides, are generally less toxic and irritating compared to the acrylate- and methacrylate-based monomers used in FRP. While FRP is limited to monomers with olefinic double bonds, CP can polymerise compounds containing epoxide or vinyl ether groups, among others.[30, 34, 35]

Cured CP materials often exhibit superior abrasion and chemical resistance, as well as better adhesion to various substrates, compared to those obtained through radical photopolymerization.[35]

However, UV photopolymerization using CP has not yet reached the commercial significance of FRP for several reasons, including the advanced development of UV curing technologies for FRP, the early use of thermally unstable initiators like PI, and patent complications related to thermally stable onium salts.[30, 34, 35]

Despite these challenges, significant progress has been made in UV curing technology for CP, particularly for epoxy-functional resins with onium salts. Optimised combinations of PI for concurrent radical-cationic polymerization are expected to enhance light absorption and utilization. In CP processes, photosensitization involves a photoinitiator (PS)/PI pair, where excited PSs activate and reduce onium salts via energy or electron transfer, as demonstrated in previous studies.[22]

Unlike FRP, CP offers notable advantages, such as the ability to continue curing even after the light source is removed, due to the long-lived Brønsted acid generated by onium salts. This phenomenon, called "dark reaction", allows further monomer conversion without termination reactions, CP also benefits from the absence of oxygen inhibition, lower toxicity, reduced irritation from monomers, and minimized volume shrinkage upon curing, making it highly attractive for both academic and industrial applications.[25, 34, 35, 59, 60]

However, a major drawback of CP is its sensitivity to water vapour, which can terminate the reaction. In dry environments, the termination rate is low, allowing photopolymerization to proceed even after irradiation has ceased.[30]

Photoinitiated CP can rapidly produce crosslinked polymer films, using approximately one-tenth of the energy required for thermal polymerization to process the same amount of monomer.[50]

Industrial applications of CP processes include multifunctional cycloaliphatic epoxy-based formulations due to their high curing rates, excellent thermal and mechanical properties, solvent resistance, and adhesion to various substrates. These applications encompass coatings, composites, adhesives, inks, medical uses, and 3DP technologies.[49]

3. Additive Manufacturing Technologies

Since the inception of the industrial era, manufacturing processes have undergone rapid evolution. Existing methods and practices have been enhanced, novel technologies have been introduced, and the magnitude and scope of industrial production have grown significantly.[7]

Among these advancements, AM has emerged as a transformative technology, bridging traditional techniques with recent digital innovations. AM is a key enabler of technology of the fourth industrial revolution, also known as Industry 4.0, which integrates cutting-edge digital technologies and automation into industrial processes. This revolution promotes the use of interconnected systems, data-driven decision-making, and intelligent technologies in industrial processes. It has the potential to significantly impact organizational structures and encourage greater collaboration between factories, suppliers, and customers, resulting in improved business operations and efficiency across the entire manufacturing network.[5, 61, 62]

AM offers numerous advantages over traditional manufacturing processes, such as the removal of design limitations imposed by conventional methods, the ability to implement precise customization on small production runs, the consolidation of components that previously required multiple parts, the optimization of geometries and the creation of lightweight components.[2, 5, 24, 61, 63, 64]

AM 3D objects are created through the successive deposition of material layers. Each layer is meticulously formed atop the previous one under the control of a computerized system, enabling the production of complex hierarchical structures with high resolution and accuracy. A key advantage of AM is its ability to minimize material waste by facilitating on-demand production of spare parts, thereby enhancing sustainability.[24, 39, 63, 65–67]

The AM process involves several steps, as illustrate in Figure 10. It begins with the creation of a 3D model using computer-aided design (CAD) software. The designed geometry is then converted into a tessellated model and saved in the standard triangulation language (STL) format, a widely accepted file format in nearly all solid modelling CAD systems. The STL file is subsequently processed by specialized software, which slices the model into a sequence of two-dimensional (2D) parallel planes that define the layers to be printed. The thickness of these layers is a critical parameter that influences the surface quality and level of detail in the final object: thinner layers produce finer resolution but increasing the production time of the object.[46, 63]

Once the slicing process is complete, the AM machine software allows users to orient the part within the printer build volume and generate the necessary supports. Once the printing parameters are optimized and set, the process then proceeds layer by layer, with each new layer bonding to the previous one to form the final structure. Once complete, the printed part is removed from the build platform and subjected to post-processing steps, including removing supports and excess material by washing in a specially selected organic solvent. Finally, the properties of the manufactured sample are analysed to assess its suitability for various applications.[63, 68]

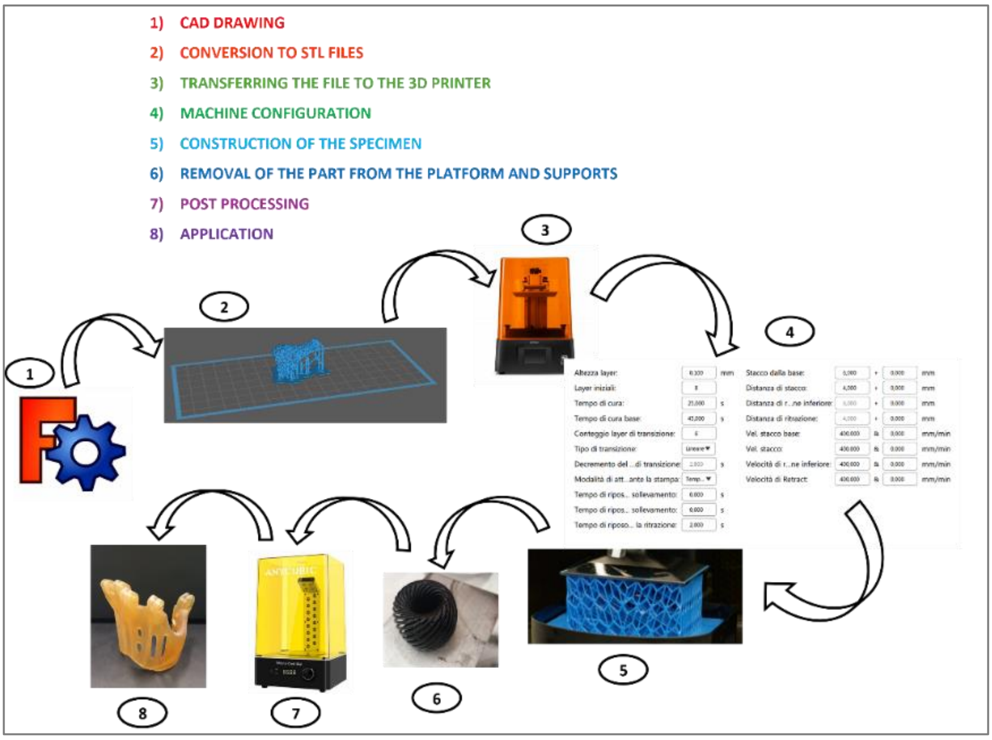

Figure 10. The eight steps of the AM process.

AM not only enables low-volume, customized production, and great design freedom, but multi-component parts can now be redesigned with improved performance and efficiently manufactured without assembly.[1,2]

This approach contrasts with conventional subtractive manufacturing technologies, which selectively remove material, and formative manufacturing technologies, which shape material via applied pressure.[2, 23, 24, 39, 63, 69, 70]

With ongoing research, new AM materials and methods are being developed, leading to an expanding range of applications. Indeed, a growing number of experts and researchers from various fields have adopted AM to fabricate complex structures, a trend reflected in the significant increase in publications over the past decade, underscoring the growing interest and potential in AM research.[23, 71]

Anderson[72] describes 3DP as a "new industrial revolution" highlighting its potential to facilitate more digitalized and localized processes within industries.

Gershenfeld[73] views 3DP as part of a societal transition that "transforms data into tangible objects and vice versa," thus contributing to a knowledge-driven economy. However, if 3DP applications experience rapid growth over the next decade, questions may arise regarding the sustainability of 3DP manufacturing processes.[7]

Despite recent progress in AM processes and technologies, significant research challenges persist, which include the need to develop new sustainable materials suitable for construction applications, optimize process parameters, advance computational modelling techniques, introduce reinforcements and enhancements to AM structures, and innovate new technologies. Current commercially available AM materials often lack the required high mechanical strength, temperature resistance, and functionalities such as thermal and electrical conductivity, biocompatibility, and shape memory behaviour for real part replacement. Consequently, extensive research efforts have been dedicated to developing new materials for polymer AM over the past decade. Conversely, ongoing improvements are continuously being made to AM systems to enable printing with a broader range of materials and achieve better resolution, higher accuracy, and significantly faster production rates.[2, 71] AM can fabricate parts ranging in size from the micro- to macro-scale and has the potential for mass production of complex geometries. Therefore, 3DP can produce lighter, more intricate, and more substantial parts.[13, 19, 63, 71, 74]

Indeed, this technology has found applications in numerous fields, including automotive, aerospace, construction, and the medical and dental industries, each utilizing AM technologies for various purposes, as summarized in Figure 11.[5, 39, 63, 75]

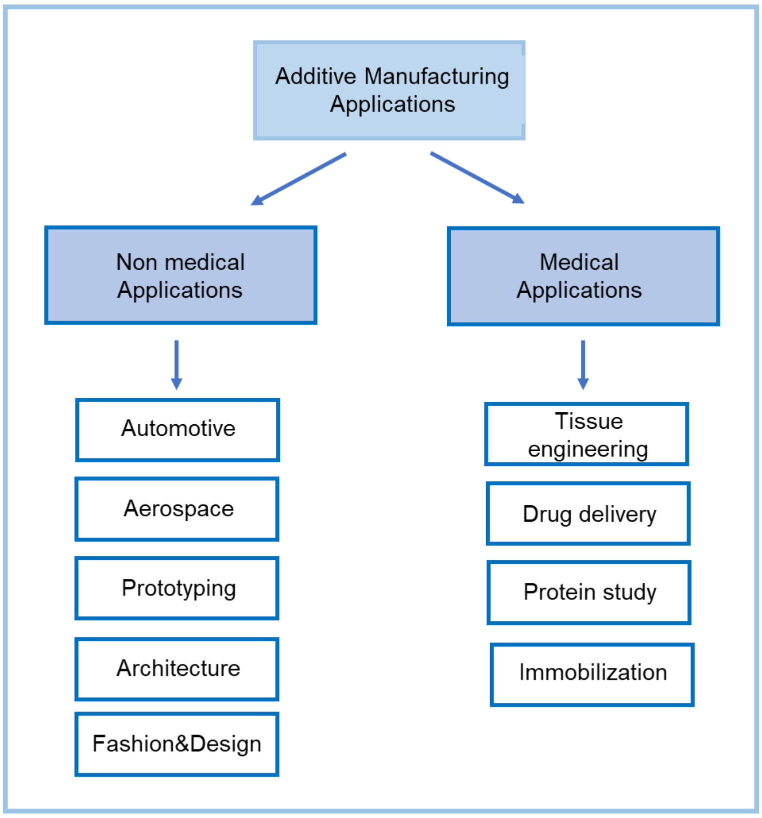

Figure 11. The applications of AM for more efficient and advanced products.

The automotive industry has adopted AM technology for designing and developing functional and structural components like engine exhausts, driveshafts, gearbox parts, and braking systems to cut down on manufacturing time and costs.[75]

The aerospace industry values this technology for its ability to produce highly complex structural parts. In the medical and dental fields, the application of AM technology has expanded to include the manufacture of complex geometrical structures such as orthopaedic implants, dental implants, tissue scaffolds, artificial organs, and maxillofacial and dental prostheses.[75]

Lakkala *et al.* suggest that addressing the limitations of mass production with AM could revolutionize healthcare, enabling doctors, pharmacists, or dentists to produce customized dosing systems or devices at their clinics.[76]

Numerous studies have compared various aspects of 3DP technologies, including power consumption, dimensional accuracy of specimens, and surface roughness. These comparative studies reflect the increasing interest in understanding discrepancies and limitations in each AM system, allowing for better technology selection based on project requirements and restrictions.[77]

Material costs for 3DP are higher compared to those of conventional processes, but this is balanced by increased material efficiency. The advancement of 3DP in manufacturing is expected in the next decade, promising to revolutionize production processes, especially for niche, customized, and high-value items. This progress is associated with a significant reduction in financial and energy inputs, leading to lower costs and reduced CO_2 emissions. Through its additive approach, 3DP notably reduces resource demands and waste.[78]

Additionally, its automated nature minimizes labour requirements, mainly focused on pre- and post-processing tasks. 3DP also impacts supply chains, fostering more direct production methods and shorter supply chains. Conversely, it presents opportunities for underprivileged remote areas, connecting them to broader markets and enhancing their quality of life. Critical technological factors like increased production speed and material availability could expand its applicability to larger production runs, enhancing its potential sustainability. In summary, AM offers significant sustainability prospects, particularly if it becomes viable for mass production markets and addresses social impacts comprehensively.[7]

On the other hand, the AM of polymers provides considerable advantages over traditional processing methods for creating 3D objects with multi-material properties. This approach enables the one-step production of complex three-dimensional products, significantly reducing processing times and garnering increased attention over the past decade. Unlike conventional methods requiring dies, moulds, or lithography masks, 3DP utilizes automated assemblies that translate computer-aided designs into intricate 3D structures with minimal material waste. Moreover, the ability to rapidly develop final products with simplified processes and lower costs has attracted attention from both academic and industrial sectors. The choice of manufacturing technology for a specific product depends largely on the physical and chemical properties of the raw materials and the intended applications of the final product.[23]

Thermoplastic granules, filaments and powders, inks and photocurable thermosetting resins are the most extensively used polymer materials for the wide AM family, which leads to a multitude of applications in different domains. The AM technologies for polymer processing can be categorized into four main types: Fused Deposition Modeling (FDM), Selective Laser Sintering (SLS), Material Jetting (MJ), and Vat Photopolymerization (VPP).[16, 63, 79]

Polyamide (PA) is extensively used in the SLS process due to its superior laser melting and bonding properties. Acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) are widely employed in the FDM process, whereas liquid photocurable resins, like acrylates and epoxy resins, are commonly used in MJ, IJ and VPP and cure when exposed to a specific laser wavelength.[2, 80]

In summary, the benefits of AM technology from an economic standpoint include the following:[5, 64]

- Producing small batches of customized items is more cost-efficient compared to traditional mass production methods.
- Direct manufacturing from 3D CAD models eliminates the need for tools and moulds, avoiding transition costs.
- Digital design files can be easily shared, allowing for quick modifications and customization of each component.
- The AM process conserves materials by reusing leftover materials (such as powder or resin) not used during production, with metal powders being estimated at 95–98% recyclability.
- It enables the creation of innovative, complex structures, including free form enclosed structures, channels, and lattices.
- Local consumers/clients can directly engage with production through distribution channels.
- Inventory risk is reduced as there are no unsold finished products, while revenue flow is improved since items are paid for before production.

4. Photopolymer-based Additive Manufacturing Technologies

Since this review focuses on thermosetting photopolymers, the most significant AM technologies involving photopolymerization are than described and discussed, specifically VPP and IJ AM technologies, able to process liquid photocurable resins by producing 3D-printed parts via light-activated photopolymerization reactions.

4.1 Vat photopolymerization

A photopolymer is a polymer that alters its properties when exposed to light, typically in the UV-Vis range of the electromagnetic spectrum. Therefore, among all AM techniques, VPP is unique in its ability to work with thermosetting polymers and produce objects with complex and hierarchical geometries. Depending on the curing source, VPP processes can be further classified into:

- Stereolithography (SLA);
- Digital Light Processing (DLP);
- Two-Photon Polymerization (2PP);
- Volumetric 3DP.

SLA is a widely used 3DP method and it was the first AM technology developed. This technology converts liquid resin into a solid via a photopolymerization reaction promoted by UV radiation, given by a laser, which selectively cures the part layer-by-layer. Traditional SLA laser printer can be divided into two main types based on the build platform movement and light source position, in a bottom-up and top-down configuration, as illustrated in Figure 12.[13, 24, 26, 76, 81]

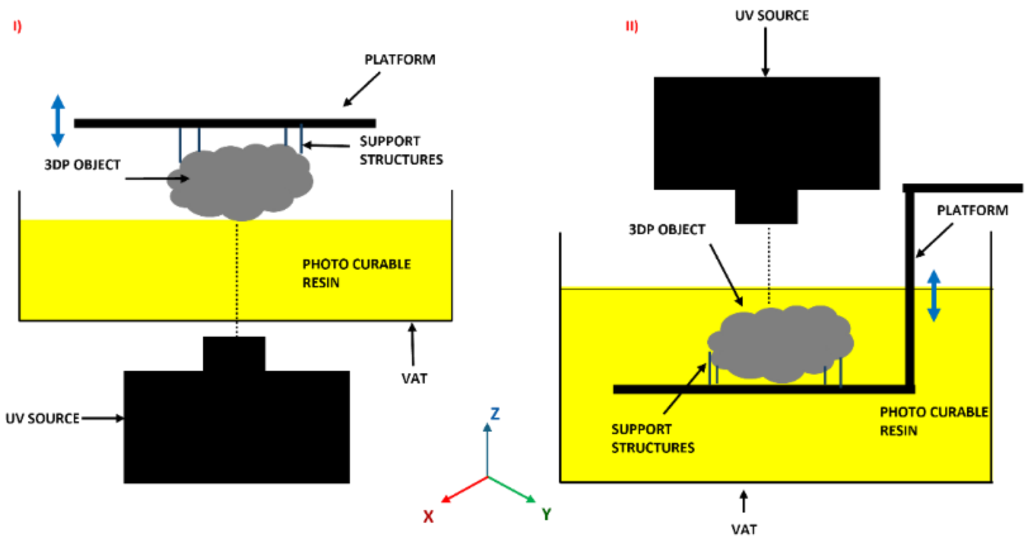

Figure 12. Schematic representation of the working principle of the SLA printers: "bottom-up" (I), and "top-down" (II) approach.

In the bottom-up approach, the vat is filled with the photocurable liquid resin, and the build platform is initially lowered until a thin layer of resin is exposed on the platform surface. The UV source emits radiation from the bottom of the vat to selectively cure and solidify a thin layer of resin, then the platform rises and falls again, and a new layer of liquid resin is cured on top of the previous layer. The process goes on until the desired object is completely created. In this type of 3DP process, the build platform is raised out of the resin vat.[39, 76]

In the top-down process, the UV source is placed above the tank containing the liquid resin. The resin is then photocured using a light source above the vat and the build platform is lowered into the resin vat. The bottom-up configuration process is preferred for several advantages. First, the UV light is positioned under the tank, safely enclosed within the machine, protecting the user from harmful exposure. Secondly, the liquid resin cures in a sealed environment, ensuring a better photocuring process. Moreover, gravity refills the liquid resin, eliminating the need of a roller. Ultimately, this process produces smoother finishes because the parts are completely immersed in the liquid resin and are in full contact with the smooth bottom of the tank. Less resin is needed to fill the tank, so it can be used less resin at once, saving material and cost.[39, 71, 76, 81]

While most of the commercially available 3D printers offer vertical resolutions between 50–200 µm, SLA machines can achieve resolutions as low as 25 µm or less. However, despite their exceptionally high resolution, SLA machines have the drawback of a slow printing process due to laser curing. Although each layer is formed quickly, significant delays occur between layers due to the time necessary for laser scanning and resin curing. This results in a noticeable time delay between the printing of each layer. Another disadvantage of SLA is the limited mechanical performance of the finished parts, which is due to a relatively limited crosslinking degree of photopolymerization that often requires post-processing of the printed components.[13]

The quality of the printed structures depends on the cure kinetics of the photopolymerization process, which is strictly influenced by light intensity, irradiation time, resin viscosity, chemical functionality, and the presence of additives in the formulations.[23]

DLP is a variation of SLA 3DP.[63] These two techniques operate similarly but differ in how light interacts with the photocurable resin. In SLA, a laser moving on the X-Y plane projects light to selectively expose the resin. In contrast, DLP uses a projector to project the entire image of each layer onto the resin, curing the entire layer simultaneously rather than point-by-point for the laser process. The projector operates on a Micro-Electro-Mechanical System (MEMS) incorporating a Digital Mirror Device (DMD). This DMD reflects UV light onto the resin layer in contact with the bottom of the vat, forming a solid layer based on the desired CAD design. DMDs are made up of tiny, individually adjustable mirrors that direct the path of the UV light. This results in a lower print time for DLP, although the expense of resolution and surface finishing.[39]

Additionally, DLP systems are often more cost-effective, making them a powerful alternative for 3DP photopolymer resins. The working principles of SLA and DLP are shown in Figure 13.[19, 81]

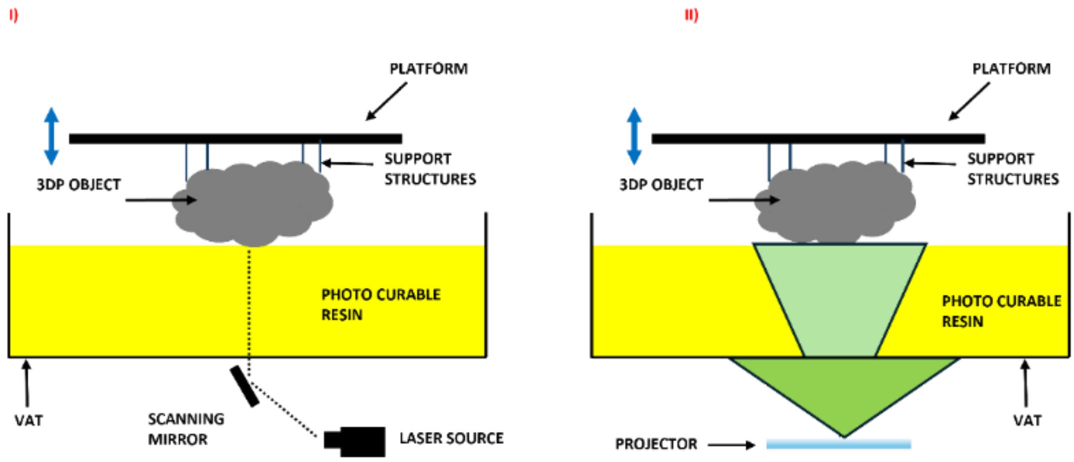

Figure 13. Working principle of SLA (I) and DLP (II) technologies.

2PP is another VPP-based printing system, like SLA and DLP, which offers better control, exceptional spatial resolution, and higher print quality. This process uses a NIR source to allow deep penetration of laser light into the material. In 2PP, two photons are absorbed simultaneously by the PI, providing energy equivalent to single-photon absorption in a photocurable formulation. Consequently, the spatially distributed photoinitiated radicals formed during the 2PP of resins follow the square law of light intensity function.[2, 19, 23] Another innovative VPP-based technique is the volumetric 3DP, which directly prints 3D structures by using a rotating vat. It projects six distinct images of the desired object from specific angles and alternates them during rotation, allowing the object to be built directly in 3D rather than layer-by-layer.[82]

The main drawback of VPP is oxygen inhibition, most significant at boundaries with air, where oxygen can diffuse in and prevent the surface from fully curing, leaving it tacky even when the interior is fully cured. To address this issue, several techniques have been developed, to increase the UV light intensity to inactivate oxygen more quickly, submerging the resin under a solvent to slow the oxygen diffusion, including oxygen scavengers in the resin, adding nanoparticle additives to bypass oxygen inhibition pathways, and curing the photocurable resin in an inert environment. This issue is more pronounced with radical photopolymerization.[2, 19, 23]

A study by Saygin *et al.* focused on the mechanical effects of oxygen inhibition, showing that the interlayer region of a material printed using VPP was softer than the bulk, due to the oxygen inhibition. Compression testing of bulk samples and nanoindentation studies of their surfaces confirmed that oxygen's mechanical influence has a remarkable surface effect.[83]

To overcome oxygen inhibition, Continuous Liquid Interface Printing (CLIP) technology was introduced in 2015 by Carbon3D company. This technology is even named Digital Light Synthesis (DLS).[82, 84, 85] The CLIP technology uses an oxygen-permeable chamber, called a "dead zone", to create an interfacial oxygen layer.[39] However, the thickness of the dead zone is a crucial factor that affects both the maximum speed and final resolution, posing challenges for scaling up to rapidly produce large objects.[84] To tackle this issue, Scot *et al.* developed and utilized wavelength-selective photoinitiation and photoinhibition in a similar SLA process.[82] This layer inhibits the radical-induced polymerization reaction, preventing the excited PIs from reacting and forming peroxides with free radicals. As a result, unreacted monomers remain at the interface between the build platform and the oxygen layer, allowing for rapid printing of polymer resins without slicing the 3D designs into layers, as illustrated in Figure 14.

CLIP technology can typically produce printed objects very quickly, with production cycles lasting only a few minutes and vertical resolutions lower than 100 µm. However, it is limited to curing systems quenched by oxygen, such as photocurable (meth)acrylate-based monomers.[23, 39, 48, 86]

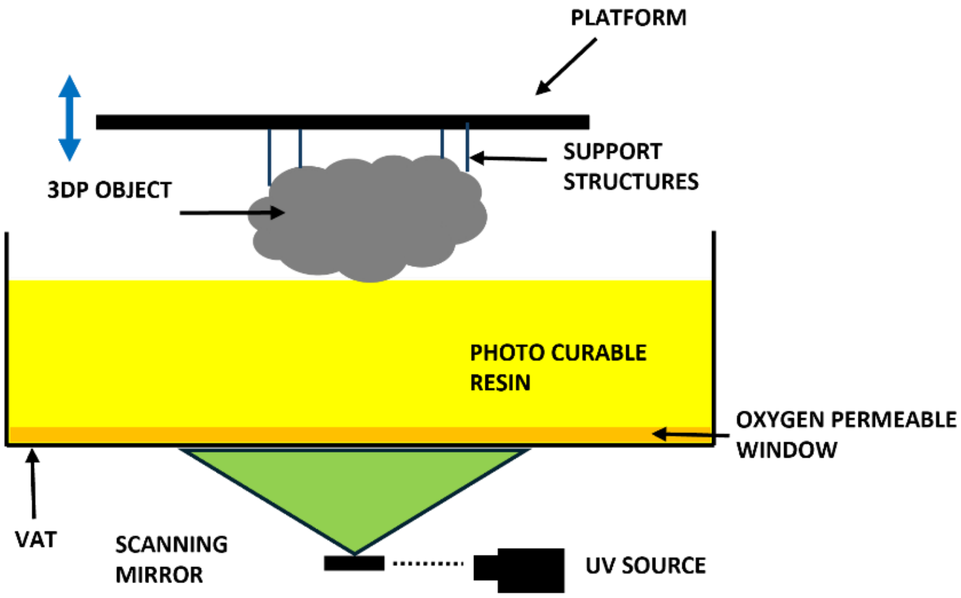

Figure 14. Schematic diagram of the CLIP process.

Another advancement in SLA is Hot Lithography (HL), which utilizes the principles of VPP technology with an added heating element in the vat to control the temperature during the printing process, as possible to see in Figure 15.[39]

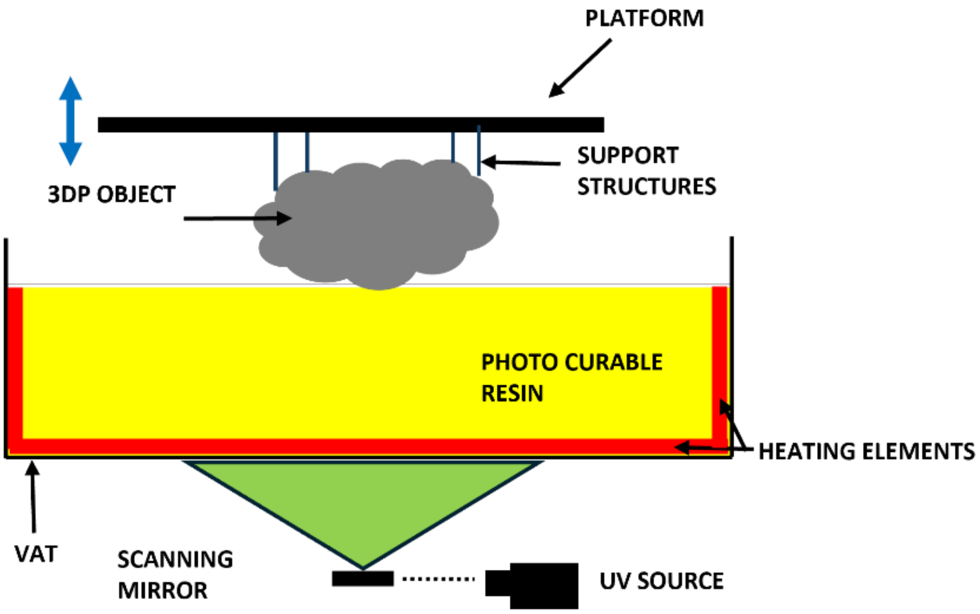

Figure 15. Schematic diagram of the HL process.

Conventional VPP processes typically maintain printing temperatures at room temperature, often limited by the high viscosity of the printing resins. By operating at higher temperatures (typically at temperatures even higher than 120°C)[87], HL reduces the resin viscosity and increases the monomer's reactivity. In this process, photocurable resins are still cured using a standard SLA laser or DLP projector, but the monomer conversion is expected to be higher compared to room-temperature curing. This technology can expand the range of resins available for VPP.[39, 87–89]

One of the recent innovations in VPP technology is the use of a liquid crystal display (LCD), also known as daylight polymer printing (DPP), a 3DP machine which relies on LCDs as the curing mechanism.[85] A key characteristic of LCD 3DP is that light is emitted directly through a flat LCD screen onto the uncured resin, preventing light from spreading and thus minimising pixel distortion compared to DLP printing. LCD printing can expose an entire layer simultaneously, eliminating the need to scan the photopolymer point-by-point as in SLA, resulting in a faster printing process.[85] Many LCD printers rely primarily on the use of UV lamps or visible LEDs as light sources. The LCD 3D printer employs a bottom-up configuration where the printing platform is completely immersed within the resin tank. Other benefits of the LCD process include the wide range of usable thermoset polymers and the capability to experiment with various polymeric resins and composites, allowing for the customisation of photopolymers by modifying the material properties or creating novel classes of materials. LCD can also produce printed parts showing substantially greater printing quality than even the most sophisticated FDM printers.[16]

Moreover, this approach efficiently uses raw materials to produce high-resolution products in an eco-friendly manner. However, the application of LCD technology is somewhat constrained by the limited availability of sustainable light-curing resins on the market.[18, 85]

3DP techniques based on photopolymerization, such as SLA, DLP, LCD, CLIP, and HL, enable the rapid and controlled creation of various structures without the need for moulds or machining.[86]

The post-processing steps can be divided into three stages:

- removal of supporting structures;
- cleaning;
- post-polymerization.

Removal involves physically detaching the sample from the build platform, and its supports if included in the print file. Support structures, designed on the CAD model to maintain the stability of the part during the manufacturing process, can be removed using a cutting device, a diamond disk, or an ultrasonic tip. During the cleaning phase, unreacted monomers are removed from the sample. The resulting 3D object is then washed with organic solvent to remove unreacted monomers and traces of PI.[66]

The post-curing step is then performed under UV light and/or through thermal curing to strengthen the object by finishing the unreacted resin groups.[39, 68]

4.2 Ink-jet photopolymerization

In the field of photopolymers for AM, IJ 3DP emerges as a particularly promising method. The integration of multi-material print heads, featuring thousands of nozzles, significantly enhances the efficiency of producing multiphase materials, commonly referred to as "digital materials".[90]

Different classes of materials have been used to produce components via IJ printing, including metals, ceramics, and polymers.[29]

The first IJ printing process to use a UV lamp for solidifying deposited droplets was the PolyJet process (Figure 16).

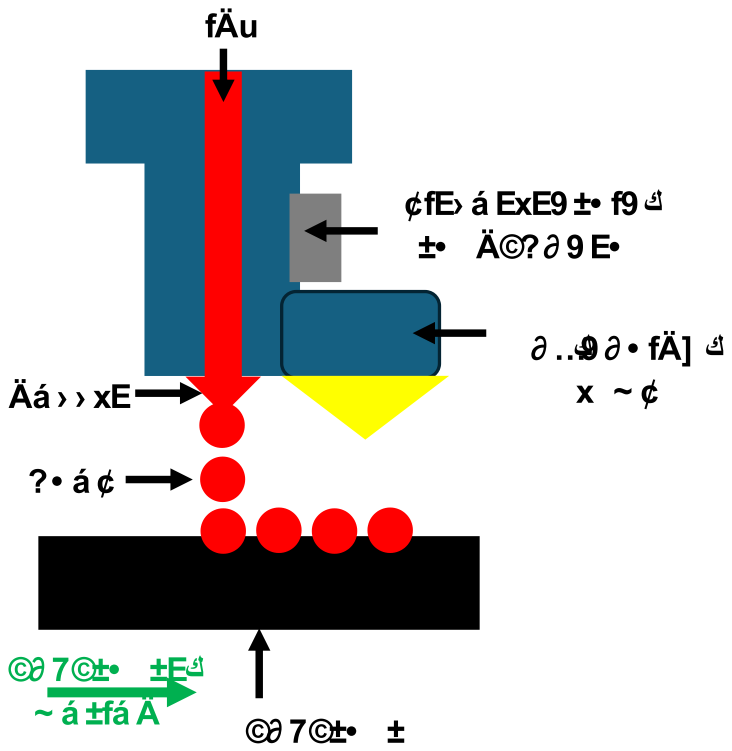

Figure 16. Schematic of the working principle of the Ink-Jet process.

Contemporary IJ printers are based on these same principles, but modifications and improvements have enabled the creation of products with higher resolution.[29]

Presently, two main methods are utilized to deposit droplets onto a substrate: continuous ink-jet printing (CIJ) and drop-on-demand (DOD) techniques.[29, 90, 91]

CIJ technology, a continuous stream of ink or resin is ejected from the nozzle. As the stream descends, it naturally breaks into a series of droplets, as also shown in Figure 16. An electrode applies an electric charge to these droplets, and the charged particles are subsequently directed onto the substrate for deposition.[29, 90]

Rishabh Magazine *et al.* employed ink jetting technology to create micro-lenses with diameters approximately between 50 and 100 µm.[29]

DOD IJ printers produce droplets only when needed. Unlike CIJ printers, DOD printers lack the electrode system used for droplet positioning, allowing the nozzles to be placed closer to the substrate and to produce smaller drop sizes. The most common types of DOD IJ printers are piezoelectric or thermal 3D printers.[20, 29, 91–93]

In a piezoelectric IJ printhead (PIP), an applied voltage causes deformation of the piezoelectric transducer, which increases pressure within the ink chamber and forces droplets to be ejected through the nozzle. PIPs can operate through different mechanisms, including squeezing, pushing, shearing, or bending, depending on the voltage waveform.[94–96]

One of the limitations of PIPs is the formation of satellite droplets, i.e. unwanted droplets that tend to separate from the primary droplet. These arise due to pressure oscillations within the ink chamber, leading to variations in the ejection process. Satellite droplets negatively impact print quality, as they are deposited inaccurately. The likelihood of satellite droplet formation is influenced by the velocity at which droplets are ejected. To mitigate this issue and achieve a sufficiently high ejection speed, a multiple-voltage waveform is often employed as a strategy to reduce the formation of satellite droplets.[97, 98]

Thermal ink-jet (TIJ) technology operates using various configurations, such as roof-shooter, side-shooter, or suspended heater systems. For example, in the roof-shooter system, the heater is positioned behind the nozzle, whereas in the side-shooter system, it is located adjacent to the nozzle, and in the suspended heater system, the heater is situated within the ink chamber.[99]

TIJ printers, however, face several limitations. A primary issue is their low durability, which arises due to heater electromigration, bubble cavitation-induced damage, and cracks resulting from thermal stress. To address these concerns, modifications such as altering the heater's geometry have been proposed to extend the lifespan of the TIJ piezoelectric components. Another challenge is the accumulation of particles on the surface of the heater, impairing bubble formation and droplet ejection. Introducing anions into the ink has been identified as a potential solution to mitigate this problem.[100–102]

For 3D fabrication, piezoelectric DOD printers are generally preferred. Individual droplets are generated by creating actuation pressure within an ink channel, either through piezo acoustic actuators or by thermally producing small gas bubbles. The characteristics of ejected droplets depend on factors such as the surface tension, density, and viscosity of the inks.[20, 29, 92]

Droplet size can be adjusted by varying the voltage applied to the piezoelectric element; lower voltages produce smaller droplets, while higher voltages yield larger ones. For high resolution and quality in ink-jet printed components, precise positioning of the droplets on the substrate is crucial.[103]

Today, several commercial DOD IJ printheads offer high resolutions of up to 1200 dots per inch (DPI), accommodating various inks, including aqueous, oil-based, solvent-based, and UV-curable inks or resins.[29, 103] DPI is a measure of printing resolution that reflects the distance between two adjacent droplets on the substrate, based on the incremental X and Y displacements of the print head or substrate.[103] DOD printing allows for precise and controlled delivery of material onto a substrate.[20]

For DOD IJ printing, the spatial resolution is typically on the order of tens of microns. Drop placement error, defined as the difference between the target location and the impact location, is influenced by the precision of nozzle manufacturing and the distance between the nozzle and substrate.[103]

The apparent contact angle of a droplet on the substrate depends on its chemical composition and the surface roughness, which surely affects the final resolution.[103, 104]

In conclusion, DOD techniques are favoured for AM applications concerning CIJ.[90]

The density, surface tension, and viscosity of fluids are critical properties in IJ printing. Surface tension arises from the cohesive forces experienced by molecules at the surface of a liquid.[92, 103]

Rheological properties are crucial in IJ 3D printing, as the inclusion of polymers, pigment particle additives, dispersants, binders, and other components can affect an ink-jet fluid viscosity and viscoelastic characteristics.[29, 103, 105]

Ejecting a certain amount of ink through a nozzle does not guarantee the formation of perfectly shaped single droplets. Drop formation depends on the nozzle structure, the ink physical properties, and the velocity and amount of ejected ink. In IJ 3DP, the fluid is subjected to high shear rates, typically over 10^4 s^{-1}, and short residence times on the order of 5–250 µs. Additionally, fluids may exhibit viscoelasticity behaviour, where stress is proportional to both the strain rate and the strain. The viscoelastic response of a fluid depends on the process characteristic time scale relative to the fluid characteristic time scale. In PIP technology, printing fluids are subjected to frequencies on the order of 10-100 kHz. Measuring the rheology of printing fluids at these relevant time scales and frequencies is important for correlating basic rheology to their actual behaviour during printing.[103]

IJ is a versatile technique capable of patterning a wide range of materials, including polymers, metals, ceramics, and biomaterials. Drop formation in IJ technology is governed by the interplay of viscous, elastic, and surface forces. The complexity of IJ printing lies in the multiple time scales and length scales involved. As the range of ink-jet fluids continues to expand, comprehending the underlying physics is increasingly important to realize IJ printing full potential.[29, 92, 103]

As described above, each IJ system possesses its unique resolution, material requirements, and distinct advantages and limitations. Overall, IJ 3DP technology has progressed significantly beyond its conventional applications and now serves as a valuable tool in various industrial processes, including polymer deposition and materials research.

5. From monomers coming from fossil origin to monomers coming from bio-sources

In recent decades, the demand for polymeric materials has increased with rapid industrial and economic growth. However, the widespread production and disposal of these materials has raised significant environmental concerns, mainly due to their resistance to degradation, which poses potential threats to human health and ecosystems.

Polymers are primarily made from petrochemical materials derived from coal, oil, and natural gas. Most of the fossil-based plastics used today are non-biodegradable. Consequently, these polymers accumulate in the environment in large quantities due to poor waste management and uncontrolled littering, posing a serious threat to our planet.[106, 107] The long-term accumulation of non-biodegradable polymers in the environment has led to a decrease in soil fertility and numerous other ecological and health problems. Additionally, the number of plastics in the oceans has exceeded that of plankton by six times, endangering aquatic birds and fish.[108] In September 2015, the United Nations adopted the 2030 Agenda for Sustainable Development, which includes 17 Sustainable Development Goals (SDGs). In this context, the use of monomers derived from renewable resources represents a promising area of research and a viable path to the creation of new polymeric materials with immense potential. This aligns with Goal 12: Responsible consumption and production, as it emphasizes the integration of eco-friendly and green technologies, such as AM, and the study of new biobased monomers to promote sustainable and responsible production practices."[109]

Bio-based polymers, particularly those derived from renewable feedstocks, are increasingly used in sectors like packaging, healthcare, and agriculture[110, 111] and new monomers, such as vegetable oils (VOs), furan-based components, lignin, vanillin, cardanol, and monomers derived from cyclodextrins, are being investigated in both academic research and the chemical industry[112] reflecting a growing commitment to sustainability and reducing dependence on fossil materials.[1, 2, 24, 107, 113–115] Among these renewable feedstocks, VOs stand out as abundant, renewable, and cost-effective, with structural characteristics that make them appealing for use in polymeric resins and composite materials. These oils are primarily composed of saturated and unsaturated fatty acids, which can undergo photopolymerization, making them a promising alternative to resins derived from petrochemicals.[116–119] The internal carbon-carbon double bonds in plant oils, called fatty acids,[118] are typically not reactive enough for most photopolymerization processes.[107] Therefore, a preliminary chemical modification, such as epoxidation or (meth)acrylation, is necessary to increase their reactivity for applications in AM.[70] Epoxidation is the simplest method to make plant oils reactive for CP, while (meth)acrylation allows them to be used in FRP.[120]

Several studies have explored the use of VO derivatives, along with other renewable feedstocks, in UV-assisted AM technologies. For example, Lebedevaite *et al.* developed innovative photo-crosslinked polymers made from acrylated epoxidized soybean oil (AESO) combined with vanillin dimethacrylate (VDM) or vanillin diacrylate (VDA).[121]

In addition to these studies, recent works from Versace's group [122–125] has demonstrated the use of soybean oil-derived acrylates combined with various natural dyes as photosensitizers for visible-light-induced 3D printing. These approaches not only enable efficient photopolymerization under LED light sources but also impart antibacterial properties to the printed objects, opening applications in biomedical and hygienic fields. For instance, methacrylated quinzaine derivatives and curcumin-based photoinitiators were successfully incorporated into VO-based formulations, demonstrating good print fidelity, mechanical performance, and antimicrobial efficacy. Moreover, Abdallah *et al.* have also contributed significantly by investigating coumarin derivatives as versatile photoinitiators for 3DP, further expanding the toolbox of bio-based photoinitiators suitable for environmentally friendly AM processes.[125]

In another study, Guit *et al.* synthesized epoxidized soybean oil methacrylates (MAESO) with varying functionalities and incorporated them into resin formulations for DLP AM technology. The MAESO resins, which contained biobased content ranging from 74% to 83%, exhibited superior mechanical properties and layer-to-layer fusion comparable to commercial counterparts.[126] Hakkarainen's research on vanillin-based epoxy thermosets demonstrated good thermal and mechanical properties, along with reprocessability and recyclability under acidic conditions.[127] Further studies by Li *et al.* focused on vanillin-phosphorus-based epoxy coatings, which exhibited high thermal stability and flame retardancy.[128] Mahajan *et al.* explored divanillin as a partial replacement for polyethylene glycol in polyurethane synthesis, where hydroxyethyl methacrylate was attached to introduce unsaturation for UV-curing.[129] Despite the higher cost of biobased vanillin-derived monomers compared to petrochemical alternatives, they could be used in specialty coatings, where price is less of a concern.[115]

In addition to vanillin, other bio-based fillers, such as lignin, have been explored for photopolymerization.[130] For instance, Sutton *et al.* functionalized lignin with methacrylate groups and incorporated it into commercial resins for SLA processes.[131] Zhu *et al.* developed soybean oil-based composites, incorporating epoxidized methylsoyate (EMS) and epoxidized allylsoyate (EAS), which exhibited improved mechanical properties and significant potential for new polymer synthesis.[107] Moreover, Miao *et al.* developed resins for 3D printing with exceptional mechanical properties by functionalizing succinic and itaconic acids with glycidyl methacrylate. Crivello et al. investigated glass fiber-reinforced composites made from epoxidized VOs, demonstrating potential for structural applications.[132] Boarino *et al.* developed thermoset coatings based on glyoxylic acid lignin and poly(ethylene glycol)diglycidylether, which exhibited antioxidant and UV-protective effects with high visible transparency, offering tunable mechanical properties and lignin content of up to 70 wt%.[133]

Today, creating soybean oil-based resins for structural applications continues to challenge the polymer and composite industries.[134]

Moreover, AESO serves not only as a bio-based monomer for thermosetting polymers, but research has also explored bio-resins derived from several bio-based precursors, even for 3DP, such as linseed oil,[135] palm oil, [136] hemp oil, [137] castor oil, [78, 138], eugenol, [139] tung oil, [140] gallic acid,[141, 142] based on rosin[143]. To cite other examples, Pezzana *et al.* utilized the diallyl ether of furan dimethanol combined with various thiols in UV-triggered thiol-ene reactions. The resulting coatings demonstrated higher T_g compared to analogous materials derived from other bio-based building blocks. The same research group also investigated mono- and diglycidyl furfuryl alcohols in UV-cured cationic coating systems.[144] VO-based polymers are commonly used in coatings, adhesives, sealants, elastomers, and foams.[107, 145] Numerous studies on the application of VOs in the photopolymerization technique have been conducted,[146] demonstrating their excellent properties for 3DP processes involving photopolymerization reactions. Researchers have developed soybean oil-based composites reinforced with functionalized calcium silicate, cellulose, vanillin, coconut, olive pit powders, or particles derived from macadamia nutshells, lignin, corn waste, or wine by-product residues.[18, 118, 147–152] In one of his studies, Liu *et al.* developed composites using AESO and microcrystalline cellulose (MCC), both derived entirely from renewable materials. By varying the weight ratio of AESO to MCC, properties such as hardness, bending strength, and bending modulus could be adjusted, showing improvements over pure AESO resin. However, the addition of MCC led to decreased thermal stability and water resistance due to MCC's low thermal decomposition temperature and high hydrophilicity. The samples were created using the solution casting method, and with further research, 3DP methods could be utilized.[153] In the study conducted by Kumar *et al.*, photopolymer resin was reinforced with cellulose nanocrystals (CNC) at concentrations of up to 5% by weight. It was observed that higher concentrations of CNC led to the formation of aggregates, which adversely impacted the mechanical properties of the resin. The incorporation of 5% CNC resulted in a moderate increase in resin viscosity, a 1 GPa increase in tensile modulus, and improvements in both the storage modulus and glass transition temperature. However, the presence of higher CNC content also caused a reduction in elongation.[154] In the study by Palaganas *et al.* different concentrations of CNC were incorporated into PEG hydrogels, but no clear patterns were observed in the mechanical properties. Nevertheless, the research successfully demonstrated the 3DP of high-resolution constructs.[155]

Cosola *et al.* explored the application of acrylated γ-cyclodextrin as a biobased material for DLP printing.[156] In the last years, the studies have verified that it is possible to photopolymerize even other natural polymers, such for example gelatine (Gel), to produce bio-based hydrogels. These systems are particularly important in the context of UV photo-curable resins for AM beyond biomedical applications.[157–161] Despite VOs gelatine attracting big attention in the biomedical field, because it has unique features like biocompatibility, low immunogenicity and low cytotoxicity, and easy acquisition. Gelatine must be functionalized to interact with UV-vis light, usually methacrylate functional groups are added by obtaining methacrylate gelatine (GelMA). After the functionalization, good biocompatibility, low immunogenicity, and the capacity to promote cellular growth are maintained, but even the property of photopolymerization is added.[160]

Therefore, by leveraging the benefits of composites made from bio-based and natural monomers, and the insertion of agricultural and industrial waste biofillers, with the advantages of AM technologies, it is possible to create high-quality objects without relying on hydrocarbons or petroleum-based monomers.[18] However, their contribution to the plastic industry remains limited, and their environmental safety and effectiveness are contingent on proper waste management and community training programs.

6. Conclusions and outlook

Critical issues in the use of polymeric materials, particularly thermosets, include the need for enhanced material properties, such as mechanical strength, thermal stability, and chemical resistance, to meet the demands of various industrial applications. Thermosets are often preferred for their excellent structural integrity and durability, but their processing and curing times can be limiting factors.

Photopolymers and photopolymerization offer significant advantages over traditional polymerization processes, to create thermoset materials. This process also enables precise control over the polymerization kinetics, leading to high-resolution and complex customized structures.

Transitioning from mercury lamps to LED lamps is crucial for health and environmental reasons. Mercury lamps are toxic and pose significant disposal and recycling challenges, while LED lamps are safer, more energy-efficient, and environmentally friendly. LEDs emit specific wavelengths of light, which can be tuned to optimize the photopolymerization process without the harmful effects associated with mercury.

Understanding the mechanisms of photopolymerization is essential to improve the efficiency and effectiveness of this process.

FRP, although widely used, has critical issues such as oxygen inhibition and incomplete curing.

Ionic photopolymerization, offers advantages like reduced sensitivity to oxygen and the ability to cure thick films and dark pigments, leading to more consistent and reliable material properties. Furthermore, as previously discussed, epoxy monomers, which follow CP, are less irritating and toxic than acrylates and methacrylates, which instead photopolymerize through the FRP mechanism. Regarding FRP, most of its aspects have been extensively studied and are well-understood. In contrast, CP, although discovered decades ago, has only seen significant study and improvement in recent years.

Shifting from fossil to bio-based sources, such as VOs and processing residues and wastes, is vital for sustainable development. Using these renewable resources supports the circular economy by reducing dependence on non-renewable materials, minimizing waste, and lowering the environmental footprint. Bio-based materials can be transformed into high-performance polymers, contributing to a more sustainable and environmentally friendly manufacturing industry. Soybean oil is the most widely used now, however, new studies and research report the use of other VOs as possible starting monomers.

At present, industrial manufacturing processes are responsible for 15% of global energy usage and 35–40% of global material consumption.[64]

AM, or 3DP, is particularly interesting due to its ability to create complex geometries, reduce material waste, and shorten product development cycles. Indeed, AM technology is increasingly being utilized in research and by companies for prototype design and the realization of 3D-printed parts with high printing resolution and complex architectures.

It offers advantages across various fields, including aerospace, healthcare, and automotive, by enabling customized and on-demand production. However, the high costs associated with AM technologies can be a significant disadvantage. These costs can be amortized by advancements in machine design, increasing production speeds, and reducing material costs, making AM more accessible and economically viable for mass production. Both the research activities and the number of published articles in this field are on the rise.

However, to improve production speed and reduce costs, advancements in machine design are necessary. Presently, the high costs and time-consuming nature of AM are significant barriers to mass production.[71, 162]

Photopolymerization technologies for thermosets, such as VPP and IJ technologies, are valid and promising methods for producing high-resolution and high-performance materials. VPP allows for the creation of intricate and detailed structures with excellent surface finish. IJ technologies enable precise material placement and multi-material printing, expanding the capabilities and applications of 3DP. These technologies are crucial for advancing the production of thermosetting polymers and overcoming current limitations in AM processes.

Further research into photopolymerization is necessary to enhance both the performance of resins and the final properties of photocured polymers. This requires a focus on mechanistic aspects to better understand and control the complex processes involved in ultrafast photocuring reactions.

However, the limitations of photosensitive resins and technological bottlenecks restrict the application of photocuring 3DP. Addressing technical issues such as rapid curing, printing with large-size and high-viscosity resins, and the development of high-performance, biocompatible, and degradable materials will broaden the prospects for 3DP.

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Declaration of Conflict of Interest

The authors declare no known conflict of interest.

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Graphical Abstract