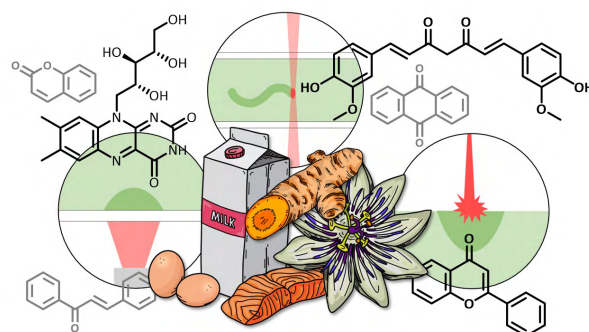


Natural and Naturally Derived Photoinitiating Systems for Light-Based 3D Printing

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Abstract Photoinitiating systems (PISs) are key components in photocurable formulations (inks) for three-dimensional (3D) printing. Natural PISs are promising and more environmentally friendly alternatives to conventional photoinitiators. These systems offer enhanced features such as less toxicity and therefore, higher biocompatibility. Furthermore, they can be found in a large “color palette” variety (absorbing in the different regions of the UV-visible spectrum) enabling new possibilities in the field of 3D printing. In this review, we outline the current efforts to implement natural and naturally derived PISs in light-based 3D printing. First, recently applied natural PISs and their performance for light-based 3D printing are discussed. In a second part, an overview of naturally derived PISs including the most common synthetic strategies are provided. Last, current challenges as well as future perspectives of the field are discussed.

Introduction

Natural Photoinitiating Systems

Naturally Derived Photoinitiating Systems

Conclusions and Outlook

Key words: natural products, photoinitiating systems, photopolymerization, 3D printing

Introduction

Light-based three-dimensional (3D) printing relies on the selective and rapid curing of photopolymers upon light exposure with a certain wavelength.^{1,2} Among other additive manufacturing technologies, light-based 3D printing is especially attractive due to superior print resolution and accuracy, surface finish, versatility, and greater efficiency.¹ Sev-

eral light-based 3D printing techniques have been developed that differ in the way in which the photopolymers, also called photocurable inks or photoresins, are cured into solid 3D material according to a digital model.³ In stereolithography (SLA), a laser scans a pattern on the ink surface to cure the layers of the object. The printing speed can be increased if the layers are exposed all at once, which is the case for digital light processing (DLP) and liquid-crystal display (LCD) 3D printing. DLP uses a digital light projector to cure the ink, whereas in LCD the light comes from an LCD screen. There are other approaches, such as volumetric 3D printing, where the entire object is simultaneously solidified by irradiating the photoresist from multiple angles with dynamic light patterns.⁴ For micro- and nanoscale printing, two-photon laser printing (2PLP) has been established as a powerful technique.⁵ In 2PLP, infrared femtosecond lasers are often utilized. Due to the non-linearity of the process, the photopolymerization occurs in a very small volume (voxel), where the laser intensity is high enough, enabling the fabrication of complex 3D structures with submicron resolution.^{1–3}

In this context, the rise of interest in light-based 3D printing has led to significant developments in the field of photocurable resins or inks. Recently, a broad range of functional polymers has been introduced allowing for new applications in fields such as soft robotics⁶, optics⁷, or biomedicine.^{3,8} These inks usually consist of (meth)acrylate and/or epoxy-based monomers/pre-polymers along further additives, which undergo radical or cationic polymerization upon irradiation with an adequate wavelength.² Although few monomers are reported in the literature which can undergo self-initiation,⁹ most printable inks require the addition of a photoinitiating system (PIS). Despite being the minority component of the formulation (sometimes even below 1 wt%), the PIS is decisive in the success of the ink formulation. The PIS governs the practical efficiency (reactivity) of the ink, since it is responsible for the generation of active initiating species starting the polymerization process

Biosketches



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Eva Blasco completed her Ph.D. studies at the University of Zaragoza (Spain) under the supervision of Prof. L. Oriol and Dr. Pinol. Thereafter, she obtained an Alexander von Humboldt Postdoctoral Research Fellowship to work in the groups of Prof. C. Barner-Kowollik (Polymer Chemistry) and Prof. M. Wegener (Applied Physics) at the Karlsruhe Institute of Technology (KIT) in Germany. Afterwards, she worked as a group leader at KIT and in 2020, she was appointed junior professor (with tenure track) at Heidelberg University. Her research interests include the design and synthesis of new smart and sustainable polymer materials for application in 3D/4D printing.

after light absorption.¹⁰ Upon illumination, ionic species or radicals should be generated which further induce either an ionic, mainly cationic, or radical polymerization. Radical photoinitiators are usually divided into Norrish type I and Norrish type II systems depending on whether one photoinitiator alone (type I) or a combination of various photoinitiators, photosensitizers, or co-initiators (type II) is required.¹⁰ A schematic representation of both mechanisms is depicted in Figure 1A. To achieve fast and precise curing during printing, the PIS should present a high molar extinction coefficient with sufficient overlap of the absorption spectrum with the irradiation profile of the light source utilized.² In addition to that, it is important to consider also the compatibility, i.e. the solubility and reactivity, of the PIS in the aqueous or organic medium.³

Due to the scarcity and rapid depletion of fossil resources, the usage of natural feedstocks has gained attention among the 3D printing research community. Extensive works are in progress exploring biobased feedstocks, such as vegetable oils¹¹, lignin derivatives¹², and terpenes¹³, for the design of

renewable photopolymers. In contrast, less consideration has been given to the sustainability of PISs. While natural or naturally derived compounds have been exploited in photopolymerization,¹⁴ their use in light-based 3D printing has not received as much attention yet. However, natural dyes exhibit several advantages: they are biobased, abundant, and less toxic compared to conventional commercially available PISs.^{10,14,15} By using natural PISs in light-based 3D printing, not only the uses of fossil resources can be reduced, but also the application fields can be expanded to other fields including food packaging¹⁵ and even to bioprinting implants and tissues due to their enhanced biocompatibility.¹⁴ In addition, natural dyes can be utilized as a source of interesting photoactive compounds covering almost the entire UV-visible regime. This mini review aims to provide with an overview of recent work on the use of pure natural compounds as PISs in light-based 3D printing (see Figure 1B and Table 1) as well as the strategies to functionalize natural molecules enabling their use as PISs. For a comprehensive overview of PISs for 3D printing in general, without focusing

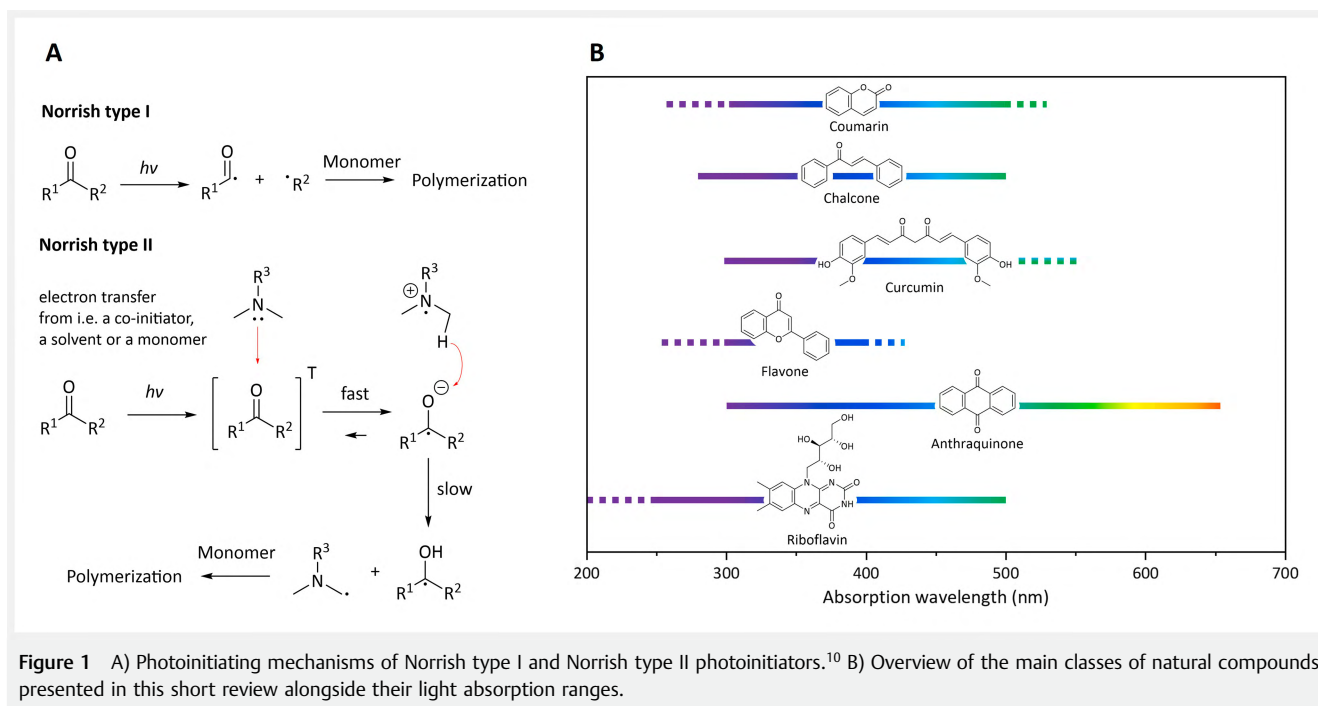


Figure 1 A) Photoinitiating mechanisms of Norrish type I and Norrish type II photoinitiators.¹⁰ B) Overview of the main classes of natural compounds presented in this short review alongside their light absorption ranges.

Table 1 Summary of the discussed printable systems including natural or naturally derived PISs.

Compound	Type	Co-initiator	Mechanism	Material system	3D printing	Wavelength	Ref.
Riboflavin							
RF	Natural	TEOHA	FRP	(Acrylate) ionic hydrogels	SLA	405 nm	31, 32
RF	Natural	TEOHA	FRP	MWCNT-loaded acrylic hydrogels	LCD	405 nm	33
RF	Natural	TEOHA	FRP	Drug-loaded (meth)acrylic hydrogels	SLA, DLP, LCD	405 nm	34–38
RF	Natural	Sodium persulfate	FRP	Keratin-based hydrogels	DLP	385 nm	43
FMN	Natural	TEOHA	FRP	Acrylate hydrogels	2PLP	780 nm	39
FMN	Natural	None	FRP	Type I collagen hydrogels	2PLP	750 nm	40
RF, FMN	Natural	None	FRP	Gelatin, silk fibroin hydrogels	DLP	Visible light	41, 42
RFT	Nat. derived	EDB	FRP	Biobased acrylates	DLP	385–405 nm	29
Flavone							
6HF	Natural	IOD, NPG, 4-DPPBA	FRP	Methacrylates	DLP	405 nm	48
3HF	Synthetic	IOD, NPG	FRP	Methacrylates	DLW, DLP	405 nm	73
3HF sulfonates	Synthetic	None or TEOHA, IOD	FRP	Methacrylates, methacrylic hydrogels	DLP	405 nm	74, 75
Curcumin							
CCM	Natural	IOD	Cationic	Epoxidized linseed oil	SLA	Visible light	57
CCM carbazyl	Synthetic	IOD	FRP	Acrylate-based Al ₂ O ₃ -slurries	DLP	532 nm	76
Anthraquinone							
QZ methacrylate	Nat. derived	None	FRP	Soybean oil methacrylate	DLP	405 nm	61
Chalcone							
Chalcone derivatives	Synthetic	IOD, EDB, TEOHA	FRP	Acrylates, acrylate hydrogels	DLW	405 nm	64, 77, 79b
Coumarin							
Coumarin derivatives	Synthetic	IOD, NPG, EDB	Cationic, FRP	Epoxy-resins, acrylates, methacrylates	DLW	405 nm	79

Abbreviations: RF, riboflavin; FMN, riboflavin-5'-phosphate, i.e., flavin mononucleotide; RFT, riboflavin tetrabutylate; 6HF, 6-hydroxyflavone; 3HF, 3-hydroxyflavone; CCM, curcumin; QZ, 1,4-dihydroxy-anthraquinone, i.e., quinizarin; TEOHA, triethanolamine; EDB, 4-ethyl-dimethylaminobenzoate; IOD, iodonium salts; NPG, *N*-phenylglycine; 4-DPPBA, 4-diphenylphosphinobenzoic acid; FRP, free radical photopolymerization; MWCNT, multiwalled carbon nanotubes; SLA, stereolithography 3D printing; LCD, liquid-crystal display 3D printing; DLP, digital light processing 3D printing; DLW, direct laser writing; 2PLP, two-photon laser printing.

on natural compounds, readers can refer to this newly published review article by Bao.¹⁶ The current mini-review is divided in two sections. In the first section, several families of natural compounds including riboflavin (RF), flavones, and curcumin (CCM) are discussed in detail along with their natural origin as well as chemical structure and (optical) properties. The systems presented herein are obtained from natural sources and used directly (or after few purification steps) in PISs for light-based 3D printing techniques. In the second part, naturally derived PISs are presented. Here, the different strategies to post-functionalize the natural compounds are given. To conclude, the challenges as well as future trends and perspectives of the presented systems are critically discussed.

Natural Photoinitiating Systems

In this section, recent examples in the literature of natural photoinitiators for 3D printing will be presented. In particular, three main classes of natural compounds are discussed: RF, flavone derivatives and CCM (Figure 1B). All these compounds are broadly present in nature and have been used for 3D printing directly, or after few extraction and purification steps, without further modification. Further, the use of other natural compounds such as anthraquinones, coumarins and chalcones in 3D printing is also described.

Riboflavin

RF is a water-soluble essential vitamin – vitamin B2 – and a precursor of the two essential coenzymes flavin mononucleotide (FMN) and flavin adenine dinucleotide, which present similar photochemical properties.¹⁷ RF is an inexpensive bright yellow pigment present in a variety of foods of both vegetable and animal origin, in highest content in salmon, liver, egg and dairy products.^{18,19} RF has been broadly used in medical applications, e.g. to treat the corneal disease keratoconus to restore vision²⁰ and to reduce viral and bacterial pathogens from platelet concentrates upon UV irradiation.²¹ The use of RF as a PIS was already reported in the 1950 s and 1960 s for the photopolymerization of vinyl^{22,23} and acrylic²⁴ monomers in aqueous media. However, it was not until the 2000 s that the photosensitizing properties of RF started to gain more interest.²⁵ RF has remarkable optoelectronic properties which are given by its chemical structure composed of two main moieties, the isoalloxazine ring and the ribityl tail. The polycyclic structure (isoalloxazine ring) is responsible for its photosensitivity, UV absorption, and redox activity.^{17,25}

The reactive hydroxyl groups in the ribityl tail can act as a reducing agent and can be easily functionalized,²⁶ as it will be discussed in the next section, making RF a multifunction-

al molecule. In aqueous media, RF exhibits photosensitivity with four absorption maxima, one in the blue light range (445 nm) and three in the UV range (373, 266, 222 nm),²⁷ making RF very attractive for photopolymerization applications and thus light-based 3D printing. RF is commonly reported as a type II photoinitiator, which, after excitation, can react with other reactants by either electron transfer or hydrogen abstraction to generate initiating radicals or radical ions.^{25,28} RF can be excited to a short-lived singlet state under illumination by UV and visible light, which efficiently generates the triplet excited state through intersystem crossing with high quantum yield.¹⁸ In the triplet state, RF can generate radical ions through triplet-triplet annihilation or undergo self-quenching.²⁹ Thus, RF can be used as a photosensitizer as well as a reducing agent due to the ribityl moiety.^{22,23} However, this mechanism is not very efficient and very often co-initiators such as amines are employed as external hydrogen donors.³⁰ The solvent can act as a hydrogen donor and therefore, the acidity of the medium plays a

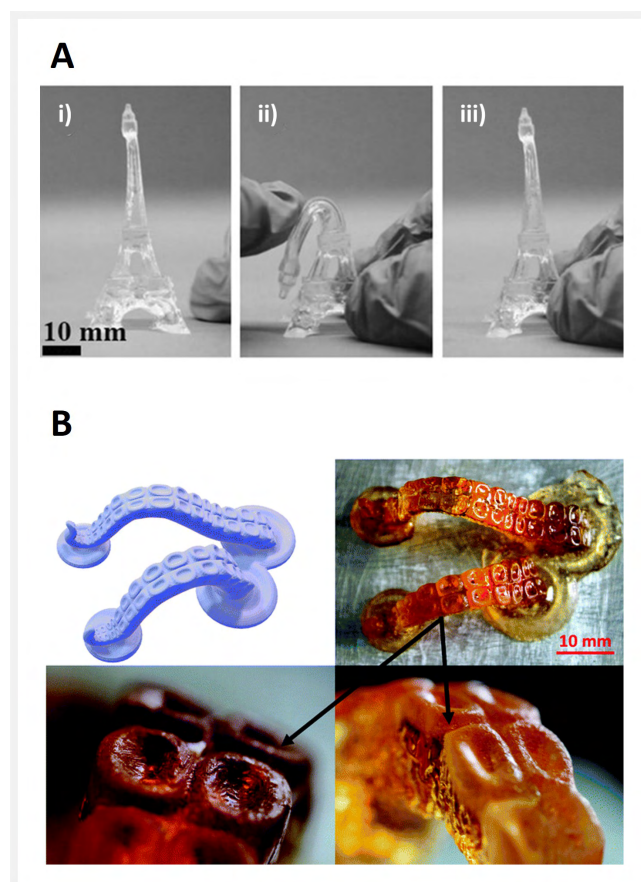


Figure 2 A) Highly flexible and resilient 3D-printed Eiffel tower (i) in which the deformation (ii) is recovered (iii).³¹ Adapted with permission from Ref. 31. Copyright 2017 Wiley-VCH. B) SLA-fabricated octopus arms based on the RF-TEOHA system.³² Adapted with permission from Ref. 32. Copyright 2019 The Royal Society of Chemistry.

significant role in the reactivity of RF. Other possible electron or hydrogen donors are amino acids, thiols, phosphines or carboxylates, among others.³⁰

In the case of 3D printing, RF was used in combination with triethanolamine (TEOHA) as a co-initiator for printing of double-network ionic hydrogels with tunable properties using a SLA printer.^{31,32} The double-network consisted of polyacrylamide together with an ionic acrylic comonomer, either [2-(acryloyloxy) ethyl]trimethylammonium chloride³¹ or [2-(methacryloyloxy) ethyl] dimethyl-(3-sulfo-propyl) ammonium hydroxide.³² Crosslinking of the linear monomer hydrogel chains was achieved with *N,N'*-methylenebisacrylamide. By adding anionic, sulfonate-modified silica nanoparticles, the authors could achieve conductivity and mechanical reinforcement.³¹ The 3D-printed structures were highly stretchable while being tough and resilient at the same time (Figure 2A, B). Moreover, the printed hydrogels presented antifouling behaviour, and due to the lower toxicity of the RF-TEOHA PIS evidencing potential for tissue engineering or biomedical devices.³² Very recently, the RF-TEOHA system was also used together with multiwalled carbon nanotubes (MWCNTs) in LCD 3D printing at 405 nm of acrylamide and other acrylic monomers (Figure 3A).³³ The system consisted of acrylamide with a small amount of polyethylene glycol diacrylate (PEGDA) crosslinker in 50 wt% of water, 0.25 wt% of MWCNTs with respect to the monomer, 1 mM TEOHA and 0.01 mM RF. The results indicated a participation of MWCNTs in the photoinitiating process by surface interaction with RF. This further positively affects the radical

generation and thus, accelerates the initiation step and 3D printing efficiency. Moreover, MWCNTs improved the mechanical properties while adding electric conductivity to the system.

Additionally, recent works have been taken advantage of the biocompatibility of RF to produce hydrogels for extended and/or controlled drug release.^{34–38} Martinez et al. used the RF-TEOHA system for the fabrication of SLA 3D-printed ibuprofen-loaded PEGDA hydrogels.³⁴ Along these lines, Madzarevic et al. prepared ibuprofen-loaded hydrogel tablets using DLP and LCD 3D printing at 405 nm.^{35,36} They applied artificial neural networks to optimize the printing parameters in terms of drug release and investigated the structure–property relationship. Karakurt et al. used the RF-TEOHA system in combination with ascorbic acid (vitamin C) as a model agent for studying the controlled release of vitamins encapsulated in polyethylene glycol dimethacrylate (PEGDMA) SLA printed networks.³⁷ The authors found that the vitamin release could be tuned by changing the 3D-printed structure without the need of modifying the ink formulation. Pyteraf et al. studied the use of vitamin C instead of TEOHA as a co-initiator for RF in LCD 3D printing of mebeverine hydrochloride-loaded hydrogels, and concluded that it leads to irregular, unreproducible results.³⁸

Furthermore, RF can be used to fabricate bioscaffolds for tissue engineering. Riboflavin-5'-phosphate (the coenzyme FMN) with TEOHA was applied in 2PLP of PEGDA to yield biocompatible scaffolds with high printing precision.³⁹ The

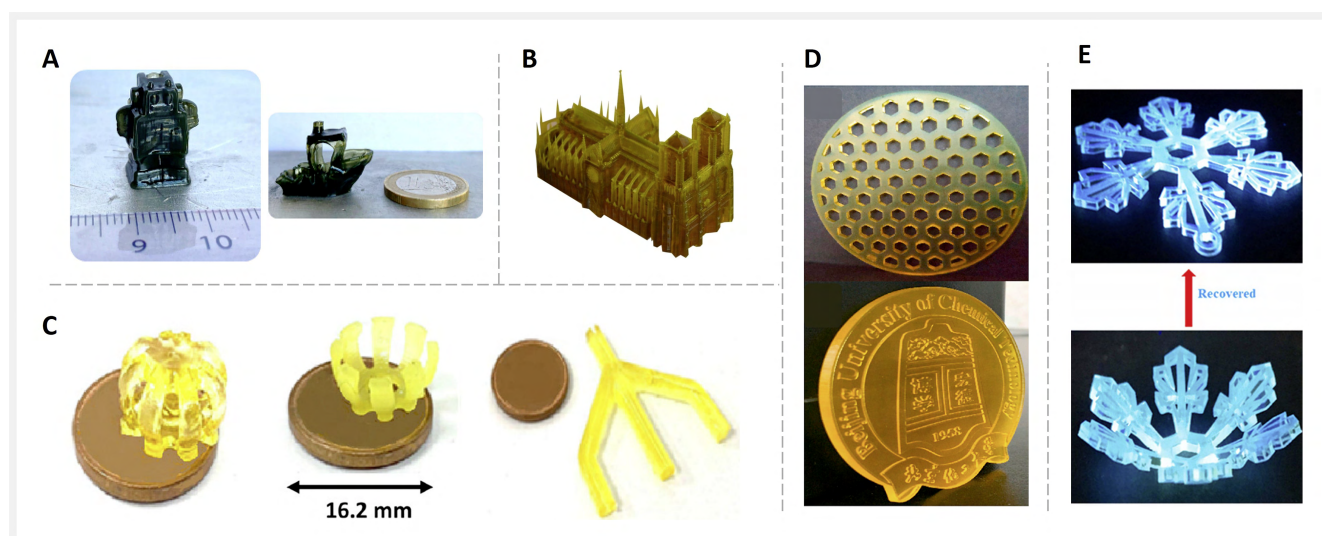


Figure 3 A) 3D-printed objects using the RF-TEOHA system together with MWCNT.³³ Adapted from Ref. 33 published under a creative commons license (CC BY). B) RFT-based 3D-printed model version of the "Notre Dame de Paris" showing high-resolution details.²⁹ Reprinted with permission from Ref. 29. Copyright 2021 Wiley-VCH. C) Different 3D-printed objects using methacrylated QZ as a photoinitiator for a biobased soybean oil-based system.⁶¹ Reprinted with permission from Ref. 61. Copyright 2021 American Chemical Society. D) Photographs of 3D-printed methacrylate-based (hexagonal grid structure) and hydrogel-based (badge structure) using 3HF sulfonate derivatives as a photoinitiator.⁷⁴ Adapted with permission from Ref. 74. Copyright 2021 Elsevier Ltd. E) Flavone-based, stimuli-responsive 3D-printed snowflake in both programmed and recovered states under UV-light excitation.⁷⁵ Reprinted with permission from Ref. 75. Copyright 2021 Elsevier Ltd.

FMN-based structures were less genotoxic than those manufactured with commercially available photoinitiators and supported the growth of bovine aortic endothelial cells. Bell et al. managed to achieve micron-scale structures consisting of type I collagen hydrogels by using FMN as a photosensitizer for multiphoton absorption 3D printing.⁴⁰ Other biomaterials, such as silk fibroin or keratin hydrogels, have been studied in combination with RF-based PISs for DLP 3D printing.^{41–43} Lee et al. added gelatin to the silk fibroin hydrogel and took advantage of its tyrosine residues for RF-mediated crosslinking through dityrosine bonding.⁴¹ In another publication, they also take advantage of the residual tyrosine in silk fibroin for manufacturing microneedles via DLP 3D printing in the visible light range.⁴² The microneedles showed high resolution (around 100 μm) and stability, even after penetration tests on animal skin. Placone et al. developed keratin-based hydrogels for DLP 3D printing of scaffolds for tissue engineering applications.⁴³ In this case, RF was used alongside sodium persulfate, which worked as a “catalyst,” and hydroquinone, as an inhibitor. The printed scaffolds showed good biocompatibility.

Several groups have also incorporated RF or FMN to a broad variety of “bioinks” for achieving photocrosslinking under visible light irradiation of extruded 3D structures.⁴⁴ Although this form of “bioprinting” uses RF-mediated photopolymerization to consolidate the structures, it is not considered a truly light-based 3D printing technology and a broad discussion is thus out of the scope of this mini review.

Flavones

Another family of phenolic compounds with high interest is flavones. Examples of naturally occurring flavones are chrysin, myricetin, tangeretin, luteolin and 6-hydroxyflavone. Flavones are ubiquitously present in plants such as cereals and herbs. Examples are vegetables like celery and parsley, yellow or orange fruits such as citrus, flowers such as passion flowers, chamomile, and crocus, or even honey and propolis.^{45,46} The formation of flavone compounds in plants is closely linked to light, so that the highest concentration of flavones occur in leaves or the skins of fruits.⁴⁵ It is known that flavones show highly beneficial physiological properties such as being anti-inflammatory, anti-allergic, anti-microbial, antioxidant, and anti-tumor and demonstrate positive vascular effect in patients.⁴⁷ Flavones exhibit high absorption in the near-UV to visible range, especially between 350 and 470 nm.⁴⁸ Therefore, the flavone family is a promising candidate for applications in light-based 3D printing. The flavone derivatives are usually reported as type II photoinitiators, which can be excited to a singlet or triplet state to afterwards react with a co-initiator to form free intermediate radicals and thus, start the polymerization. It has been shown that the nature and position of the substituents, such

as hydroxy groups, affect the initiation properties of flavones. Recently, Al Mousawi et al. explored five flavone derivatives – flavone, 6-hydroxyflavone, 7-hydroxyflavone, chrysin and myricetin – in two- and three-component PISs for the free-radical polymerization of methacrylates and the cationic photopolymerization of epoxides with application in blue-light 3D printing.⁴⁸ All flavone derivatives except for 7-hydroxyflavone are naturally available. In this thorough study, they established relationships between the structure of the flavone compounds and the effectivity in photoinitiation. It was demonstrated that the location and number of hydroxy groups determine the photophysical properties of the compound: a higher number of phenolic functionalities in the flavone skeleton reduces the photoinitiating efficiency. Indeed, the phenolic functionalities show scavenging properties and thus inhibit the (radical) initiation process. This effect explains why myricetin, despite having the highest absorption, was less reactive, whereas 6-hydroxyflavone (6HF) showed the best photoinitiation performance. Moreover, oxygen inhibition competes with radical production. Oxygen inhibits the radical process by quenching the excited flavones. In this context, additives could increase the oxygen tolerance of the inks. The results show that the systems containing *N*-phenylglycine (NPG) perform very efficiently due to the electron transfer from NPG to flavones in a photoreduction process. Moreover, oxygen inhibition can be prevented using more viscous monomers. Further, the solubility of the flavone compounds in the monomers highly affected the effectivity in PIS. Myricetin shows poor solubility in the studied methacrylate formulations. In conclusion, 6HF was the most promising of the naturally occurring flavones and could be successfully used for 3D printing of well-defined structures with different thicknesses.

Curcumin

CCM is a hydrophobic, phenolic natural substance which has also gained interest as a natural photoinitiator. CCM is an inexpensive yellow-orange natural dye derived from the rhizomes of the plant turmeric (*Curcuma longa*) and present in culinary spices such as curry. Further, CCM has been used in traditional Indian and Chinese medicine for centuries.⁴⁹ Therefore, CCM has been extensively studied due to its beneficial pharmacological properties, among which the following stand out: anti-inflammatory, anti-bacterial, anti-viral, anti-oxidant, and even anti-cancer or anti-Alzheimer applications.⁵⁰ It is not until the beginning of the 2000 s that CCM started to gain interest among the scientific community due to its interesting photochemical properties. CCM exists predominantly as a keto-enol tautomer, providing a highly conjugated system responsible for its long wavelength absorbance between 340 and 535 nm.⁵¹ However, due to its keto-

enol tautomerism, its properties are strongly dependent on the solvent or medium.^{52,53} Further, differently to RF and flavone derivatives, CCM is highly soluble in a broad variety of polar and nonpolar monomers and polymers. These assets, apart from its low toxicity, make CCM an interesting compound for photopolymerization applications. Until now, CCM has been reported in mechanisms such as the free radical polymerization of styrene⁵⁴ or methacrylate monomers,^{55,56} or the cationic polymerization of epoxides.^{57,58} In general, CCM is commonly also presented as a type II photo-initiator: after illumination with an adequate wavelength, CCM can be excited to a short-lived singlet state, which generates a triplet excited state with relatively low quantum yield due to intramolecular or intermolecular hydrogen bonding.⁵³ From the excited state, CCM abstracts a hydrogen from a co-initiator, e.g. an amine or even a polyol such as glycerol.⁵⁶ Interestingly, Oliveira et al. proposed a mechanism for photoinitiation with CCM acting without a co-initiator, forming radicals directly from a methacrylate monomer, which then initiates polymerization.⁵⁶ Despite the great interest in CCM for photopolymerization, its use in PISs for light-based 3D printing is very scarce. Branciforti et al. performed SLA 3D printing of epoxidized linseed oil using a PIS consisting of CCM and iodonium salts.⁵⁷ After excitation with visible light, CCM generates radicals that are then oxidized by the iodonium salts, generating the ionic species necessary to start the cationic photopolymerization of the epoxides. The use of natural dyes with electron acceptors such as iodonium salts is less usual than electron/hydrogen donors such as amines.³⁰ This work is one of the few examples using a combination of biobased monomers and with biobased photosensitizers. The novelty of this work opens new perspectives for fully biobased inks for light-based 3D printing.

Other Natural Compounds

In addition to the already discussed natural compounds, there are other classes with interesting optoelectronic properties such as anthraquinones, coumarins and chalcones (Figure 1B). Anthraquinones are a family of natural dyes derived from medicinal plants such as Liliaceae and Polygonaceae that can be functionalized to increase their solubility in organic media.⁵⁹ Among them, quinizarin (1,4-dihydroxy-anthraquinone, QZ) stands out due to its fungicidal, pesticidal and anti-tumor properties.⁶⁰ QZ presents strong absorption in the near-UV to blue region; however, it presents slow initiating properties.⁶¹ The underlying reason for this lies in the hydroxy groups, which reduce solubility in organic media while acting as radical scavengers that might inhibit the photopolymerization. Coumarin and chalcone derivatives are being studied as interesting photoactive substances. Their use in photopolymerization has been widely

reported by Dumur and coworkers.^{62,63,64} Coumarins are flavonoid type of secondary metabolites present in (green) plants and have been intensively studied due to promising antioxidant and anti-cancer properties.⁶⁵ Moreover, coumarins have been used in sensing, detecting or fluorescence applications.⁶⁶ The coumarin scaffold, which is a benzopyrene derivative, is characterized by broad and high (visible) light absorbance and can readily be tuned through derivatization.⁶⁷ Chalcones or chalconoids are a structurally diverse group of natural phenolic compounds occurring in a broad part of the plant kingdom with antibacterial, anti-inflammatory and even anti-tumor properties.⁶⁸ Chalcones are closely related to flavonoid compounds, with absorbance mainly in the UV-blue region. However, with proper derivatization and substitution of the chalcone core, the photoelectric properties can be fine-tuned and shifted to the blue-green region.⁶³

However, anthraquinones, coumarins and chalcones have not been used directly but rather derivatized through more synthetic functionalization pathways and will be discussed in detail in the next section.

Naturally Derived Photoinitiating Systems

Current limitations of natural PISs such as low photoinitiation efficiency as well as poor solubility in the ink formulation need to be overcome in order to increase their applicability in 3D printing. For this aim, there are two main synthetic strategies that have been explored so far: a) (post-) functionalization of the pure natural PISs and b) purely synthetic route yielding a new structure that is related to the core of the natural compound which in contrast cannot be considered as biobased anymore.

Functionalization of Natural PIS

The first strategy consists of small molecular modifications in the PIS, conserving the main structure of the natural compound. These modifications include the incorporation of functional side groups to achieve either an increased solubility of the PIS in the desired media or an introduction of polymerizable groups. All these changes do not significantly affect the optoelectronic properties except for solvatochromism.

For example, functionalization of RF has been performed to overcome the limited solubility in organic solvents. Several hydroxy groups in the ribityl tail make this compound difficult to dissolve in aprotic media, hence, the hydroxy groups could be functionalized with butyrates leading to riboflavin tetrabutryrate (RFT).⁶⁹ This compound has a higher solubility in organic solvents compared to pure natural RF. Aiming for these properties, Champion et al. could success-

fully perform DLP 3D printing of a biobased acrylate formulations in the presence of RFT and an amine co-initiator.²⁹ The 3D-printed structures show enhanced resolution and level of detail (Figure 3B). This work is the first employing RF-derived PIS in other than hydrogel 3D printing. Their work further proves that side-group functionalization does not necessarily influence the photoinitiation process in 3D printing. This functionalization could be also equipped in other compounds to achieve increased solubility in photocurable inks.

In another work, the two hydroxy groups of QZ from the anthraquinone family were functionalized with methacrylate groups by Breloy et al. to dissolve it in soybean oil acrylates.⁶¹ This two-component photocurable ink was entirely bio-based and could be DLP 3D printed with an LED wavelength of 405 nm. Geometries with different levels of complexity and overhanging structures were printed using the novel QZ derivative demonstrating its photoinitiating properties (Figure 3C). The functionalization of the PIS with methacrylate groups further yielded covalent incorporation into the polymer network during the printing process. The printed material exhibited antibacterial properties when exposed to visible light. The strategy of covalent incorporation of the PIS in the 3D printing process has been described by Sautrot-Ba et al. in 2021 with a purpurin-derived PIS.⁷⁰ The covalent incorporation of the dyes into the polymer network prevents the release of the PIS in the application. This might reduce the toxicity of the material or influence other (optoelectronic) properties of the printed materials.

Synthetic Routes Yielding Substructures of Natural PIS

The (post-)functionalization step yields a biobased PIS while complex synthetic routes can be assigned to entirely synthetic PIS carrying a conjugated system which was nevertheless inspired or derived from a natural compound and is therefore not biobased. Synthesis of these derivatives is more demanding since it often implements rather significant changes in the conjugated system. These changes mainly target a shifting of the absorption spectrum or influence the optoelectronic properties by either reducing competitive photoelectronic side pathways or creating new ones. These significant molecular changes can go along with the investigation of inter- and intramolecular photoreaction pathways to enhance the photoinitiation efficiency.

In this context, the development of flavone-based PISs can be highlighted since in this case the empirical and theoretical investigation of the photoinitiation pathway had a major impact on the research progress. The previously described pure natural flavones have a well-described competitive photoexcitation pathway by intramolecular proton transfer (ESIPT).⁷¹ In this pathway, the excited state is

present in two tautomeric states. After a proton transfer, the decay of the arisen charge transfer species yields two fluorescence emission bands. This photoreaction pathway makes flavones excellent fluorescent probes for sensing and imaging applications.⁷² However, the predominant tautomerism and thus the described fluorescence pathway competes with the photoinitiation. Nevertheless, the photoinitiation process efficiency can be improved by controlled functionalization of the aromatic core in flavones. The success of this functionalization can be seen by comparing the early flavonoid PIS, reported by Al Mousawi et al.⁷³ with recent developments. You et al. have for example tuned flavones at various positions to enhance their applicability in DLP 3D printing.⁷⁴ Most recently, the esterification of the 3-hydroxy group in combination with a 3-carbazolyl π -extension has notably improved the efficiency in multi-component PISs for DLP 3D printing of PEGDA hydrogels.⁷⁵ Herein, the authors replaced the phenyl group with a carbazole moiety to yield a larger bathochromic shift enabling light-based printing with a photoinitiation at 405 nm. These flavone derivatives could successfully be used for printing detailed geometries (Figure 3D, E).

Similar functionalization was also applied to CCM. Altering the absorption spectrum of CCM with two carbazyl moieties was performed by Wang et al. to achieve DLP 3D printing of ceramic PEGDA slurries under green 532 nm irradiation.⁷⁶ Herein, the bis-carbazyl-modified CCM was synthesized and used as a PIS in combination with an iodonium salt. Both carbazyl substituents were important to achieve an enormous bathochromic shift improving the penetration depth of the light in the dispersion and the print fidelity.

In a similar approach, Lalevée and coworkers had performed several studies focusing on the influence of the functionalization of the conjugated system in mono-chalcone^{64,77,78} or coumarin⁷⁹ on the efficiency in direct laser writing and 3D printing with a wavelength of 405 nm. All these PISs possessed two- or three-component PISs with an iodonium salt or/and an external amine. Further empirical and theoretical studies are necessary to gain deeper understanding of the fundamental photoreaction pathway in these naturally derived PIS.

More complex changes of the conjugated systems, such as embedding them in π -donor-acceptor(–donor) structures, have been reported for anthraquinones,⁸⁰ bis-chalcones,^{77,81} and (keto-) coumarins.⁸² These structures can be very efficient PISs in 2PLP as well as in DLP/SLA. However, the resulting PIS differs considerably from natural and naturally inspired PISs. Thus, detailed discussion of these structures is out of scope of this short review.

Conclusions and Outlook

Natural alternatives in photocurable inks for light-based 3D printing have gained considerable research interest in recent years. Until now, the attention has rather been paid to natural or biobased monomers and pre-polymers. However, the variety of photoactive compounds found in nature offers an excellent source for the development of new PIS that might cover the entire visible spectrum. These compounds have already proven the potential to enable light-based 3D printing in the visible spectral range. Development of new natural and natural-derived PIS could expand the first promising results to further extend.

This short review has highlighted recent progress in the implementation of the three natural compound families – RF, flavone, and CCM – in light-based 3D printing. The three classes of natural compounds do not only compete with commonly used, commercially available, fossil-fuel based photoinitiators in terms of their photoinitiation performance, but they can also add biocompatibility, color, antifouling, and other properties with physiological relevance to the 3D-printed materials. In addition to that, this review has given an overview of other natural compounds such as anthraquinones, coumarin, and chalcones, which have been successfully used after functionalization. This targeted functionalization was employed to overcome existing limitations such as poor solubility in the photocurable ink or low photoinitiation performance. Future improvements could be achieved by combining theoretical and empirical work since a detailed understanding of the fundamental photoinitiation process could facilitate the design of highly efficient naturally derived PIS. A summary of the reported natural, naturally derived, and synthetic compounds is given in Table 1.

In addition to the current efforts to overcome the described limitations, attention should be paid to more sustainable synthesis including atom-economic few-step synthesis to reduce solvent use and hazardous by-products. Furthermore, exploring the potential of more sustainable or purely natural co-initiators could be a promising alternative approach to enhance the photoinitiation performance which has not been discussed here. This strategy could allow for an increase in existing interplay within the PIS and not only enhance photoactive properties in one component as it has been performed until now. Finally, new efficient and natural PISs for use in the red region could facilitate handling of the light source as well as enable the 3D printing of bioinks with enhanced biocompatibility.

Despite the outlined challenges, the use of natural and naturally derived derivatives as PISs in 3D printing is promising and we believe that natural PISs are a more sustainable alternative that will have a big impact in the field in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

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