Naturally Derived Photoinitiators for Dental and Biomaterials Applications

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Abstract

Biocompatibility of materials used in dental and biomaterials applications is very important and depends on the components of these materials. Photopolymerized materials for dental and biomaterials applications have been progressively used since the 1970s. One of the crucial components in these materials is the photoinitiator (PI) that initiates the polymerization reaction. Synthetic PIs are the most commonly used types, but owing to their drawbacks such as cytotoxicity, insolubility in water, and high cost, research on naturally derived (bio-sourced) PIs is growing, to find an alternative to these synthetic types, especially in the growing field of three-dimensional (3D) printing and bioprinting of biomaterials for tissue engineering applications. Naturally derived PIs are biocompatible, highly water-soluble, and abundant. Naturally derived PIs have been used to prepare experimental dentine bonding agents, dentine primers, photo-crosslinked hydrogels for tissue engineering applications, antibacterial coatings, guided tissue regeneration membranes, and 3D printed biomaterials. An electronic search was done using MEDLINE/PubMed and Scopus databases using the keywords naturally derived, bio-sourced, photoinitiators dental, biomaterials, 3D printing, and 3D bioprinting, to review potential naturally derived PIs for dental and biomaterials applications. There are a variety of naturally derived PIs with various colors and absorption spectra to choose from, according to the intended application. Most of naturally derived PIs can be used with modern conventional dental light curing units, making them applicable for experimental studies for potential dental and biomaterials applications. Due to their biocompatibility and availability it is expected that in the upcoming years, research on naturally derived PIs and their dental and biomaterials applications will increase especially in the growing field of 3D bioprinting in which cell viability is essential; thus this review was done.

Keywords

- naturally derived
- bio-sourced
- photoinitiators
- dental
- biomaterials
- 3D printing
- 3D bioprinting

Introduction

Photopolymerization is a process in which a liquid monomer changes into a solid material by a chain reaction initiated by reactive species (radicals, cations, or anions), which are generated from photoinitiators (PIs), upon ultraviolet (UV) or visible light irradiation.[1] Photopolymerization has been used in dentistry since the 1970s. It started with the use of a UV light-cured pits and fissure sealant,[2] then UV-cured dental resin-based composites (RBCs). However, due to the drawbacks of UV-light curing such as short depth of cure, long curing time per increment, heat generation, and potential hazards to the eyes,[3] visible light-cured (RBCs) progressively replaced UV-cured (RBCs) after the introduction of camphorquinone PI in 1978.[4]

Visible light photoinitiation then included different dental materials such as dentine bonding agents, resin cements, glass ionomer cements, denture base polymers, and epoxy resins. Nowadays, photopolymerization is being used to prepare hydrogels, three-dimensional (3D) printed and 3D bioprinted scaffolds, for tissue engineering applications, such as bone and cartilage regeneration.

A PI is a synthetic or naturally derived substance with a chromophore group that absorbs light and takes part in initiation of polymerization reaction, alone or through primary or subsequent reactions, involving one or more additional compounds such as coinitiators and accelerators. Thus a photoinitiating system (PIS) can be a one-component system with the PI only, or a two-component system with the PI and one additive mainly a coinitiator, or a three-component system with the PI plus a coinitiator and an accelerator.[5]

PIs can either be of type I or type II. Type I PIs generate initiating radicals by a unimolecular cleavage reaction, while type II PIs undergo bimolecular hydrogen abstraction reactions by the transfer of a hydrogen atom from a second compound, which is the coinitiator. The generation of radicals from type II PIs is slower in comparison to type I PIs because this initiation is based on a bimolecular reaction;[6] thus accelerators are used with type II to enhance polymerization kinetics and lower the irradiation timec Synthetic PIs have several drawbacks such as limited solubility in water, high cost of synthesis, and cytotoxicity.[8] On the contrary, naturally derived (bio-sourced) PIs are highly soluble in water, biocompatible, abundant, and of lower cost.

The most common mechanisms of photoinitiated polymerization used in dental and biomaterials applications are free radical or ionic polymerization. In free radical polymerization, upon light irradiation, the PI generates active free radicals that attack the monomer and convert it into a free radical that propagates the reaction and is terminated by either reaction of two free radicals (coupling) or by hydrogen transfer from a free radical to another. Photoinitiated ionic polymerization is similar to free radical polymerization but is characterized by the propagation of anionic or cationic species. Upon light irradiation, PIs produce an electron-donating compound (cationic polymerization) or an electron-withdrawing compound (anionic polymerization). Ions attack the monomer and propagation occurs by the addition of monomers to the initial ion pair. Termination of polymerization can occur by the transfer of the ion pair to a monomer or a polymer or combination with a counter ion.[9]

Three-dimensional printing is an additive manufacturing technology that allows fabrication of dental materials and biomaterials by adding successive layers of materials (e.g., polymers) on top of each other through computer-aided design. Photochemistry-based 3D printing uses monomers and PIs either by free radical or ionic polymerization.[10] Also, 3D bioprinting is based on deposition of biomaterials, either encapsulating cells or loaded with cells, for tissue engineering applications. Thus, using biocompatible monomers and PIs by visible light stereolithography techniques to prepare 3D bioprinted biomaterials is crucial for cell viability.[11]

Naturally derived PIs have been used to prepare experimental dentine bonding agents, dentine primers, methacrylates, photo-crosslinked hydrogels for tissue engineering applications, antibacterial coatings, guided tissue regeneration membranes, 3D printed and 3D bioprinted biomaterials (►Fig. 1).

An electronic search was done using MEDLINE/PubMed and Scopus databases using the keywords naturally derived, bio-sourced, photoinitiators, dental, biomaterials, 3D printing, and 3D bioprinting, and using operators or modifiers such as AND, NOT, and OR with the different keywords to review the potential naturally derived PIs for dental and biomaterials applications. Articles were chosen according to the following inclusion criteria: full text available or obtained in English language and the applications are for either dental or biomaterials uses. Structure of each naturally derived PI is shown in (►Fig. 2) and the type, color, and uses of each are summarized in ►Table 1.

Fig. 1 Uses of naturally derived photoinitiators for dental and biomaterials applications.

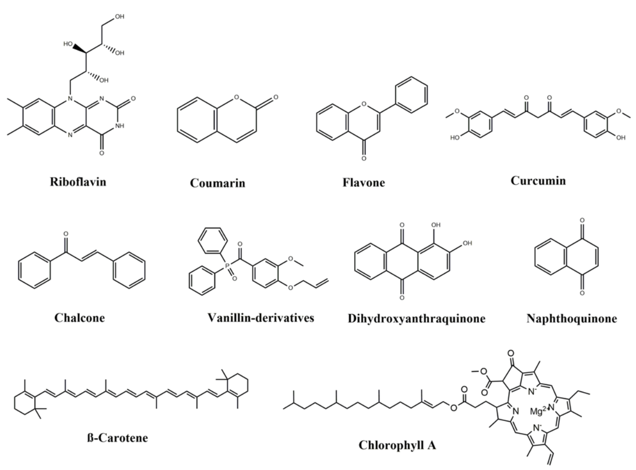

Fig. 2 Structure of naturally derived photoinitiators for dental and biomaterials applications.

Table 1 Summary of types, color, and potential uses of naturally derived photoinitiators for dental and biomaterials applications

Naturally derived photoinitiator	Type	Color	Uses
Riboflavin	I or II	Orange-yellow	• Dentine primers
			• Hydrogels
			• 3D printing/bioprinting
Coumarins	II	Colorless or white	• Polymerization of acrylates, methacrylates, and epoxy resin
			• 3D printing
			• Dentine bonding agents
Flavones	II	Colorless	• Polymerization of methacrylates
			• 3D printing
Curcumin	II	Orange-yellow	• Anticariogenic photodynamic therapy
			• Polymerization of methacrylates
			• Antibacterial coatings
Chalcones	II	Yellow	• Polymerization of acrylates and epoxy
			• 3D printing
Vanillin derivatives	I	White	• Polymerization of acrylates
			• 3D printing
Dihydroxyanthraquinone	II	Orange	• Polymerization of methacrylates and epoxy
Naphthoquinones	I or II	Yellow, red, orange, purple	• Polymerization of acrylates
β-Carotene	II	Red-orange	• Antibacterial coatings
Chlorophylls	II	Green	• Photodynamic therapy disinfection in endodontics
			• Polymerization of MMA

Abbreviations: 3D, three-dimensional; MMA, methyl methacrylate.

Riboflavin (Vitamin B2)

Riboflavin, or vitamin B2, is derived from plant origins, such as asparagus, broccoli, and spinach, or animal origins such as kidneys and liver. Riboflavin is important for energy production, enzyme function, and normal fatty acid and amino acid synthesis.[12] It is orange-yellow in color and absorbs light in the range of 200 to 470 nm, that is, in the UV and visible light ranges, with maximum absorption (λ max) at 223 nm, 267 nm, and 373 nm in the UV region, and 444 nm in the visible light region.[13] Riboflavin has the ability to produce superoxide radicals that can consequently initiate a polymerization reaction.[14] When used with UV, riboflavin acts as a type I PI while when used with visible light, it acts as a type II PI; thus a coinitiator is needed as a proton donor.

Riboflavin is the most commonly used naturally derived PIs in dental and biomaterials applications. Riboflavin has been used either with UVA (315–400 nm) or visible light as a primer to cross-link dentinal collagen before the application of dentine bonding agents to increase the bond strength and decrease nanoleakage. Application of riboflavin also inactivates matrix metalloproteinase (MMP) through direct cross-linking of MMPs, thus preventing degradation of the hybrid layer.[15] Riboflavin has also been used to prepare photo-crosslinked membranes for guided tissue regeneration,[16] hydrogels for bone,[17] and cartilage regeneration.[18] It is also used in corneal collagen cross-linking to treat keratoconus, using UVA light.[19]

Riboflavin has also been used in 3D printing of polyethylene glycol diacrylate for the potential use in tissue engineering applications.[20,21] It has also been used in the 3D bioprinting of collagen/chondrocytes bioinks using extrusion-based bioprinting and visible blue light.[22] A drawback of riboflavin as a PI is its orange-yellow color that might change the color of the final photo-crosslinked material.

Recently, riboflavin has been used with UV, using photodynamic therapy to reduce the count of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), the causative agent for coronavirus disease 2019, while maintaining blood product quality.[23]

Coumarins

Coumarins and keto-coumarins are naturally derived compound of plant origin, especially tonka beans, strawberries, cherries, apricots, cinnamon, and vanilla grass. They possess antimicrobial, antioxidant, anticoagulant, and anti-inflammatory properties.[24] They are colorless or white solids that absorb light in the near UV and visible light spectra (270–510 nm) with the (λ max) of some types at 405 nm and 421 nm. Coumarins are type II PIs that can initiate the free radical polymerization of methacrylates such as bisphenol-A-glycidyl methacrylate and triethylene glycol dimethacrylate (Bis-GMA/TEGDMA) and cationic polymerization of epoxy resins. Also, they can be used to photopolymerize photosensitive 3D printing resins and epoxy silicones using laser diode irradiation at 405 nm and hydrogels for tissue engineering applications.[25-27]

Being colorless or white gives coumarin an advantage over other colored naturally derived PIs, as it can be used easily without changing the color of the material to be photopolymerized.

Coumarin-based iodonium hexafluoroantimonate is a white-colored PI with a light absorption spectrum near blue light (λ max at 347 nm) and has been used in the photopolymerization of experimental dental adhesive resin based on Bis-GMA, TEGDMA, and hydroxyethyl methacrylate, both in presence of solvent and acid monomer content.[28] Coumarin oxime esters have strong absorption in the range of 400 to 480 nm and can initiate free radical polymerization of acrylates.[29] High concentration of coumarin can be hepatotoxic,[30] thus care should be taken to use the least efficient amount to photoinitiate polymerization reaction.

Flavones

Flavones are colorless naturally derived compounds that belong to flavonoids and are derived from food sources such as spices and red-purple fruits and vegetables and have antioxidant, anti-inflammatory, antimicrobial, and anticancer properties.[31] Certain types of flavones have proven their antibacterial activity against cariogenic bacteria.[32] They can be used as PIs using near UV and visible light irradiation (350–470 nm) with λ max at 405 nm. The family of flavones includes compounds such as 3-hydroxyflavone, 6-hydroxyflavone, 7-hydroxyflavone, chrysin, and myricetin. Flavones are type II PIs that are used with coinitiators and accelerators to enhance photopolymerization. Flavones can be used to photopolymerize Bis-GMA/TEGDMA composites and 3D printed biomaterials.[8,33]

Curcumin

Curcumin is a yellow-orange natural dye derived from the rhizomes of *Curcuma longa*. It has anti-inflammatory, antibacterial, and antioxidant properties,[34] and antiviral properties against several viruses among which is SARS-CoV-2.[35] Curcumin has been proven to reduce dental bacterial biofilm formation,[36] and photodynamic therapy using blue visible light and curcumin as a photosensitizer has led to 99.99% reduction in the bacterial count of *Streptococcus mutans* and *Lactobacillus acidophilus*.[37] It has also proven to be efficient in the treatment of chronic gingivitis.[38]

It is a panchromatic PI that absorbs light in the UV-visible light (blue, green, yellow, red, and warm white) range (350–750 nm), with an intense light absorption maximum (λ max) at 417 nm. It is a type II PI that is used with coinitiators and accelerators in three-component PIS for free radical polymerization of methacrylates such as urethane dimethacrylate and BIS-GMA, leading to highly cross-linked polymers with high thermal stability and mechanical strength.[39-41]

Curcumin has been used to prepare visible light photo-induced stainless steel antibacterial coatings against *Escherichia coli* and *Staphylococcus aureus*, with the ability to reduce bacteria by 99% and 95%, respectively.[42] The drawback of curcumin is its yellow-orange color, which may limit its application, especially in dental applications.

Chalcones

Chalcones are a class of natural compounds that belong to flavonoids and are present in many edible plants such as fruits (tomatoes, apples, citrus), nuts, and vegetables (potatoes, shallots, bean sprouts) with anti-inflammatory, antibacterial, antiviral, anticancer, and antioxidant properties.[43] Chalcone derivatives have been proven to promote osteogenic differentiation of cells,[44] thus are candidates to be used in photo-crosslinked hydrogels for bone regeneration. They have also proven to have inhibitory effects against *S. mutans* cariogenic bacteria.[44]

Chalcones are yellow colored and are type II PIs that absorb light in the near UV and visible light region with λ max of some types at 423 nm, 363 nm, 362 nm, and 344 nm. Chalcones can be used in the photopolymerization of acrylates by free radical polymerization, cationic polymerization of epoxy, and preparation of 3D printed biomaterials for tissue engineering applications.[45,46]

Vanillin Derivatives

(4-Allyloxy-3-methoxybenzoyl) diphenylphosphine oxide is a vanillin-derived type I PI that is white in color and can be used to induce free radical polymerization of acrylates using UV light as it absorbs light in the UV region (385 nm).[47] Vanillin-derived PIs have the potential to be used in the photopolymerization of 3D printed scaffolds for tissue engineering applications. Vanillin derivatives are known to possess antimicrobial properties.[48] Being of type I, vanillin-derived PIs can be used without coinitiators and accelerators, thus the biocompatibility of the PIS increases.

Dihydroxyanthraquinones

Dihydroxyanthraquinone derivatives are naturally derived dyes of plant origin and are orange in color with anticancer properties. They are blue-light-sensitive with λ max of some types at 477 nm, 417 nm, and 426 nm. They are type II PIs and have the potential to initiate free radical polymerization of methacrylates (Bis-GMA/TEGDMA) and cationic polymerization of epoxy.[49]

Naphthoquinones

Naphthoquinone derivatives, such as 5-hydroxy-1,4-naphthoquinone, are naturally derived PIs of plants, microbes, and marine origins,[50] and possess antibacterial properties.[51] They are yellow, red, orange, or purple in color and show maximum absorption (λ max) at 420 nm in visible blue light region. They are type II PIs that can initiate the free radical polymerization of acrylates.[52,53] 1,4-Naphthoquinone-2,3-dithiol can be used as a type I PI using visible light (478 nm) to initiate the free radical polymerization of acrylates.[54]

β-Carotene (Provitamin A)

β-Carotene is a naturally derived PI that is commonly synthesized by plants, fungi, and photosynthetic bacteria. It is red-orange in color and absorbs light between 400 and 500 nm with maximum absorption at 450 nm. It has photobactericidal, antioxidant properties and is a precursor of vitamin A.[55] It is a type II PI that has been used in the cationic photopolymerization of limonene-derived polymer network with addition of eugenol, to prepare antibacterial coatings.[56]

Chlorophylls

Chlorophyll and its derivatives are naturally derived green-colored PIs that are found in plants, eukaryotes, and cyanobacteria, and are essential for photosynthesis process. It has proven antimicrobial activity against *Candida albicans* and *Enterococcus faecalis*[57] and can be used as a photosensitizer in root canal disinfection, using photodynamic therapy.[58] Chlorophyll derivatives have proven antiviral activity against SARS-CoV-2 virus.[59] Chlorophyll A absorbs light in the violet-blue region (430–450 nm) and is a type II PI that can initiate the free radical photopolymerization of methyl methacrylate, to produce cross-linked polymethyl methacrylate.[60]

Conclusions

Many naturally derived PIs have proven their ability to be used as biocompatible alternatives to synthetic PIs for dental and biomaterials applications. There are a variety of naturally derived PIs with various colors and absorption spectra to choose from, according to the intended application. Most of naturally derived PIs can be used with modern conventional dental light curing units, making them applicable for experimental studies for different dental and biomaterials applications. Due to their biocompatibility and availability it is expected that in the upcoming years, research on naturally derived PIs and their dental and biomaterials applications will increase especially in the growing field of 3D bioprinting in which cell viability is essential.

Conflict of Interest

None declared.

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