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3D printing algae-based materials: Pathway towards 4D bioprinting

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ABSTRACT

Algae is a renewable source of various materials that are suitable for 3D printing. Taking a step towards sustainability, the continuously growing industry of 3D printing calls for novel green materials/inks with stable mechanical properties. This paper aims to investigate the 3D printability of algae-based materials and their potential for 4D bioprinting. The sources, printability, and properties of algae-based synthetic polymers, natural hydrogels, and algae cells were reviewed. 4D printability was also explored in terms of hydrogel responsiveness to various types of stimuli and in terms of cell/tissue maturation, and relevant recent progress was reviewed. Results show that PHAs (Polyhydroxyalkanoates) from algae can replace fossil-derived PHAs because they have similar mechanical properties whilst being more environmentally friendly. Algae can also produce a wide range of hydrogel-forming polymers, of which many are already being used as 3D printing inks while others are yet to be developed to suit the printing specifications. Several hydrogels also demonstrate stimuli-responsiveness which make them suitable for 4D printing. Further research is required to overcome the mechanical instability and slow stimuli-responsiveness of natural hydrogels.

1. Introduction

The current environmental state of the earth is driving industries to replace the current unsustainable toxic products (e.g. fossil-based plastic and fuel) with green alternatives that are renewable and biodegradable. For example, from the energy side, the global renewable electricity generation increased by around 7% in 2021 [1]. Green materials are also gaining increasing attention. For instance, the global production of biodegradable bioplastics increased from ~1.2 million tonnes in 2020 to ~1.6 million tonnes in 2021, and is expected to reach up to ~5.3 million tonnes by 2026 [2]. Production of non-biodegradable bioplastics is also increasing since it is renewable, but its disposal stage is still concerning.

Bioplastics are typically produced from plant based sources such as starch or from agricultural residues and food waste. The downsides of these types of feedstock include the need for large areas of fertile lands for cultivation. Using food crops to produce bioplastics and other renewable materials also poses a threat to the food supply. Algae feedstock is an alternative source that overcomes the aforementioned limitations. Algae finds its applications in many fields owing to its natural production of various classes of materials including lipids, proteins, and carbohydrates [3–5]. Each class of these materials can be converted to several types of end products. For example, lipids can be converted to biofuels such as biodiesel and bioethanol [6]. Among all algae-sourced products, biofuel has been the main focus of research until the concept of algae-based biorefinery started emerging. Valorizing other types of products from algae such as proteins and polysaccharides not only yields higher economic value, but also helps supply the increasing demand for renewable materials. Fig. 1 shows general fields and categories of applications of algae-based materials, and the corresponding Sustainable Development Goals which they serve.

One of the growing industries that have started utilizing algae-based materials is the 3D printing industry [7–9]. 3D printing makes detailed prototyping easier and faster [10,11], makes printing precise scaffolds for tissue regeneration possible [12,13], aids in drug delivery and other biomedical applications [14–16], facilities fabricating customized water nanofilters and adsorption systems [17], and many more. Each application requires the printing material (ink) to have a specific combination of mechanical and biological properties, therefore, a wide range of novel materials are continuously being developed. Typically used inks include polymers [18], metals [19,20], ceramic [21,22], and biomaterials [23–25]. Smart and responsive materials are also gaining increasing interest as inks for 4D printing [26,27]. 4D printing functional materials

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serves biomedical applications, smart devices and biosensors, smart packaging, etc. [28,29]. However, the nature of most available printing materials imposes a trade-off between mechanical integrity and biological compatibility. On the other hand, algae-based materials are renewable, biodegradable, and have various favorable mechanical properties.

This paper explores the 3D and 4D printability of algae-based materials and algae cells. It starts with discussing the general categories of 3D printing technologies available in the industry and highlighting the ones suitable for printing algae-based materials, according to the literature. Then, algae-based synthetic polymers, natural hydrogels, and algae cells are discussed in terms of structure, mechanical and biological properties, printability, and applications. Finally, the potential of algae-based materials to be used in 4D bioprinting is highlighted.

2. General description of 3D printing processes and materials

This section describes the 3D printing technologies commonly used in the industry and specifies the ones that can be suitable for printing algae-based materials, according to the available literature. It also highlights the favorable mechanical and biological properties which the printing ink should possess. The terms 3D printing, 3D bioprinting, 4D printing, 4D bioprinting, ink, bioink, and hydrogel will be used according to the following definitions.

(1) 3D printing: precise layer-by-layer deposition of a material to form a previously designed three-dimensional digital model. Also called: additive manufacturing [30].
(2) 3D bioprinting: precise layer-by-layer deposition of a biocompatible material that contains living cells to form a previously designed three-dimensional digital model. Also called: biological printing [31].
(3) 4D printing: three-dimensional printing using smart or responsive materials which have the ability to change shape or property over time under certain stimuli.
(4) 4D bioprinting: three-dimensional printing of responsive materials containing living cells and have the ability to change shape or property in a controlled way under certain stimuli.
(5) Ink: any material suitable for three-dimensional printing.
(6) Bioink: any material suitable for bioprinting.
(7) Hydrogel: a network of hydrophilic polymers that can hold their 3D shape due to different types of crosslinking [32,33]. Not all hydrogels can form bioinks.

2.1. 3D printing processes

Fig. 2 shows the seven categories of 3D printing technologies as per the ISO/ASTM 2021 classification. According to the standard definitions, both binder jetting and powder bed fusion start with a powder bed, after which the former uses liquid as a binding agent to fuse the powder into desired shapes while the latter uses a thermal source as a binding agent. Selective laser sintering is one type of powder bed fusion in which a laser beam is used to fuse powdered materials such as polymers [34]. Direct energy deposition is another 3D printing technique

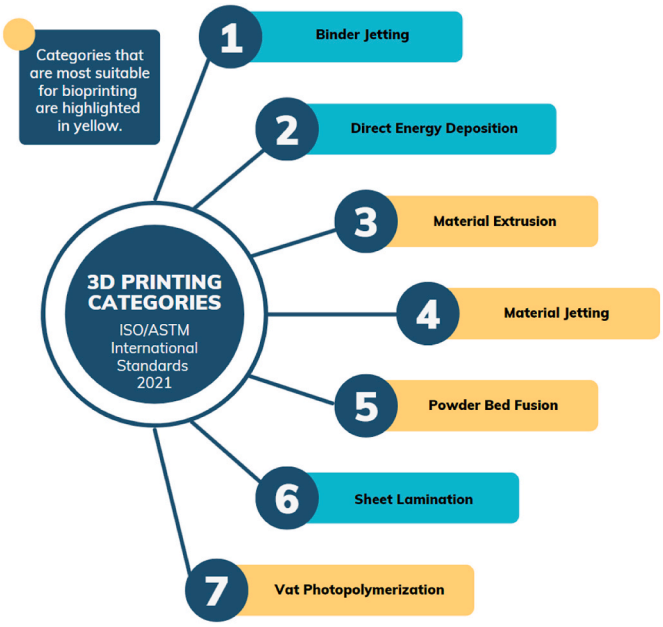

Fig. 2. 3D printing categories according to the ISO/ASTM International Standards 2021.

Fig. 1. Applications of algae-based materials and their respective Sustainable Development Goals.

which uses a thermal source to melt materials and fuse them into the desired shape. Sheet lamination fuses thin sheets of material together to form a print. Since most of the aforementioned techniques are not commonly used in printing biomaterials they are not described in detail here. Refer to Ref. [35] for more on the description of each process.

The four categories highlighted in yellow in Fig. 2 and summarized in Table 1 are among the most commonly used methods for printing biomaterials. Material extrusion dispenses material in a continuous line while material jetting dispenses drops of the material. Using material extrusion, thermoplastic, viscoelastic, or viscoplastic material goes through a nozzle in which it is melted and printed as required, once it is printed it rapidly solidifies. Sometimes additional postreatment using a thermal source is applied to enhance the mechanical stability of the print [34]. A wide variety of materials are compatible with extrusion printing, including thermoplastic polymers (e.g. PLA, PC, PET, etc), thermoset polymers (e.g. epoxy-based materials) hydrogels (e.g. alginate, nanocellulose, etc), cell-laden material, nanocomposites, etc [34,36]. Advantages of material extrusion include affordability, possibility of using nano-fillers, and ability to control parameters such as printing angle, layer thickness, etc [37]. Disadvantages include nozzle being prone to blockage, printed structure requiring support, and material viscosity should be around the high range of 30×10^7 to 6×10^7 mPa s [34,38].

On the other hand, material jetting, also called inkjet printing, requires lower viscosities of around 1–300 mPa s, which can be achieved by heating the ink [36,38]. Low viscosity cell-laden hydrogels can also be used with inkjet printing [31]. In this method, drops can either be dispensed through pressure in a continuous line or discontinuously in a drop-on-demand manner. Each layer of drops should solidify or be cured before the next layer is dispensed [39]. Inkjet printing is affordable and readily available but the technology that allows bioprinting various cell fabrications is limited. High heat and/or pressure also impacts the cell life and functionality. Like with extrusion printing, inkjet printing nozzles are also prone to clogging [39].

Vat photopolymerization and powder bed fusion, unlike extrusion and inkjet, do not involve the use of heat or pressure that damages living cells. Vat photopolymerization uses radiation sources such as laser or ultraviolet light to selectively solidify parts of a liquid photopolymer to form the desired shape, while powder bed fusion uses the same energy source to fuse the powder ink to form the desired shape. Although the accuracy of vat photopolymerization prints can reach up to 1.2 μm, mechanical properties are relatively low and liquid materials compatible with this process are mainly limited to thermoset polymers such as resin-based or acrylic-based materials. Similarly, powder bed fusion yields high accuracy but is costly and polymers, steel, or ceramic to be in a powder form only [34,40].

2.2. Inks and bioinks: materials and properties

The main determinant of the desired print properties and printing technology to be utilized is the application of the final product. For example, degradability is favored for a piece that will be used inside a human body for medical purposes while it is irrelevant in the textile or food industry. Generally, factors that define the final quality of a 3D print include the accuracy of the printing technology and the consistency of the printing ink. Consistency is a result of surface tension and rheological properties such as viscosity [41]. Thermophysical properties such as density and thermoplasticity are also crucial for the selection of the most suitable printing technology for a certain material. Favorable mechanical properties involve shear thinning, viscoelasticity, and shape fidelity [41,42]. Materials that are suitable for 3D printing include but are not limited to polymers, metals, ceramic, and biomaterials. Polymers are commonly used as 3D printing ink because of their high adaptability, strength, and lightness. Biopolymers from plant and algae sources can also be used as inks. They are more environmentally friendly but their mechanical properties are lower than those of polymers [36]. To enhance the properties of biopolymers, they can be reinforced with fillers such as carbon-fillers. Fillers can also enhance thermal and electric conductivities [43]. Section 4 will discuss the 3D printability of biopolymers which can be extracted from algae.

In addition to the mechanical properties required for regular 3D printing inks, bioinks should meet additional biological requirements. A good bioink should have high cell viability meaning cells are able to function properly inside the bioink medium. To be used for biomedical purposes, bioinks should be biocompatible. They should not cause damage to the host cells or alterations to the DNA. They should also exhibit desirable cell proliferation and mimic real tissues. In addition, they should prove controlled degradability that does not release toxic byproducts [40,44]. For food applications, bioink should be edible, has stable thermal properties, and has a low tendency for agglomeration. For textile products, flexibility is a key property.

Algae are powerful microorganisms that can produce a wide variety of materials, including lipids, proteins, and carbohydrates. 3D printing algae-based materials can be divided into three types as shown in Fig. 3.

The first type (3D printing bioplastics) is mainly aided with bacteria to produce plastic-like materials suitable for 3D printing such as PLA and PHAs while the second type (3D printing hydrogels) involves a natural process in which algae produce biomaterials that can form hydrogels suitable for 3D printing such as alginate, carrageenan, etc. The third type

Table 1
Summary of 3D printing techniques suitable for algae-based materials.

	Material extrusion	Material jetting	Vat photopolymerization	Powder bed fusion
Mechanism	Nozzle-based continuous material dispensing	Nozzle-based drop-by-drop material dispensing	Radiation used to solidify the printing ink.	Radiation used to fuse the powder ink.
Common types	Fused deposition modeling (FDM), direct ink writing (DIW), fused filament fabrication (FFF).	Drop on demand (DOD).	Stereolithography (SLA), digital light processing (DLP).	Selective laser sintering (SLS), electron beam melting (EBM).
Materials	Thermoplastic, thermoset, thermoelastic, viscoplastic, hydrogels, nanocomposites, etc.	Low viscosity materials and hydrogels.	Thermoset polymers (e.g. resin-based or acrylic-based)	Polymers, steel, ceramic in powder form.
Required viscosity	30×10^7 to 6×10^7 mPa s	1–300 mPa s	Not of utmost importance as these techniques are nozzle-free.	Not of utmost importance as these techniques are nozzle-free.
Resolution	Mm up to 5 μm	~50 μm	High (micro scale)	
Printing speed	Slow	Fast (up to 10,000 droplets per second	Medium to fast	
Cell density	High	Low (10^6 cell/ml and below)	Medium	
Cell viability	Medium (up to 85–90%)		High (up to 95%)	
Advantages	Affordability, small-scale accuracy, ability to change many printing parameters.	Affordability.	High accuracy, no nozzle issues.	High accuracy, no nozzle issues.
Disadvantages	Nozzle clogging, need for material support, high viscosity requirement.	Nozzle clogging, limited bioprinting techs, high temperature/pressure impacts cell viability, low speed.	Limited compatible inks, expensive.	Expensive, slow.

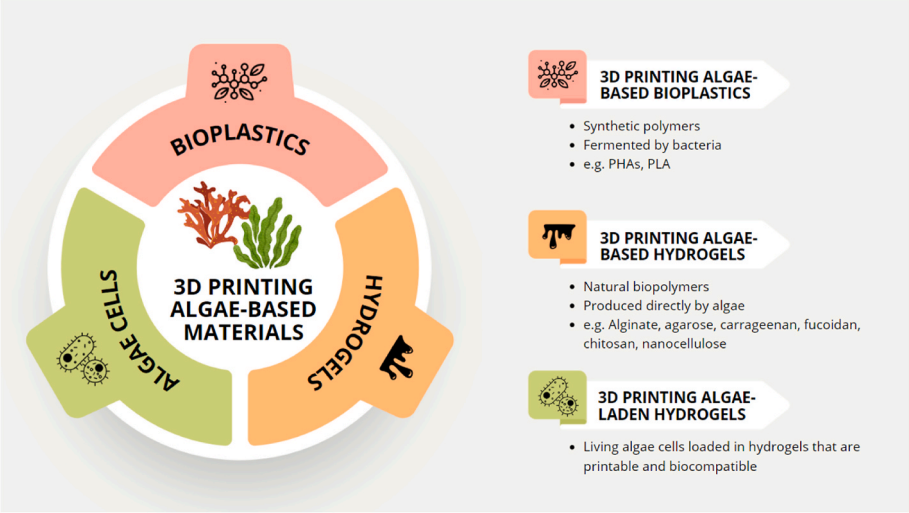

Fig. 3. Overview of 3D printing algae-based materials.

involves printing algae cells in biocompatible hydrogels not necessarily from an algae-based source. The following sections will discuss the suitable materials for each type.

3. Printability of algae-based bioplastics

3.1. Algae-derived PHAs

Polyhydroxyalkanoates, known as PHAs, is a family of polymers, specifically polyesters that are produced from renewable bio-based sources. Unlike some biobased plastics which are not biodegradable, PHAs have the ability to degrade through depolymerization in an interval of three to nine months [45,46]. The structure of PHAs is very diverse as this polymer can be made of 150 different monomers, which results in different properties. The most commonly used types of PHAs from algae are poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), also known as PHB and PHBV, respectively. Fig. 4 shows the structures of PHB, PHV, and PHBV.

Algae species that have high carbohydrates content are a suitable source of carbon which can be fermented by bacteria into PHAs. Studies have investigated the potential of red algae (*Gelidium amansii* [48,49], *Corallina mediterranea* [50], *Pterocladia capillaceais* [50]), green algae (*Chlorella* [51,52], *ulva* [53], *Botryococcus braunii* [54]), brown algae (*Laminaria japonica* [55]), and cyanobacteria [52,56,57] in combination with various marine bacteria to produce PHAs. Fig. 5 shows the types of algae and cyanobacteria that are suitable for PHA production. A study

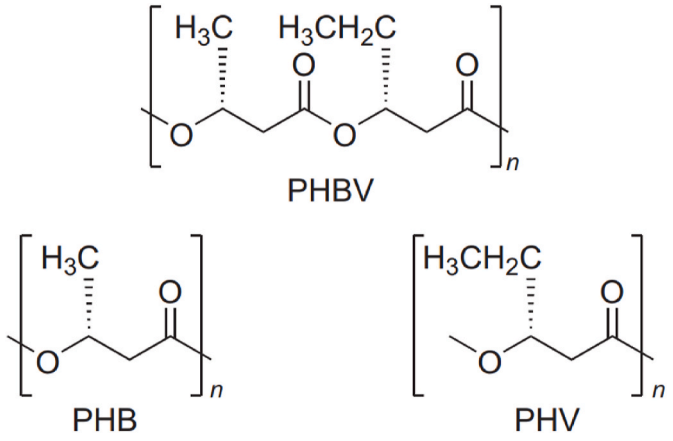

Fig. 4. Structures of different type of PHA [47].

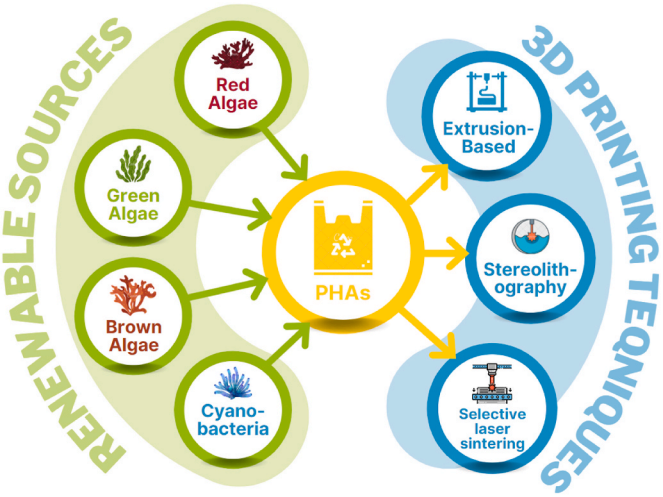

Fig. 5. Sources of PHAs from algae and cyanobacteria and the suitable 3D printing techniques.

also explored the use of a mixed culture of different bacteria and algae strains and were able to produce up to 20% PHA content in the form of PHB [58]. Another study obtained a similar result of 17%–27% dry cell weight content of PHB from red algae [48]. Specific structure and properties of the obtained PHA is determined by factors such as algae and bacteria species, carbon content, dissolved oxygen and nitrogen content, pH, etc [45,52,59,60].

In addition to being biodegradable, PHAs were proven to be highly biocompatible when tested on the skin and muscles of mice [61,62]. PHAs have mechanical properties similar to their petroleum-based counterparts. For example, PHB have properties (i.e. Young's modulus and tensile strength) similar to polypropylene while PHBV have properties similar to low density polyethylene [45,63]. Study [45] reports mechanical properties of different PHA structures. Although PHAs in general are semi-crystalline, their crystallinity varies depending on their structure. PHBV are less crystalline than PHB and PHAs with short side chains are more crystalline and brittle than PHAs with long side chains which tend to be elastic [45].

PHAs can be 3D printed through extrusion-based techniques such as fused deposition modeling (FDM). Pure PHA prints have excellent biodegradability and biocompatibility but have relatively average mechanical properties. Composites of PHA and other materials such as

palm fibers, wood flour, lignin, PLA, cellulose nanocrystals and nanofibrils, etc are typically used to enhance the mechanical properties of the prints [45]. PHAs can also be printed through laser-assisted techniques such as stereolithography and selective laser sintering, which give higher quality results that can be used as biomedical scaffolds and implants, among other uses [45]. Fig. 6 shows scaffolds made of PHBV nanocomposites printed through selective laser sintering [64]. Table 2 summarizes the key points of algae-based PHAs printability.

3.2. Algae-based PLA

Polylactic acid, also known as PLA, is a bio-based polyester polymer produced by fermenting crops with high sugar content such as corn, potato, sugarcane, and beet. PLA production process produces lactic acid first, then lactide, and finally polylactic acid (PLA) [44,74]. As far as the authors know, there are no experimental studies proving the ability of fermenting PLA from algae. However, a few studies theoretically mention the possibility of fermenting PLA from algal biomass with very limited details [46,75].

PLA has favorable mechanical properties which make it a popular ink in the 3D printing industry. It has a reasonable price and a low melting temperature which facilitates the printing process. 3D printing using PLA results in relatively less carbon emissions because this material does not produce toxic fumes when heated [36]. PLA can be used for end products and applications that require different degrees of transparency because of their transparent structure. High rigidity is another advantage of PLA as it makes the print/scaffold hold its shape for a long time and under various load conditions. However, in addition to having a semi-crystalline and a brittle structure, PLA has low biodegradability [76].

To strengthen the weak points of PLA, the polymer matrix is often reinforced with filler materials such as natural fibers that have properties which PLA lacks. Studies investigated the use of algae as a filler to make PLA-algae composites and found that algae has good adhesion to the PLA polymer matrix and the end material demonstrates enhanced properties [76,77]. Adding algae biomass to PLA increases its biodegradability as proven by Ref. [78]. Faster degradation was explained by the high nitrogen content available in the algal biomass. Young's modulus can also be increased by adding algae to pure PLA, however sacrificing tensile strength [76].

Reinforcing PLA using algae fillers results in a composite with properties that are suitable for biomedical applications. A study [79] investigated the cytocompatibility of various PLA-algae composites and established positive cell viability and proliferation results.

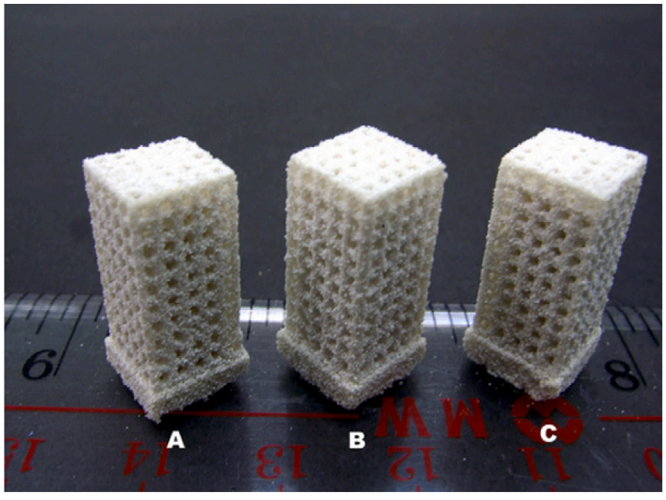

Fig. 6. PHBV nanocomposites printed using selective laser sintering technology [64].

Table 2
3D printability of algae-based PHAs.

	Properties/examples	Details	Refs
Examples of suitable sources	Red algae		[48,49]
	Green algae		[51–54]
	Brown algae		[55]
	Cyanobacteria		[52,56,57]
	Mixed cultures of algae and bacteria		[58]
Biological properties	Biodegradable	Aerobic and anaerobic degradation	[65]
	Biocompatible		[61,62]
Mechanical properties	Young's modulus	0.008–3.5 GPa	[45]
	Tensile strength	9–43 MPa	[45]
	Semi-crystalline		
Common composites	Palm fibers		[66]
	Wood flour		[67]
	Lignin		[68]
	PLA		[69]
	Cellulose nanocrystals and nanofibrils		[70,71]
Suitable printing techniques	Extrusion-based	FDM	[67,70,71]
	Laser-assisted	Stereolithography Selective laser sintering	[72,73]

PLA composites are typically more economically attractive than pure PLA because of their low processing costs. PLA-algae composites are compatible with many processing technologies including the most common extrusion and nozzle-based 3D printing [36,80]. 3D printing makes customized scaffold fabrication easier. PLA composites can be used to repair and replace torn meniscus parts or be used as tools (screws, pins, needles, etc) for biomedical purposes. They can also be used for packaging and other applications that would otherwise use petroleum-based plastics [36,63,81].

4. Printability of algae-based hydrogels

Algae naturally produce various types of hydrogel-forming materials that have diverse properties and applications. This section presents an overview of the materials that can be extracted from algae and have shown a potential for 3D printing, highlighting their properties, printability, and applications.

4.1. Alginate

Alginate is one of the most used biomaterials produced by algae. It is typically extracted from the cell walls of brown seaweed. It can also be extracted from red and green algae [7]. According to their chemical structure, alginates are classified as natural polysaccharide polymers. The monomers of the alginate polymer are G-blocks, M-blocks, and GM-blocks, arranged in linear chains, as shown in Fig. 7. The arrangement and percentages of these blocks result in alginates with different properties such as different molecular weights and viscosities [82,83].

Since alginates are negatively charged (anionic), their gelation mechanism is activated in the presence of cations such as calcium ions (Ca^{2+}) made possible by immersion in calcium chloride ($CaCl_2$) which is often used as a crosslinking agent with alginates such as Na-alginate. The process of cations binding to the anionic alginate is called ionic crosslinking and is the typical method of producing alginate hydrogels [82]. Fig. 8 illustrates how the cations tend to bind to the G-blocks more than the M-blocks and GM-blocks. Alginate gelling can be achieved through other mechanisms such as covalent crosslinking, photo-crosslinking, and thermal crosslinking which are discussed in detail in Ref. [82]. Crosslinking duration has the ability to alter the properties of the hydrogel. For example, a study [85] demonstrated a significant increase in the elastic modulus of the hydrogel when the

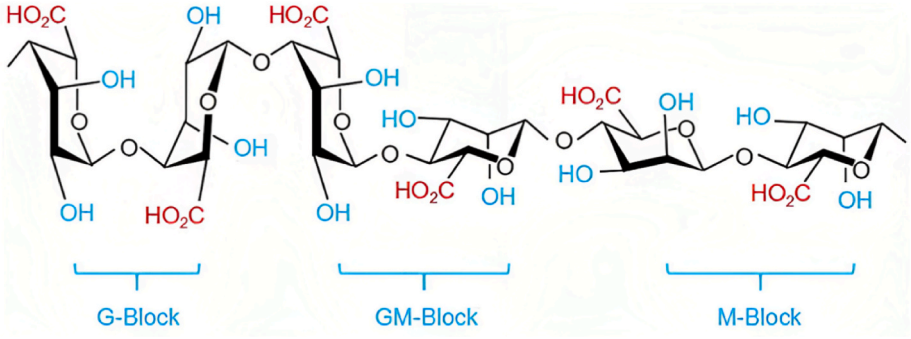

Fig. 7. Monomer blocks of the alginate polymer [84].

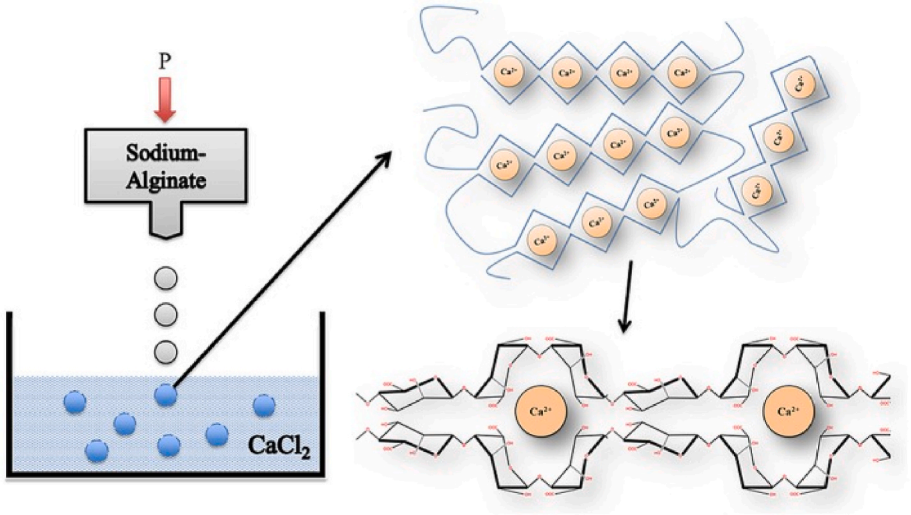

Fig. 8. Calcium ions binding to the G-blocks of alginates [87].

crosslinking time was increased. Slow and controlled crosslinking also results in better mechanical properties [86].

Alginate hydrogels have high biocompatibility and low cytotoxicity [88] which make them suitable hosts to encapsulate living cells. They are also biodegradable, but ionic crosslinking slows their degradability [40]. It is preferred that degradation occurs at the rate at which the

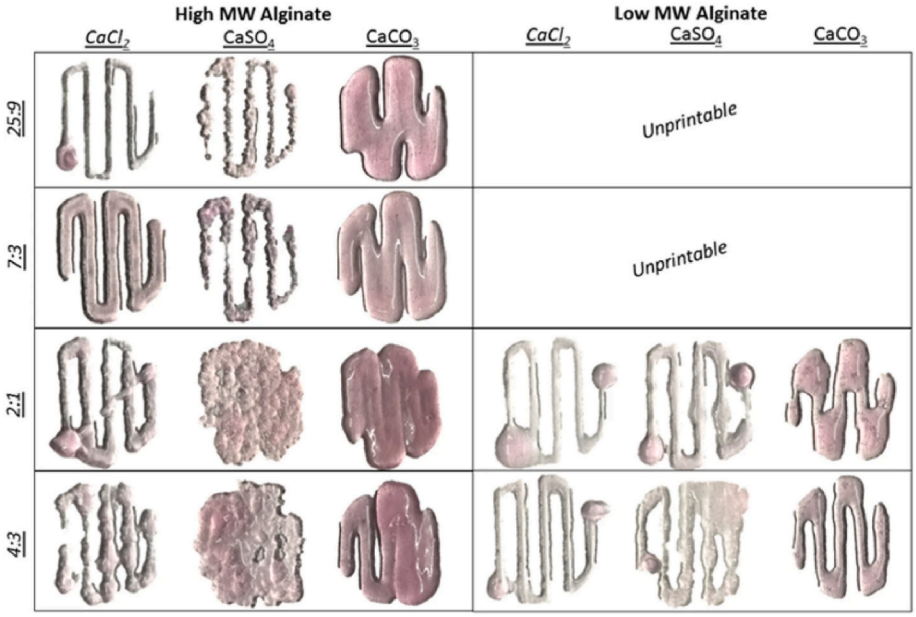

Fig. 9. Printability of alginates. Numbers to the left show crosslinking ratios [90]. Available under a CC-BY license.

extracellular matrices of cells are rebuilt [31]. In addition to favorable biological properties, alginates have good mechanical/rheological properties. Alginates have a wide range of viscosities depending on their molecular weight, composition, pH, temperature, among other factors [31,82]. Fig. 9 shows viscosities of alginates with different molecular weights and crosslinkers. Although alginates undergo shear thinning under high shear rates, at no shear rate their viscosities are too low to print 3D scaffolds. Another drawback of pure alginate hydrogels is that they cannot hold their shape for a long time. Properties of alginates can be enhanced by combining them with other materials such as gelatin, chitosan, and nanocellulose or by nanocoating [36]. Alginate composites were reviewed elsewhere [89].

Since alginates have a wide range of viscosities, they can be bioprinted using various 3D printing technologies. Shear thinning and rapid gelation properties make alginates suitable for nozzle-based techniques such as extrusion bioprinting. However, shape retention is the main challenge associated with alginate printing through extrusion. Additionally, heat and pressure used in this method decrease the viability of the cells encapsulated within the hydrogel. Inkjet bioprinting has higher cell viability and laser assisted methods have the highest cell viability percentages of 95% and above [36,83]. Alginates are used for biomedical applications such as bone and tissue regeneration, wound dressing, and drug delivery [82,91]. Edible alginates are also used in the food industry. Alginates can also act as adsorbents to treat water by removing metal ions and dyes [92]. Table 3 summarizes the 3D printability of alginate.

4.2. Agarose

Agar consists of agarose and agaropectin, which are shown in Fig. 10. Agarose is the purified form of agar that has the gelling ability while agaropectin is more complex and only contributes to the viscosity of agar. Like alginate, agarose is a linear polysaccharide made of repeating monomers. However, one of agarose's different characteristics is its charge neutrality [39,44]. Agarose has self-gelation ability due to the presence of hydrogen bonds between the chains of agarose. This property can be controlled using heat and shear [104] and it eliminates the need for crosslinking agents. However, cells encapsulated within an agarose hydrogel can interfere with the functions of hydrogen bonds and disrupt the mechanical stability of the gel [31,105]. Agarose is typically extracted from the cell walls of red algae. Common algae types that produce agarose include Gelidium and Gracilaria species [106].

Generally, agarose has favorable and stable mechanical and rheological properties. However, the gel's properties vary significantly depending on the agarose concentration and source. For example, agarose gels are known to be elastic yet according to various studies, their Young's modulus can range anywhere between 5.6 kPa and 3000 kPa [31]. Although agarose is highly viscous even at high shear rates, it demonstrates shear-thinning behavior which makes it suitable for extrusion-based printing to some extent [31,104]. Agarose hydrogels are thermoreversible, thus the printed hydrogel scaffold should not be exposed to high temperatures to avoid returning to the solution state. Also, an above-atmospheric temperature (~37 °C) is required to prevent the solution from gelling in an uncontrolled manner. Agarose hydrogels are responsive to pH. This property makes them suitable for pH-controlled drug delivery applications [108] and perhaps opens the door for 4D bioprinting.

The biological properties of agarose hydrogels are less attractive than their physical properties. Their biocompatibility is limited by the interference of cells with the hydrogen bonds that hold the gel together, as mentioned earlier. It is also limited by the poor cell adhesion that is provided by the agarose hydrogel matrix [39]. Despite these challenges, researchers are attempting to develop agarose-based materials that have suitable properties for biomedical applications [109]. In addition to limited biocompatibility, agarose tends to demonstrate uncontrolled and very limited biodegradation. It can only be degraded by agarolytic enzymes which are produced by limited sources [110,111]. To enhance the properties of agarose hydrogels, they are typically coupled with other materials that have the biological properties which agarose lacks. For example, a composite of agarose and hyaluronic acid showed no cytotoxicity and had an improved degradation time of 4–8 weeks [112]. Agarose can also be combined with chitosan, cellulose, and other biocompatible materials. Table 4 summarizes the 3D printability of agarose.

Agarose can be 3D printed mainly through nozzle-based methods. For example, a study printed an enhanced bioink made of carboxylated agarose through a nozzle-based printer using low shear stress [115]. Another study prepared a functionalized carboxylated agarose hydrogel which can be extruded [116]. Fig. 11 shows another example of a 3D printed scaffold made of an agarose ink coupled with gelatin and alginate [117]. Applications of agarose-based prints include cartilage repair and other biomedical applications [115,118]. They can also be used as a plant growth medium because of their excellent water retention capability which acts as a continuous water supply for the plant [119].

4.3. Carrageenan

Carrageenan is a linear anionic polysaccharide produced by red algae species such as Chondrus, Gigartina, Eucheuma, and Kappaphycus [32,39]. Properties of carrageenans vary slightly depending on the number and places of sulfate groups in the monomer unit. Out of six main types, kappa-carrageenan, iota-carrageenan, and lambda-carrageenan are the most used types [40]. Fig. 12 shows their structures. κ-Carrageenan and ι-carrageenan form brittle and soft hydrogels, respectively while λ-carrageenan is mainly used as a creamy thickener.

Carrageenan can easily undergo thermoreversible gelation at low temperatures and ionic gelation at low salt concentrations. Some types of modified carrageenan can also undergo gelation under ultraviolet radiation with or without the presence of ions [40]. Examples of ions used to crosslink carrageenan chains are calcium (Ca^{2+}) and potassium (K^{+}) ions [121].

Carrageenan (esp. κ-carrageenan) forms a brittle hydrogel with high viscosity and shape fidelity. However, viscosity and other rheological and mechanical properties of carrageenan hydrogels depend on their chemical structure, concentration in the solution, crosslinking agent, temperature, and other factors [32,122]. Ionic crosslinking gives carrageenan hydrogels properties similar to alginate. Carrageenans also have favorable biological characteristics such as antitumor and antioxidant properties [123]. They are nontoxic and biocompatible [7,124].

Table 3
Summary of 3D printability of alginate.

	Properties/examples	Refs
Examples of suitable sources	Cell walls of brown seaweed Red algae Green algae	[93–96]
Biological properties	High biocompatibility Low cytotoxicity Biodegradability	[88,97,98]
Mechanical properties	Elastic modulus increases by increasing crosslinking time Wide range of viscosities Shear thinning under high shear rate Low viscosity at under zero shear rate Poor shape fidelity	[85]
Common composites	Gelatin Chitosan Nanocellulose Nanocoating	[89]
Suitable printing techniques	Nozzle-based (Commonly used) Inkjet bioprinting (Higher cell viability) Laser-assisted (Highest cell viability <95%)	[99,100] [101] [102,103]

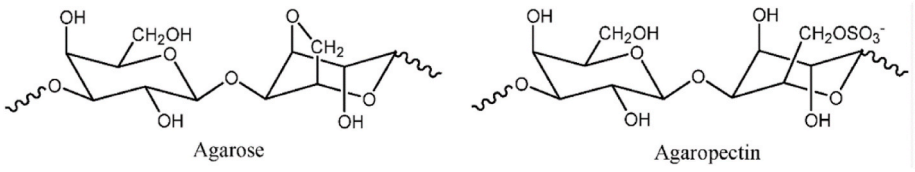

Fig. 10. Structures of agarose and agaropectin [107].

Table 4
Summary of 3D printability of agarose.

	Properties/examples	Refs
Examples of suitable sources	Cell walls of red algae	[106]
Biological properties	pH-responsive	[108]
	Limited biocompatibility	[39]
	Uncontrolled biodegradation	[110,111]
Mechanical properties	Depend on the agarose concentration and source	[31]
	Young's modulus (5.6 kPa–3000 kPa)	
	Shear thinning	
	Thermoreversible	
Common composites	Materials with favorable biological properties such as hyaluronic acid, chitosan, and nanocellulose	[112–114]
Suitable printing techniques	Extrusion-based	[115–117]

Mihaila et al. [125] created a carrageenan-based hydrogel that was able to host cells for up to 3 weeks with a cell viability of around ~75%. Additionally, carrageenans have tunable biodegradability. For example, Martiny et al. [126] created a carrageenan-based biodegradable film which can be used for food packaging purposes.

Carrageenan can be modified using hydroxyl/sulfate to improve the hydrogel's physiochemical properties and printability [39,40]. It can also be coupled with materials such as gelatin, chitosan, cellulose, and alginate to enhance the properties that are required for the targeted application [123,127,128]. Another technique used to improve the printability of carrageenan scaffold is employing multilayered structures typically consisting of alternating layers of carrageenan (which is anionic) and another cationic hydrogel such as gelatin and nanosilicates [129,130]. Fig. 13 illustrates the process of 3D printing layered structure of carrageenan and gelatin. The strong bonds between the layers result in an improved structural integrity. Interlayers can also consist of materials that have favorable biological properties to enhance the biological applicability of the carrageenan-based hydrogel, such as calcium phosphate which was used as a biological binder in Ref. [131].

Although various carrageenan-based hydrogels are studied, the literature available on 3D printing those hydrogels is limited. However, their properties suggest that they can be printed using nozzle-based techniques like agarose. Another possible 3D printing technique for carrageenan-based hydrogels is stereolithography in which the hydrogel is photocrosslinked to produce a solidified scaffold [40]. Carrageenan prints can be used in regenerative medicine, tissue engineering, drug delivery [121,123,124]. The food-grade version of carrageenan is widely used as a thickener and a gelling agent in the food industry. It can also be used in pharmaceuticals and cosmetics [39,123]. Table 5 summarizes the 3D printability of carrageenan.

4.4. Fucoidan

Fucoidan is another group of anionic sulfated polysaccharides, which are particularly rich in fucose. They are typically produced by brown algae such as Fucus, Sargassum, and Laminaria in response to dryness. The structure diversity of fucoidans depends on the algae type, harvesting season, and extraction method [135]. Fig. 14 shows a general structure of fucoidan. Although limited literature is available on the gelation mechanism and hydrogel formation of fucoidans, it is believed to act similar to carrageenan since their structures are very similar [136].

Fucoidan is typically combined with mechanically stable gels such as alginate, gelatin, or chitosan to enhance the biological and pharmacological properties of the final composite. Fucoidan is cytocompatible and nontoxic. Studies show that adding fucoidan to a hydrogel composite increases its cell proliferation ability [137]. Additionally, bioactive properties of fucoidan include being antioxidant, antibacterial, anticancer, antiinflammatory, anticoagulant, etc. [138,139].

This cluster of favorable properties allows fucoidan to be used for various biomedical and nanomedical applications such as cancer therapy [140,141], wound healing, bone tissue engineering, and drug delivery [142]. Fucoidan is also used in the cosmetic industry because of the protection and soothing that it provides for the skin [143]. It is also used in the food industry [144].

Although there is not enough literature about 3D printability of fucoidan, its structure similarity to carrageenan makes it seem promising. Also, it demonstrates viscoelastic and shear-thinning properties at room temperature and low concentrations [145]. Table 6 pinpoints the key characteristics that make fucoidan printable.

4.5. Chitosan

Chitosan is derived from chitin which is the most abundant

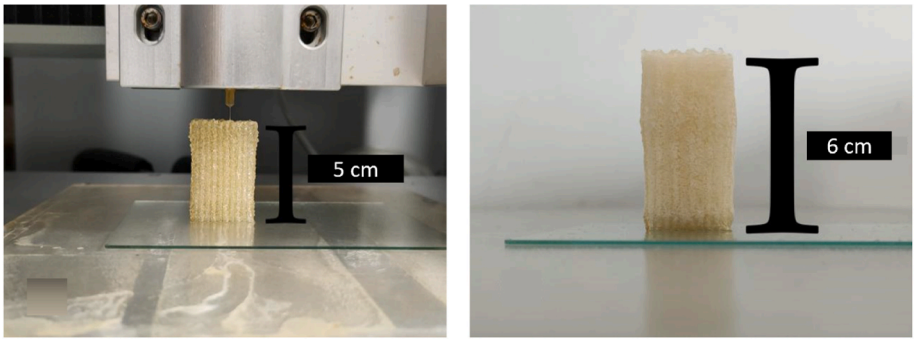

Fig. 11. 3D printed gelatin/alginate/agarose composite [117]. Available under a CC-BY license.

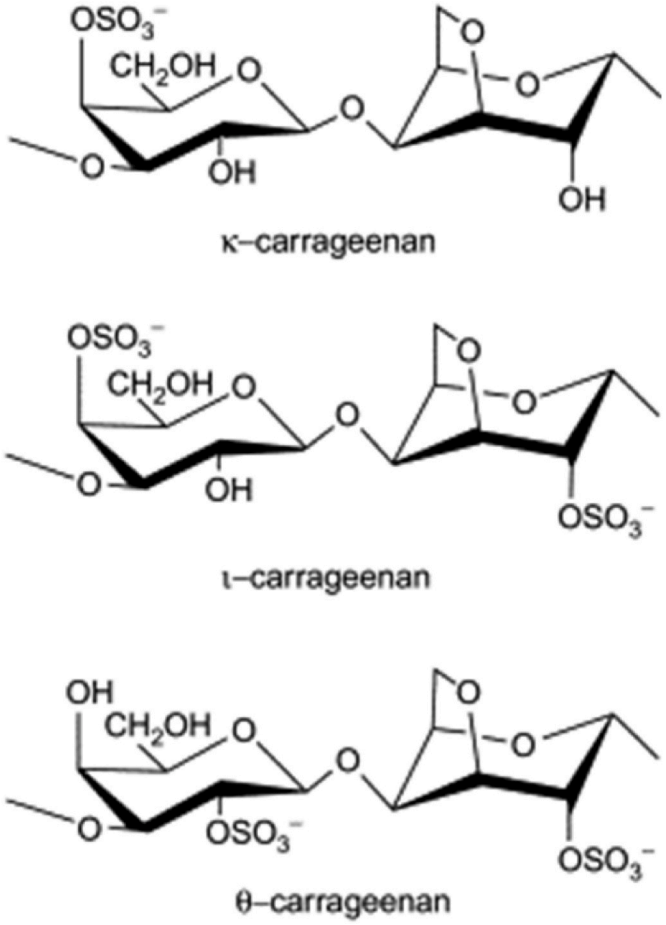

Fig. 12. Structures of kappa-carrageenan, iota-carrageenan, and lambda-carrageenan [120].

polysaccharide in nature after cellulose. Fig. 15 shows the chemical structures of chitin and chitosan. Although chitin is mostly obtained from fungi and from shells of crabs, shrimps, and some insects, some studies suggest that it can be extracted from some types of algae as well. These types include coralline algae [149], diatoms [150], green and brown algae [151]. Chitosan nanofibrils from microalgae were also studied [152]. Chitosan is unique because unlike other hydrogel forming polysaccharides, it is cationic [44].

Chitosan can form a printable hydrogel through physical or chemical crosslinking. Physical crosslinking occurs through hydrogen bonds, electrostatic forces, and/or ionic interactions and is activated by changes in pH, temperature, magnetic fields, and/or the addition of ions. Although this type of crosslinking is reversible and nontoxic, it yields relatively low mechanical strengths. On the other hand, chemical crosslinking through covalent bonding forms hydrogels that are more stable and less prone to dissolution which happens due to interactions with ions. However, chemically crosslinked hydrogels are potentially cytotoxic. Photocrosslinking also enhances the shape retention of the hydrogel [154,155].

In addition to being abundant in nature, chitosan has many favorable biological properties. It is one of the most used biomaterials in biomedical applications such as drug delivery. Its biocompatibility and noncytotoxicity allow it to be widely adopted as a matrix forming hydrogel [156]. It is also anti-inflammatory, anti-oxidant, and antimicrobial [154]. Additionally, chitosan has been widely explored for the production of antimicrobial packaging films because of its excellent biodegradability [157,158]. Chitosan-based materials are also used as adsorbents and flocculants in the wastewater industry [151,159]. Besides, they have applications in the biomedical, agricultural, and cosmetics industries [151,152,160]. Chitosan composites for various applications are widely explored and reviewed elsewhere [161–164].

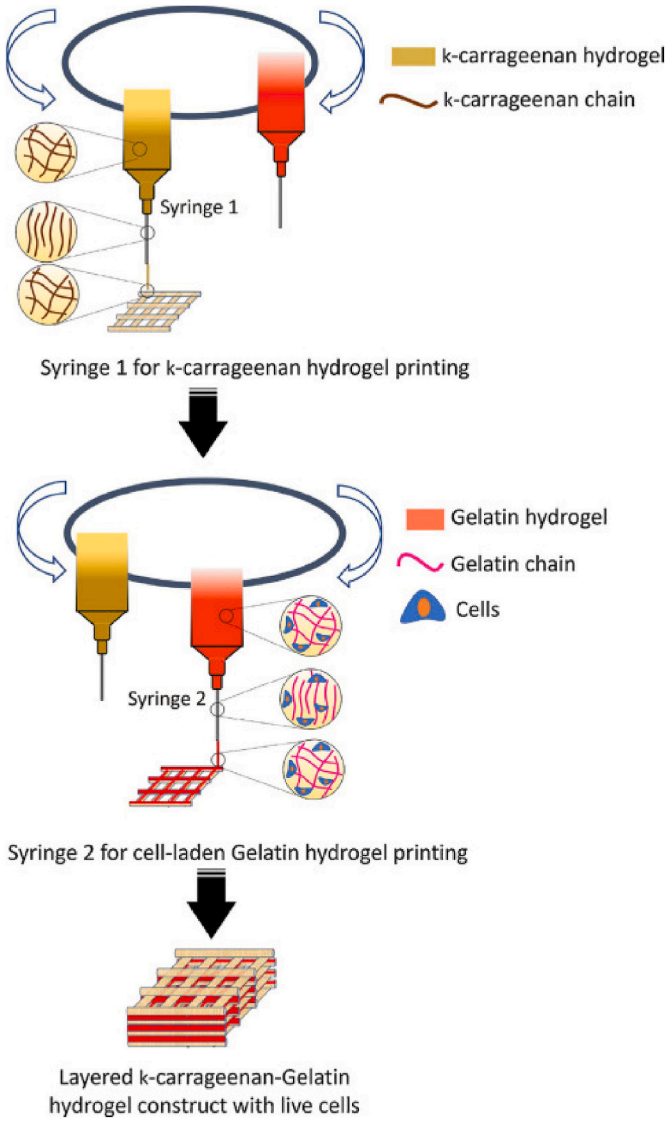

Fig. 13. Process of 3D printing a layered structure of carrageenan and gelatin [132].

Table 5
Summary of 3D printability of carrageenan.

	Properties/examples	Refs
Examples of suitable sources	Red algae	[32,39]
Biological properties	Antioxidation Antitumor	[123]
	Biocompatible	[7,124]
	High cell viability (up to 75%)	[125]
	Tunable biodegradability	[126]
Mechanical properties	Brittle hydrogel	[133]
	High viscosity	
	High shape fidelity	
Common composites	Gelatin	[123,129,130]
	Chitosan	
	Cellulose	
	Alginate	
	Multilayered composites	
Suitable printing techniques	Nozzle-based	[131,134]
	Laser assisted	[40]

Chitosan-based materials can be printed using various 3D printing techniques. They demonstrate shear thinning behavior which facilitates

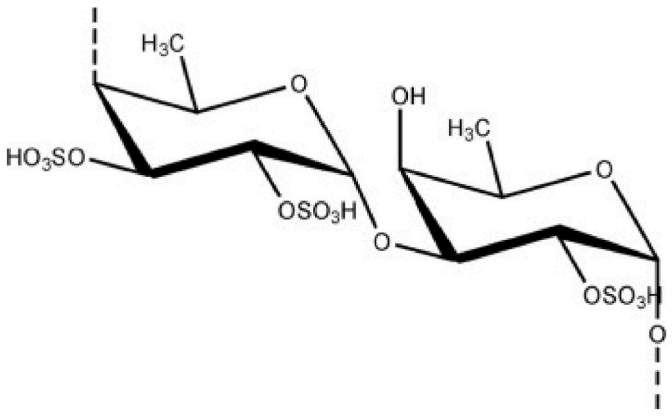

Fig. 14. Structure of fucoidan [120].

Table 6
Key points of 3D printability of fucoidan.

	Properties/examples	Refs
Examples of suitable sources	Brown algae	[146–148]
Biological properties	Biocompatible	[137]
	Antioxidation	[138,139]
	Antibacterial	
	Anti-inflammation	
Mechanical properties	Properties similar to carrageenan	
	Viscoelastic and shear thinning	[145]
	Shear thinning	[145]
Suitable printing techniques	Limited literature available	

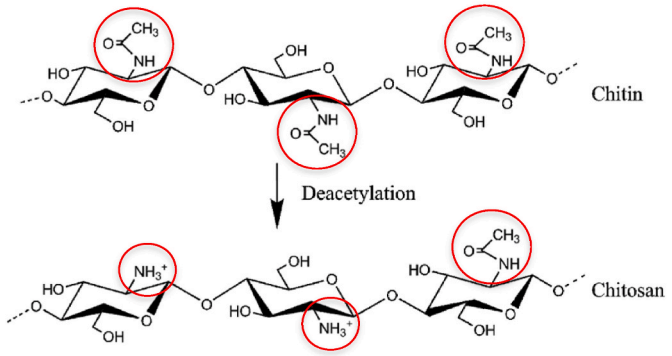

Fig. 15. Structures of chitin and chitosan [153]. Available under a CC-BY license.

nozzle- and micronozzle-based printing. Upon the deposition of the chitosan ink, the solvent evaporates leaving the hydrogel to solidify [165]. Specific 3D printing techniques applicable for chitosan-based bioinks include extrusion-based methods [165–169], inkjet printing [170], binder jetting [171], and laser-based printing [172–176]. Fig. 16 shows flexible scaffolds made of chitosan/nanocellulose inks. Pictures of stretchable chitosan scaffolds can also be viewed in Ref. [165]. Table 7 summarizes the key points of chitosan 3D printability.

Since chitosan-based materials are sensitive to changes in factors such as pH, temperature, and magnetic fields, they can be developed for 4D printing. More on the development of chitosan smart inks and bioinks for 4D will be discussed in Section 6.

4.6. Nanocellulose

Nanocellulose is another linear polysaccharide that mainly comes from plants in abundant amounts. However, studies show that it can also be extracted from some types of algae. One study [182] reported the average cellulose content on a dry basis to be 9.67% in green algae, 7.88% in brown algae, and 4.75% in red algae. Nanocellulose can also be extracted from brown algae residue after alginate extraction [183].

Algal nanocellulose comes in the forms of cellulose nanocrystals and cellulose nanofibers, wherein nanofibers have better printability than nanocrystals [184,185]. The process of producing nanocellulose from cellulose typically starts with purifying cellulose, yielding amorphous nanocellulose. Then, depending on the desired end product, cellulose fibers can either be further processed under high shear to obtain cellulose nanofibers or it can be treated with acid hydrolysis to give cellulose nanocrystals [184,186].

Compared to cellulose from lignocellulosic crops, algal cellulose is easier to extract because of the absence of lignin and other components that require additional purification steps. Purity and in turn crystallinity of cellulose decreases going from microalgae up to macroalgae and then to higher plants [186,187]. The high crystallinity of algal cellulose is defined by the rigid network of hydrogen bonds that holds the chains together. Although this crystalline nature does not facilitate hydrogel

Table 7
3D printability of chitosan.

	Properties/examples	Refs
Examples of suitable sources	Coralline algae	[149]
	Diatoms	[150]
	Green algae	[151]
	Brown algae	[151]
Biological properties	Biocompatibility	[156]
	Antioxidation	[154]
	Antimacrobial	
	Anti-inflammation	
	Biodegradability	[157,158]
Mechanical properties	Shear thinning	
	Tensile strength (<18 MPa)	[177–179]
Common composites	Cellulose	[161–164,180]
	Gelatin	
	PVA	
	Titanium dioxide	
Suitable printing techniques	Extrusion-based	[165–169]
	Inkjet printing	[170]
	Binder jetting	[171]
	Laser-assisted	[172–176]

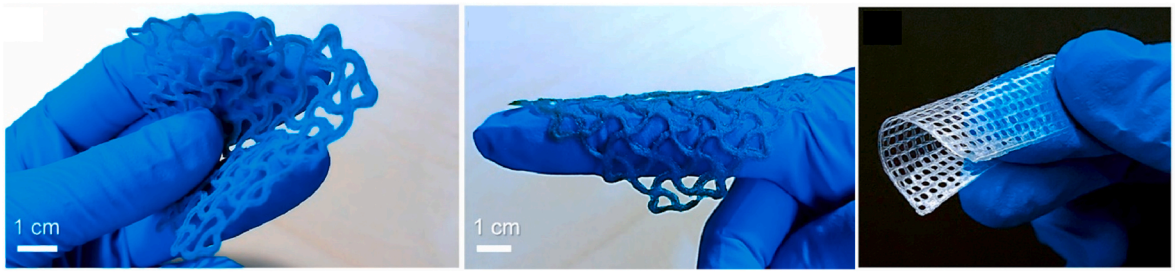

Fig. 16. Flexibility of 3D printed chitosan structures [181]. Available under a CC-BY license.

ink formation, the availability of many hydroxyl groups suitable for functionalization allows plenty of room for modification and development of nanocellulose composites capable of forming hydrogels. Fig. 17 shows scaffolds made of pure nanocellulose versus functionalized nanocellulose. Ionic and chemical gelation can also be used to enhance nanocellulose gelation [8].

The properties of algal nanocellulose are highly affected by many factors. The extraction and preparation methods play a huge role in shaping the mechanical, rheological, and biological properties of the end product [184]. The aspect ratio is also critical in determining the rheological properties of the nanocellulose [185]. Generally, cellulose nanocrystals have a lower aspect ratio than cellulose nanofibers and thus are less viscous [185]. The concentration of nanocellulose in the mixture also impacts its properties. Low concentrations typically form fluids while high concentrations are capable of forming gels. Unlike other hydrogel forming polysaccharides, nanocellulose is insoluble in water. Therefore, crosslinking agents are typically used to aid its gelation process [189].

Nanocellulose-based inks have favorable rheological properties such as thixotropy. They are viscous at no shear while when high shear rate is applied, their hydrogen bonds break resulting in a shear thinning behavior [190]. Additionally, nanocellulose has good mechanical and thermal stability [191]. Although the mechanical properties (e.g. crystalinity, tensile strength, Young's modulus, etc.) of nanocellulose vary depending on many factors, cellulose nanocrystals are generally known to be stiff while cellulose nanofibers are more flexible [184]. Nanocellulose is also lightweight (Fig. 18), biodegradable, and biocompatible [192].

Cell viability of the nanocellulose hydrogel can be enhanced by combining it with alginate [194] or other biomaterials that have favorable biological properties [195]. Nanocellulose can also be coupled with other materials such as nanocarbons, conducting polymers, metals, and organic polymers for various applications [196,197]. Applications of nanocellulose span a wide variety of domains, including biomedicine [189], energy storage [198], electronics and sensors [198], water filtration [199], packaging films [200,201], etc. Its thixotropic and shear thinning properties make it attractive for 3D printing applications. 3D printing of nanocellulose-based materials is reported using several 3D printing techniques such as extrusion-based methods (e.g. fused deposition modeling FDM [202,203], and direct ink writing DIW [204]), inkjet printing [205], stereolithography SLA [206], and digital light processing DLP [207–209]. Nanocellulose-based inks are also being investigated for 4D printing because of their responsiveness to several types of stimuli such as pH, illumination, and magnetism (discussed in Section 6) [204,210]. It is worth noting that most of the literature available about nanocellulose, its applications, and printability is about nanocellulose from plants and crop residues. Although there is limited literature exploring algal cellulose, it is believed to have similar characteristics to nanocellulose from higher plants, as mentioned earlier. Table 8 summarizes the 3D printability of nanocellulose.

5. 3D printability of algae-laden hydrogels

Algae-laden hydrogels are scaffolds made of hydrogels loaded with living algae cells. The hydrogel can be from a non-algae source, but it should be fully biocompatible with the algae cells to allow cell growth and proliferation. It should also be mechanically stable to serve the intended application and be rheologically printable. Although immobilization of mammalian cells is widely studied, immobilization and bioprinting of plant cells are still in their early stages [211–213]. Former literature reports immobilizing algae cells in hydrogel beads [214–216]. Only recently, bioprinting algae-laden hydrogels started emerging. Studies show that bioprinted cells are more efficient in many applications than beads which are in turn more efficient than suspended cells [217].

Although there are limited studies about 3D printing algae-laden hydrogels, they show a promising potential to be used in various fields. For example, they can replace suspended cultures which are used in photobioreactors to produce biofuels and other high value products because immobilized algae cells are easier to control and harvest [218]. Cell-laden printed hydrogels also allow organized coculturing. In the biomedical field, algae-laden scaffolds have shown the potential to be a sustainable supply of O_2 to encapsulated human cells [211]. However, more research is required to prove and develop this concept.

Additionally, algae-laden printed structures can replace open algae wastewater treatment to avoid uncontrolled invasion of the algae blooms into the water bodies and to facilitate the collection of algae colonies posttreatment [217]. Also, printing algae-laden hydrogels and observing their proliferation and response to the environment builds knowledge blocks for the advancements of soilless plant cultivation [219]. Since algae has a faster growth rate yet a similar behavior to plants, it is more convenient to experiment with algae cells before applying the same techniques to higher plants. Fig. 19 summarizes the potential applications of 3D printed algae-laden hydrogels.

Preparation of algae-laden scaffolds can be done by two ways.

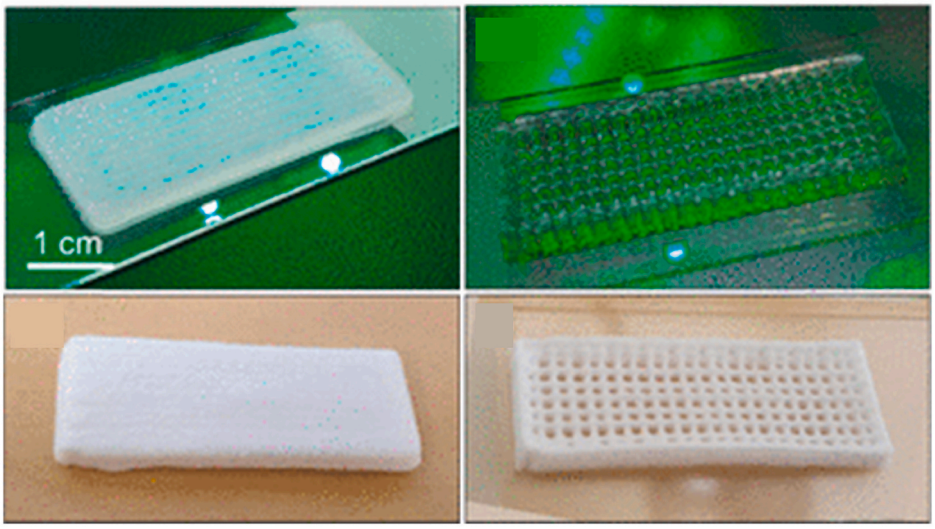

Fig. 17. Structure fidelity of cellulose nanofibers (left) and acetylated cellulose nanofibers (right), undried (top) and dried (bottom) [188]. Available under a CC-BY license.

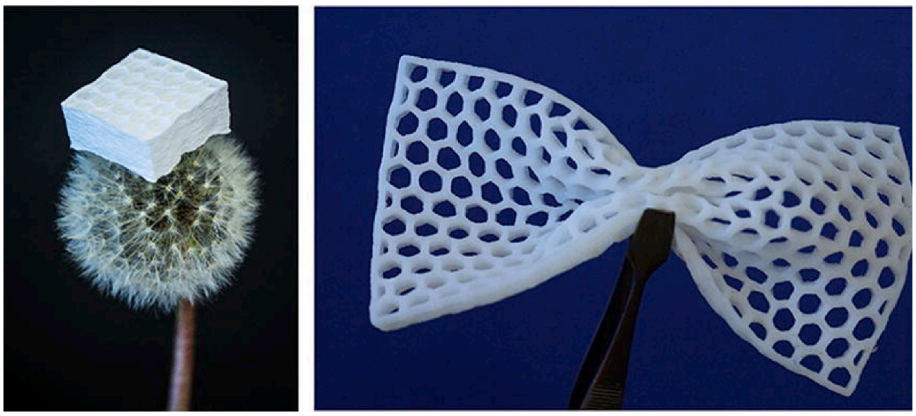

Fig. 18. Flexible and lightweight 3D printed cellulose [193].

Table 8
3D printability of nanocellulose.

	Properties/examples	Details	Refs
Examples of suitable sources	Green algae	1.5–34% dry weight	[182]
	Brown algae	2.2–10.2% dry weight	
	Red algae	0.85–18% dry weight	
Biological properties	Cell viability	Enhanced by coupling with biologically favorable materials	[194]
Physical properties	Crystallinity	High, but hydroxyl groups allow functionalization to decrease rigidity	[191]
	Gel formation	High concentration required	
	Solubility	Insoluble in water	
	Thixotropic		
	Shear thinning		
	Thermal stability	Depends on algae source	
Common composites	Alginate		[194,195]
	Nanocarbons, conducting polymers, metals, and organic polymers		[196,197]
Suitable printing techniques	Extrusion-based	FDM	[202,203]
		DIW	[204]
	Inkjet printing		[205]
	Laser-assisted	SLA	[206]
		DLP	[207–209]

(1) Seeding algae cells into a printed hydrogel scaffold.
(2) Bioprinting ink loaded with algae cells (bioink).

Our focus will be on the recent advancements regarding the second way, which are shown on a timeline in Fig. 20. A summary of the printing details is also presented in Table 9. The earliest 3D bioprinting of algae cells was reported in 2015 by Lode et al. [211]. They used a bioink consisting of algae cells loaded in a hydrogel made of alginate and methylcellulose to bioprint a simple 3D scaffold. Pictures of the scaffold can be viewed in Ref. [211]. Printing was performed at room temperature using a bioprinter with a nozzle diameter of 250 μm, pressure of 0.8 bar, and printing speed of 10 mm/s. Scaffolds were crosslinked using $CaCl_2$ post-printing. The encapsulated algae cells were able to grow and proliferate changing the scaffold's color from colorless to green, meaning the hydrogel and the printing process are biocompatible with algae cells. The same team also utilized the multichannel feature of the bioprinter to print a scaffold containing an organized coculture of algae cells and human cells. Although the oxygen production rate of algae cells reached up to 0.25 mg/L.h, the cell viability of the human cells decreased gradually. More studies are required to optimize this process and facilitate the human cells' consumption of oxygen produced by algae cells inside a confined environment.

Although alginate was successfully used in the aforementioned study, Zhao et al. [220] highlight the constraints of natural-polysaccharide-based hydrogels such as alginate as a hosting environment for algae living cells. To overcome the instability of alginate in wet environments, they used a protein-based polymer to host the cells. Protein-based polymers are typically mechanically weak, but silk in particular showed favorable properties. They used a bioink consisting of a silk solution (silk and hydroxypropyl methylcellulose) and algae cells to bioprint scaffolds through a 0.5 mm nozzle into an H_2O_2 solution which induced hydrogel crosslinking. After crosslinking, the scaffold was moved to a medium suitable for cultivating algae cells. The proposed hydrogel was proven biocompatible as it supported cell proliferation for up to 4 weeks and cell viability for up to 3 months. Also, the algae culture produced around 3–8 mg/L of oxygen every 3 days. However, the behavior of the scaffold and the encapsulated algae culture independent from the culturing solution was not reported.

Another hydrogel that proved good compatibility and protection for the hosted algae culture is Pluronic F127-bisurethane methacrylate (F127-BUM) [221]. In their study, Johnston et al. studied the biological behavior of not only algae cells, but bacteria and yeast as well. They prepared three versions of ink, each containing the special hydrogel loaded with one of the aforementioned types of cells, and printed them in layers creating a 3D scaffold. A picture of the structure can be viewed at [221]. The 3D printing technique used was direct ink writing (DIW) through a 0.41 mm nozzle and a 5 mm/s printing speed. The print was cured with UV for 3 min post-printing to avoid uncontrolled degradation. Results show that the used hydrogel has a high biocompatibility with the three types of cells, characterized by cell viabilities which stayed around 90% for a week. Interestingly, despite the inks of different cultures being in touch, no significant cell contamination occurred. This protective feature of the hydrogel makes it a suitable choice for co-culturing colonies of different types of cells in a controlled way.

Another study [218] investigated the 3D printability of algae cells in a set of hydrogels made of alginate and different types of viscosity modifiers such as methylcellulose and carrageenan. Alginate combined with methylcellulose showed the best printability and biocompatibility with algae cells. This supports the work of Lode et al. [211] mentioned above. In this study, Malik et al. [218], 3D-printed a multilayered structure that replicates the branched structure of a plant leaf to facilitate water flow, as shown in Fig. 21. The layers have different concentrations of algae cells and were printed through nozzle diameters between 2 and 7 mm. The extrusion pressure was maintained between 2 and 4 bar. $CaCl_2$ was used to crosslink each layer independently not later than 10 min post-printing, and the whole structure was later immersed in the crosslinking solution as well. The hydrogels maintained cell growth for at least 14 days and cell viability was not affected by the printing process.

Fig. 19. Applications of 3D printed algae-laden hydrogels.

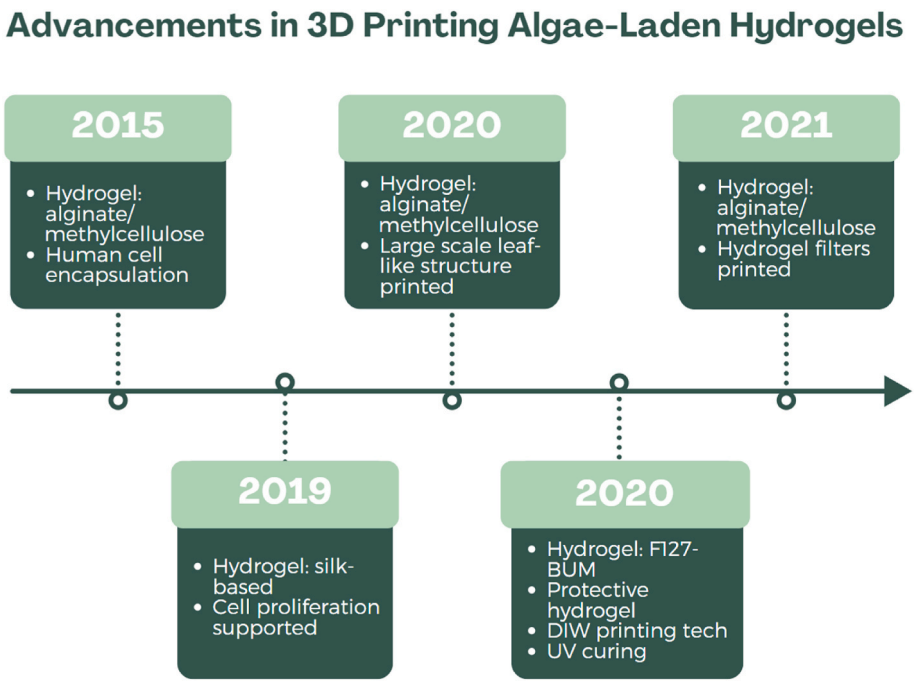

Fig. 20. Highlights of the recent advancements in 3D printing algae-laden hydrogels (Data as per March 2023).

Similarly, Thakare et al. [217,222] printed algae cells loaded in a hydrogel made of alginate and methylcellulose for the purpose of filtering copper from water. The square algae-laden hydrogel filters were printed through a 30-gauge needle with 6 mm/s printing speed and 95 psi pressure. Several filters were placed on top of each other, separated by a custom-made platform. Pictures of the platform can be viewed in Ref. [217]. The algae-laden hydrogel filters showed a copper reduction efficiency of 83% as compared to the pure hydrogel efficiency of 50%. It is also more efficient than adsorption using suspended algae. Further studies are required to optimize the parameters of this filtration process to enhance its efficiency and make it applicable for other types of metals and contaminants.

6. Pathway towards 4D bioprinting

Since the literature does not provide experimental examples of 4D bioprinting algae-based materials specifically, the studies available on printing biomaterials discussed in Section 4 will be taken as a guide in this section, regardless of the source of the material used in each study. For example, studies mentioning alginate will be considered regardless of the actual source of alginate in the study.

4D bioprinting is an emerging technology that has a wide range of applications in the biomedical field and other areas. The key feature of 4D bioprinting is the ability to induce a controlled change over time in the shape or properties of a 3D printed structure containing living cells. Fig. 22 shows the two categories of 4D bioprinting. The change in the printed structure can be induced by (1) utilizing smart materials or responsive hydrogels or (2) harnessing the natural maturation of living cells.

Table 9
Summary of the details of recent work on 3D-printing algae-laden hydrogels.

Authors & Ref.	Lode et al. [211]	Zhao et al. [220]	Malik et al. [218]	Johnston et al. [221]	Thakare et al. [217]
Year	2015	2019	2020	2020	2021
Cell type	Algae & human cells	Algae cells	Algae cells	Algae, bacteria, & yeast cells	Algae
Hydrogel	Alginate/methylcellulose	Silk/hydroxypropyl methylcellulose	Alginate/ methylcellulose[b]	Pluronic F127-BUM	Alginate/methylcellulose
Crosslinking agent	$CaCl_2$	H_2O_2	$CaCl_2$	UV curing	$CaCl_2$
Printing specifications	D_N = 250 μm P = 0.8 bar S = 10 mm/s	D_N = 0.5 mm	D_N = 2–7 mm P = 2–4 bar	D_N = 0.41 mm P = S = 5 mm/s	D_N = 30-gauge P = 95 psi S = 6 mm/s
Reported cell viability	12 days[a]	3 months	21 days	90% viability for a week[a]	Not mentioned
Potential applications	Biotechnology/ biomedicine	Various applications	Photobiore-actors	Controlled coculturing	Copper removal from water

D_N: nozzle diameter, P: printing pressure, S: printing speed.
[a] Period of the study.
[b] Other hydrogels were tested but alginate/methylcellulose showed the best results.

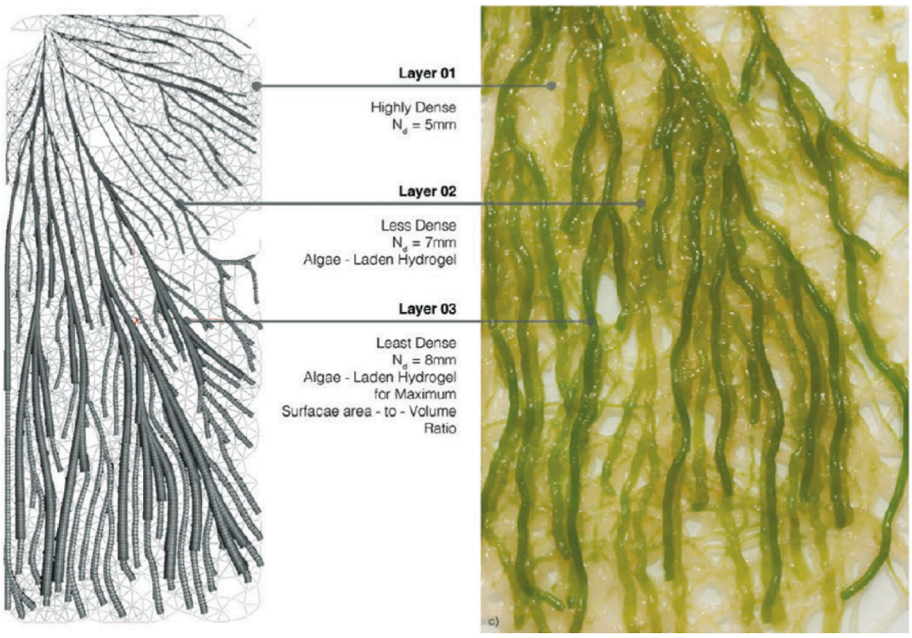

Fig. 21. 3D-printed multilayered algae-laden hydrogels with different concentrations [218]. Available under a CC-BY license.

6.1. Responsive hydrogels

Responsive hydrogels are attractive in 4D bioprinting because they have the ability to respond in specific ways (bend, twist, swell, etc.) to certain types of stimuli such as change in temperature, moisture, or other factors that are discussed below. The functionality of structures made of responsive hydrogels is typically shaped by combining the material's smart properties with smart design. Responsive hydrogels are also called dynamic hydrogels [223] and are used as actuators in soft robots and devices [224,225].

6.1.1. Moisture responsiveness

Although the responsiveness of hydrogels to moisture is not considered a "smart" property, it can be tailored to serve specific functions in 4D printing. Swelling mismatch in the printed structure makes certain parts bend or twist when they absorb or desorb specific solutions. Different degrees of swelling are achieved by inhomogeneous crosslinking, hybrid hydrogel composites, or other means [226].

6.1.2. Temperature responsiveness

Temperature change is widely used to trigger responsive behavior from smart hydrogels. When polymers are exposed to a high temperature, they release water out of their matrices resulting in a shrinking size. On the other hand, when they are exposed to a low temperature, the polymeric matrix takes in water molecules resulting in an expanded size. Various types of polymers have different critical temperatures at which the phase transition occurs. For example, PNIPAm, Poly(N-isopropylacrylamide), is commonly used because its lower critical solution temperature is safe for the human body (32 °C) [227,228]. Coupling PNIPAm with alginate results in enhanced mechanical properties while maintaining the thermal responsiveness of PNIPAm. For example, Bakarich et al. [229] used a PNIPAm/alginate hydrogel to fabricate a valve that responds to low and high water temperatures by opening and closing, respectively. Agarose is another thermoresponsive hydrogel that can be extracted from algae. Guo et al. [230] used an agarose-based hydrogel to 4D-print octopus- and whale-like shapes that are soft and deformable at high temperatures and hard at temperatures below 35 °C. They proved the reversibility of the responsiveness by deforming the structures at high temperatures and then cooling them. The structures maintained their deformed shape until they were heated again, upon which they restored their original shapes. Other biomaterials that can be extracted from algae and were investigated for

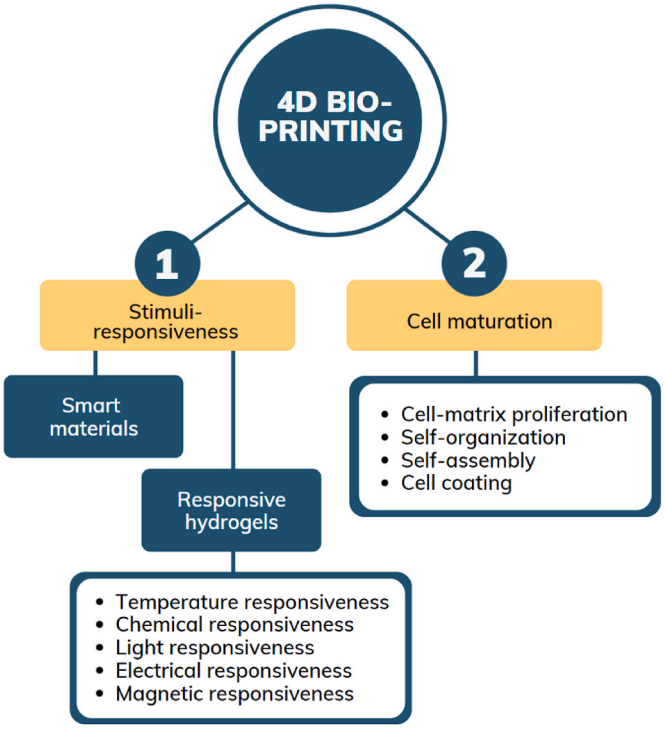

Fig. 22. 4D Bioprinting categories.

thermoresponsiveness are chitosan [231], carrageenan [232], and nanocellulose [233].

6.1.3. Chemical responsiveness (pH, ion concentration)

Changes in pH and ion concentration are other commonly used stimuli to trigger controlled change in chemically responsive hydrogels. The presence of ions or change in the pH of the scaffold's environment impacts the crosslinking of the polymer chains and thus alters the properties of the structure. pH-responsive hydrogels are particularly important in controlled drug delivery applications. For example, several studies fabricated alginate-based hydrogels that are capable of releasing certain drugs such as diclofenac sodium only at high pH levels [234, 235]. This means the drug capsule can pass by the acidic environment of the stomach without releasing anything until it reaches the high-pH intestinal environment where it starts releasing the drug.

Immersing hydrogels in ionic solutions can also evoke certain responses. For example, Kirillova et al. [236] 4D-printed an alginate based hydrogel that folds and unfolds in response to changing Ca^{2+} ion concentration in the solution. They used green light to create a gradient in the crosslinking of the hydrogel, which aids in shape morphing once the stimulus is applied. This crosslinking difference causes swelling mismatch in the scaffold and thus makes the flat structure fold to become a hollow tube. Similarly, Fig. 23 show scaffolds made of alginate/methylcellulose printed in different designs to evoke various folding patterns when immersed in $CaCl_2$ solution.

Other biomaterials that can be extracted from algae (e.g. carrageenan [237], chitosan [238], agarose [239]) are also used to make chemically responsive hydrogel composites.

6.1.4. Light responsiveness

The response to light typically comes not from the hydrogel itself but from photosensitive particles such as carbon- or graphene-based particles that are embedded inside the hydrogel, or inside parts of it. Unlike most of the aforementioned responsive properties which require the hydrogel to be immersed in a fluid and are governed by the diffusion rate, response to light is noninvasive and can be instantly triggered in partial sections of the scaffold. Light responsiveness can also be coupled with thermoresponsive materials to achieve localized temperature sensitive response through the conversion of light energy to heat [226,241]. Among algae-based materials, nanocellulose [242], chitosan [231], carrageenan [243], agarose [244,245], and alginate [246–248] were used to fabricate photosensitive composites. However, photoresponsive particles limit the use of the hydrogels in biomedical applications because of their toxicity.

6.1.5. Electrical responsiveness

Electrical responsiveness is another attractive property in 4D printing which can be activated in a noninvasive and noncontact way. Applying an electric field around an electroactive hydrogel stimulates a bending response towards the positively charged electrode. Bending of thin rods/flat pieces is explained by the rearrangement of ions on the two halves of the scaffold and consequent shrinking on one side and swelling on the other side. An advantage of this method is that it works with homogeneously crosslinked structures. Fig. 24 (a) shows the bending of an alginate-based specimen under an electric field strength of 500 v/mm, (b) shows another example using an agarose-based hydrogel, and (c) using a carrageenan hydrogel.

6.1.6. Magnetic responsiveness

As with light responsiveness, magnetic responsiveness is achieved by embedding magnetic materials such as ferromagnetic particles inside the hydrogel. This property allows controlling the hydrogel remotely and without changing its properties. McCracken et al. [252] 4D-printed alginate-based structures (loaded with Fe_3O_4 nanoparticles) that mimic aquatic organisms in shape and certain behaviors under external stimuli such as magnetic fields. Pictures of the printed hydrogels can be viewed in Ref. [252]. Chitosan was also used in another study in combination with magnetite nanoparticles for controlled drug delivery applications [253]. Limited information is available on using other algae-based materials in magnetic responsive hydrogel composites. Table 10 puts together the algae-based responsive hydrogels according to the available studies.

6.2. Cell/tissue maturation

In addition to the use of smart polymers and responsive hydrogels, harnessing the living cells' natural dynamic activity is another path towards 4D bioprinting. Naturally, after the living cells are bioprinted into a specific structure, they mature, fuse, and adjust to form grafts that are as similar as possible to real tissues. One example of cell maturation over time (4D) is the proliferation of cells that are bioprinted into a biocompatible matrix. Ideally, the cell culture should proliferate at the same rate at which the hydrogel matrix decomposes. Anticipating and controlling those rates are aspects of 4D bioprinting that are currently under development. Another example of 4D bioprinting using cell maturation is the process of self-organization (or self-assembly) which the bioprinted cells go through postprinting. Fig. 25 shows two examples of bioprinted cells before and after they adjust and fill the gaps to form a stable tissue-like structure. Fig. 26 also shows the self-assembly of cells printed in an agarose scaffold. Making this process directed aids in 4D bioprinting [254].

Although there are other methods to control cell maturation such as cell coating for vascularization and vessels grafting [255], the majority of the related literature that is available to date is on human and mammalian cells. The domain of bioprinting plant/algae cells is still in its infancy. However, as demonstrated in Section 5, algae bioprinting is gaining more attention recently, and 4D bioprinting techniques developed on mammalian cells are being tested and applied to plant cells. Algae-based hydrogels serve as sustainable biomaterials to make biocompatible scaffolds. Algae cells are also suitable for experimenting purposes because of their availability and high proliferation rate.

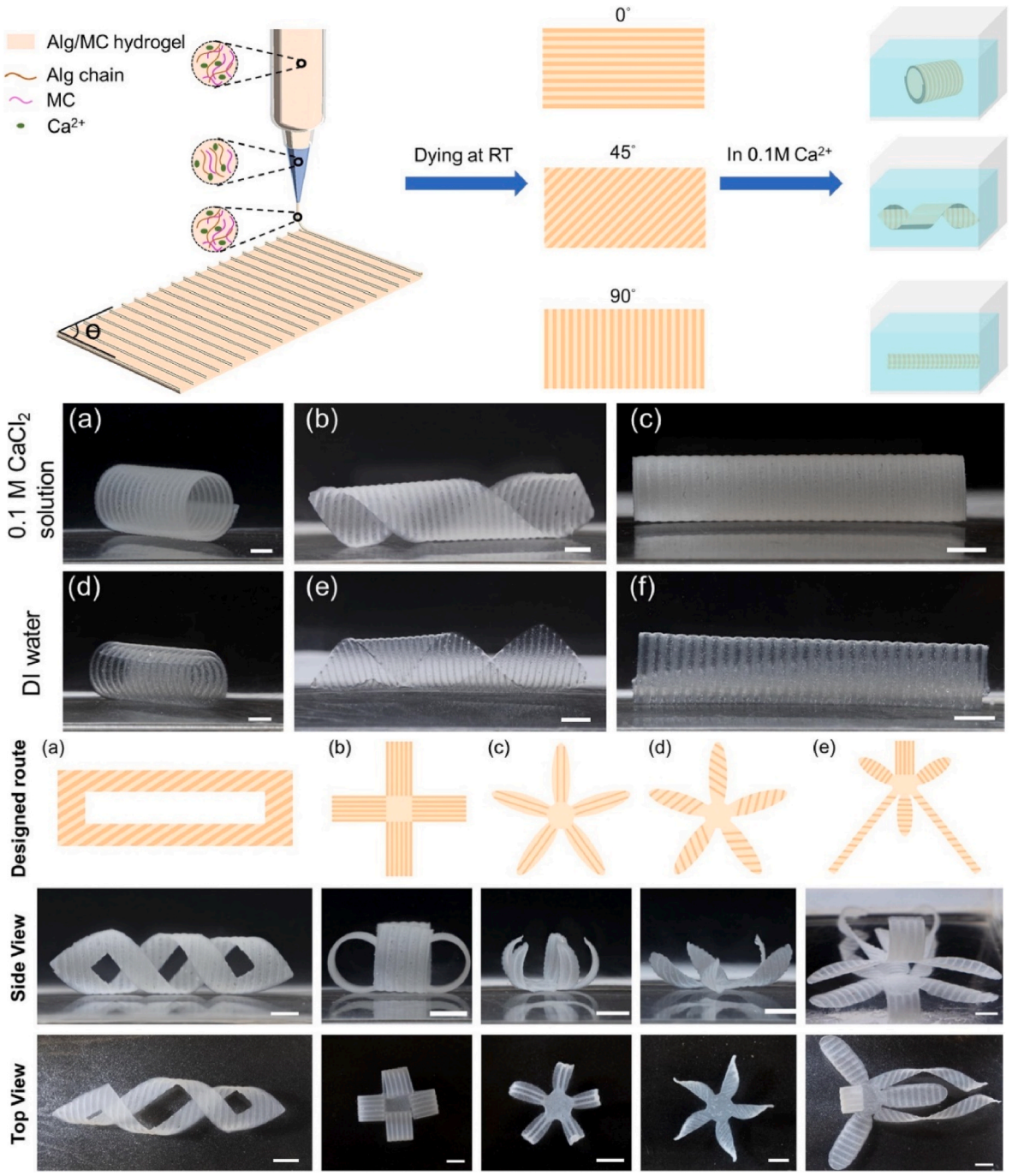

Fig. 23. Alginate/methylcellulose scaffolds 4D-printed in various designs and patterns. Folding responses are activated when immersed in $CaCl_2$ solution [240].

7. Conclusion

Since the demand for sustainable and environmentally friendly materials is increasing, it is important to explore untapped renewable feedstocks. Algae naturally produce a wide variety of materials that can help make the 3D printing industry 'greener'. The aim of this paper was to investigate the 3D and 4D printability of algae-based materials. This was achieved by reviewing the literature available on algae-based synthetic polymers (PHAs, PLA), natural hydrogels (alginate, agarose, carrageenan, chitosan, fucoidan, nanocellulose), and algae cells.

PHAs can be fermented from algae by bacteria and have shown mechanical properties similar to fossil-based PHAs, as discussed earlier. Although PLA from various sources is frequently blended with algae powder to increase the filament's degradability, there is no experimental proof that algae can be a source of PLA. From the algae-derived hydrogels, alginate, agarose, carrageenan, chitosan, nanocellulose, and their composites are already used in the 3D printing industry for various uses of which biomedical applications are the most common. The printability of fucoidan was not experimentally proven yet its properties suggest that it is printable. Recent progress in printing living algae cells was also reviewed. It is noticed that the most used printing techniques for algae-based materials are extrusion-based techniques, after which come inkjet techniques and laser-assisted techniques.

The path towards 4D printing using algae-based materials starts with the controlled responsiveness of certain hydrogels and the cell maturation of printed algae cells. Different types of stimuli that can be used to trigger anticipated hydrogel response were reviewed. Several algae-

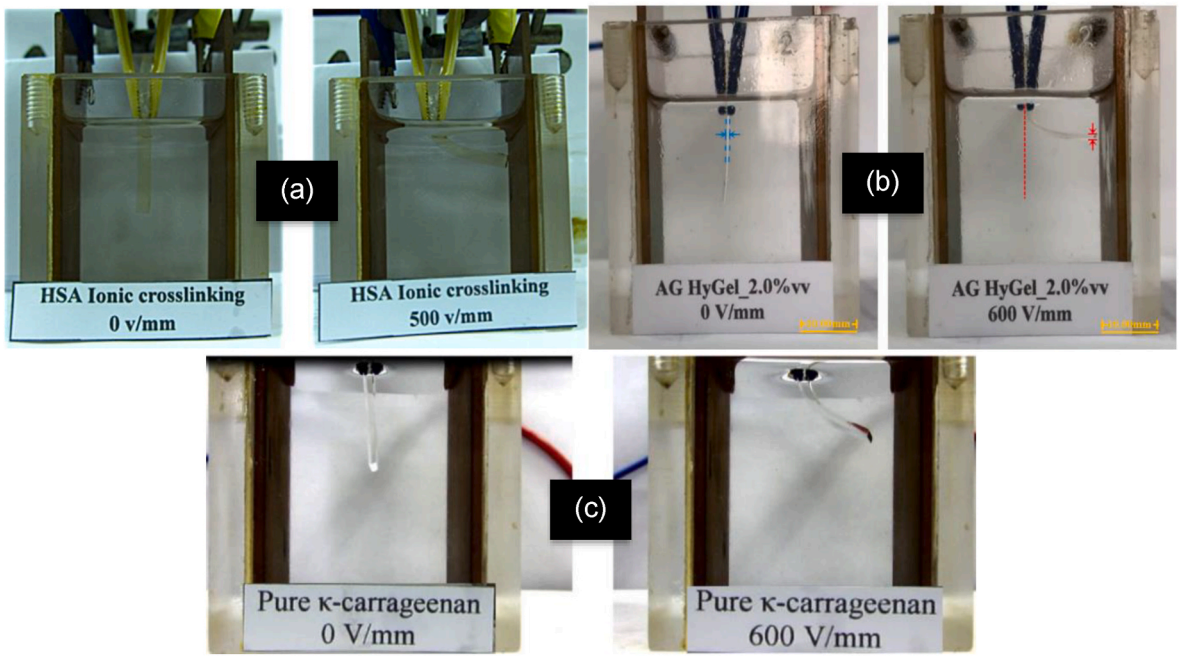

Fig. 24. Electrical responsiveness of hydrogels made of (a) alginate [249] (b) agarose [250] and (c) carrageenan [251].

Table 10
Summary of algae-based responsive hydrogels.

Property	Hydrogel	Ref.
Moisture responsiveness	Swelling is an inherent property of hydrogels.	
Temperature responsiveness	Alginate/PNIPAm	[229]
	Agarose	[230]
	Chitosan	[231]
	Carrageenan	[232]
	Nanocellulose	[233]
Chemical responsiveness	Alginate	[234–236]
	Carrageenan	[237]
	Chitosan	[238]
	Agarose	[239]
Light responsiveness	Composites of photosensitive particles (e.g. carbon or graphene based) and:	[242] [231]
	- Nanocellulose	[243]
	- Chitosan	[244,245]
	- Carrageenan	[246–248]
	- Agarose	
	- Alginate	
Electrical responsiveness	Alginate	[249]
	Agarose	[250]
	Carrageenan	[251]
Magnetic responsiveness	Composites of magnetic materials (e.g. ferromagnetic particles) and:	[252] [253]
	- Alginate	
	- Chitosan	

based hydrogels have shown the potential to be used in 4D printing. For example, alginate swells and shrinks when the ion concentration changes, agarose demonstrates reversible deformation when temperature is changed, and carrageenan can bend when an electric field is applied. There is limited information on harnessing cell and tissue maturation to 4D-print algae cells in particular. However, the relevant progress on 4D-printing mammalian cells using that way is reviewed, for the sake of setting a potential model to follow and to investigate its applicability on algae cells in future research.

It is typically difficult to find natural hydrogels that combine good printability, stable mechanical properties, and favorable biological compatibility. To overcome this limitation, different algae-based hydrogels can be combined with each other to enhance the overall

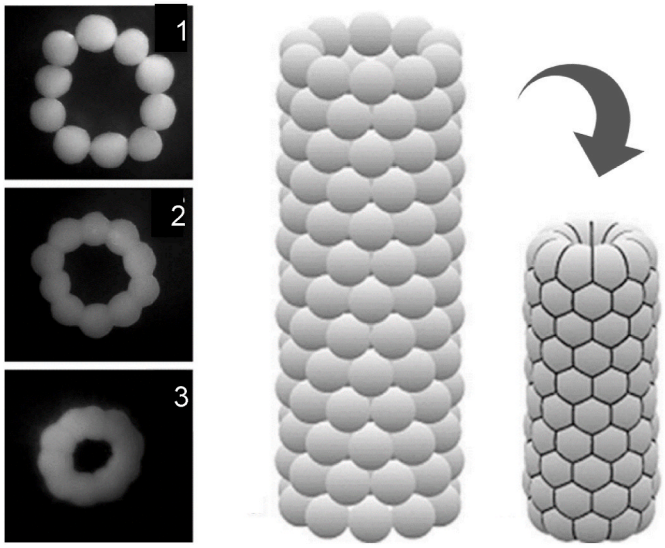

Fig. 25. 4D-bioprinted structures before and after cell maturation [254].

properties of the final inks. They can also be coupled with materials from other sources when required. It is worth highlighting that when selecting a material to incorporate in a 'green' ink, one should take into consideration that not all bio-based materials are biodegradable. More research is required to explore and discover printable materials from algae, and to develop the properties of the existing materials. Algae-based materials are very diverse and have a huge potential but their properties need to be tailored and improved to serve specific applications. Further investigation is also needed to tackle the challenge of the slow response to the stimuli in 4D bioprinting of hydrogels and living cells.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

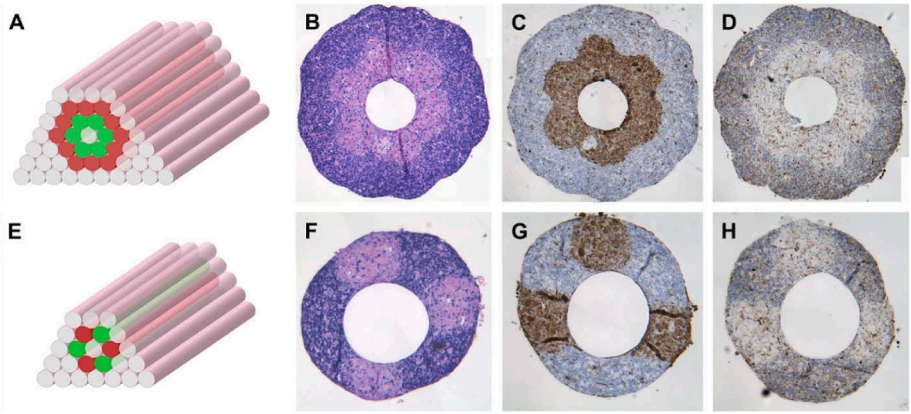

Fig. 26. Self-assembly of cells printed in an agarose scaffold [256].

the work reported in this paper.

Data availability

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

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References

[1] P. Bojek, Renewable Electricity, International Energy Agency Website, 2022. https://www.iea.org/reports/renewable-electricity. (Accessed 6 December 2022).
[2] Bioplastics Market Data, European Bioplastics, 2022. https://www.european-bioplastics.org/market/. (Accessed 6 December 2022).
[3] B.R. Kumar, et al., A state of the art review on the cultivation of algae for energy and other valuable products: application, challenges, and opportunities, Renew. Sustain. Energy Rev. 138 (Mar. 2021), 110649, https://doi.org/10.1016/j.rser.2020.110649.
[4] R.C. Anyanwu, C. Rodriguez, A. Durrant, M. Ramadan, A.-G. Olabi, Micro-macroalgae properties and applications, in: Encyclopedia of Smart Materials, Elsevier, 2022, pp. 732–758, https://doi.org/10.1016/B978-0-12-815732-9.00129-7.
[5] S. Grira, H. Abu Khalifeh, M. Alkhedher, M. Ramadan, The conventional microalgal biofuel production process and the alternative milking pathway: a review, Energy 277 (Aug. 2023), 127547, https://doi.org/10.1016/j.energy.2023.127547.
[6] M. Kumar, Y. Sun, R. Rathour, A. Pandey, I.S. Thakur, D.C.W. Tsang, Algae as potential feedstock for the production of biofuels and value-added products: opportunities and challenges, Sci. Total Environ. 716 (May 2020), 137116, https://doi.org/10.1016/j.scitotenv.2020.137116.
[7] H.N.P. Vo, C. Chaiwong, L. Zheng, T.M.H. Nguyen, T. Koottatep, T.T. Nguyen, Algae-based biomaterials in 3D printing for applications in medical, environmental remediation, and commercial products, in: Algae-Based Biomaterials for Sustainable Development, Elsevier, 2022, pp. 185–202, https://doi.org/10.1016/B978-0-323-96142-4.00011-7.
[8] S. Mandal, G.K. Nagi, A.A. Corcoran, R. Agrawal, M. Dubey, R.W. Hunt, Algal polysaccharides for 3D printing: a review, Carbohydr. Polym. 300 (Jan. 2023), 120267, https://doi.org/10.1016/j.carbpol.2022.120267.
[9] Muskan, D. Gupta, N.P. Negi, 3D bioprinting: printing the future and recent advances, Bioprinting 27 (Aug. 2022), e00211, https://doi.org/10.1016/j.bprint.2022.e00211.
[10] S.A. Vasilescu, S.R. Bazaz, D. Jin, O. Shimoni, M.E. Warkiani, 3D printing enables the rapid prototyping of modular microfluidic devices for particle conjugation, Appl. Mater. Today 20 (Sep. 2020), 100726, https://doi.org/10.1016/j.apmt.2020.100726.
[11] S.L. Sing, C.F. Tey, J.H.K. Tan, S. Huang, W.Y. Yeong, 3D printing of metals in rapid prototyping of biomaterials: techniques in additive manufacturing, in: Rapid Prototyping of Biomaterials, Elsevier, 2020, pp. 17–40, https://doi.org/10.1016/B978-0-08-102663-2.00002-2.
[12] T. Li, J. Chang, Y. Zhu, C. Wu, 3D printing of bioinspired biomaterials for tissue regeneration, Adv Healthc Mater 9 (23) (Dec. 2020), 2000208, https://doi.org/10.1002/adhm.202000208.
[13] Y. Sun, A.D. Juncos Bombin, P. Boyd, N. Dunne, H.O. McCarthy, Application of 3D printing & 3D bioprinting for promoting cutaneous wound regeneration, Bioprinting 28 (Dec. 2022), e00230, https://doi.org/10.1016/j.bprint.2022.e00230.
[14] S. Beg, et al., 3D printing for drug delivery and biomedical applications, Drug Discov. Today 25 (9) (Sep. 2020) 1668–1681, https://doi.org/10.1016/j.drudis.2020.07.007.
[15] G. Pagnotta, S. Kalia, L. Di Lisa, A.F.G. Cicero, C. Borghi, M.L. Focarete, Progress towards 3D bioprinting of tissue models for advanced drug screening: in vitro evaluation of drug toxicity and drug metabolism, Bioprinting 27 (Aug. 2022), e00218, https://doi.org/10.1016/j.bprint.2022.e00218.
[16] S. Kanwar, S. Vijayavenkataraman, Design of 3D printed scaffolds for bone tissue engineering: a review, Bioprinting 24 (Dec. 2021), e00167, https://doi.org/10.1016/j.bprint.2021.e00167.
[17] L.D. Tijing, J.R.C. Dizon, I. Ibrahim, A.R.N. Nisay, H.K. Shon, R.C. Advincula, 3D printing for membrane separation, desalination and water treatment, Appl. Mater. Today 18 (Mar. 2020), 100486, https://doi.org/10.1016/j.apmt.2019.100486.
[18] M. Guvendiren, J. Molde, R.M.D. Soares, J. Kohn, Designing biomaterials for 3D printing, ACS Biomater. Sci. Eng. 2 (10) (Oct. 2016) 1679–1693, https://doi.org/10.1021/acsbiomaterials.6b00121.
[19] H.W. Tan, J. An, C.K. Chua, T. Tran, Metallic nanoparticle inks for 3D printing of electronics, Adv Electron Mater 5 (5) (May 2019), 1800831, https://doi.org/10.1002/aelm.201800831.
[20] L. Wang, J. Liu, Liquid metal inks for flexible electronics and 3D printing: a review, in: Advanced Manufacturing, 2B, American Society of Mechanical Engineers, Nov, 2014, https://doi.org/10.1115/IMECE2014-37993.
[21] Z. Chen, et al., 3D printing of ceramics: a review, J. Eur. Ceram. Soc. 39 (4) (Apr. 2019) 661–687, https://doi.org/10.1016/j.jeurceramsoc.2018.11.013.
[22] L. del-Mazo-Barbara, M.-P. Ginebra, Rheological characterisation of ceramic inks for 3D direct ink writing: a review, J. Eur. Ceram. Soc. 41 (16) (Dec. 2021) 18–33, https://doi.org/10.1016/j.jeurceramsoc.2021.08.031.
[23] W. Li, L.S. Mille, J.A. Robledo, T. Uribe, V. Huerta, Y.S. Zhang, Recent advances in formulating and processing biomaterial inks for vat polymerization-based 3D printing, Adv Healthc Mater 9 (15) (Aug. 2020), 2000156, https://doi.org/10.1002/adhm.202000156.
[24] M. Mobaraki, M. Ghaffari, A. Yazdanpanah, Y. Luo, D.K. Mills, Bioinks and bioprinting: a focused review, Bioprinting 18 (Jun. 2020), e00080, https://doi.org/10.1016/j.bprint.2020.e00080.
[25] Z.U. Arif, M.Y. Khalid, M.F. Sheikh, A. Zolfagharian, M. Bodaghi, Biopolymeric sustainable materials and their emerging applications, J. Environ. Chem. Eng. 10 (4) (Aug. 2022), 108159, https://doi.org/10.1016/j.jece.2022.108159.
[26] M.Y. Khalid, Z.U. Arif, R. Noroozi, A. Zolfagharian, M. Bodaghi, 4D printing of shape memory polymer composites: a review on fabrication techniques, applications, and future perspectives, J. Manuf. Process. 81 (Sep. 2022) 759–797, https://doi.org/10.1016/j.jmapro.2022.07.035.
[27] R. Suriano, R. Bernasconi, L. Magagnin, M. Levi, 4D printing of smart stimuli-responsive polymers, J. Electrochem. Soc. 166 (9) (2019) B3274–B3281, https://doi.org/10.1149/2.0411909jes.
[28] X. Kuang, et al., Advances in 4D printing: materials and applications, Adv. Funct. Mater. 29 (2) (Jan. 2019), 1805290, https://doi.org/10.1002/adfm.201805290.
[29] K. McLellan, Y.-C. Sun, H.E. Naguib, A review of 4D printing: materials, structures, and designs towards the printing of biomedical wearable devices, Bioprinting 27 (Aug. 2022), e00217, https://doi.org/10.1016/j.bprint.2022.e00217.
[30] S.K. Bhatia, K.W. Ramadurai, 3D Printing and Bio-Based Materials in Global Health, Springer International Publishing, Cham, 2017, https://doi.org/10.1007/978-3-319-58277-1.
[31] T.H. Jovic, G. Kungwengwe, A.C. Mills, I.S. Whitaker, Plant-derived biomaterials: a review of 3D bioprinting and biomedical applications, Front. Mech. Eng. 5 (Apr. 2019), https://doi.org/10.3389/fmech.2019.00019.
[32] M. Beaumont, et al., Hydrogel-forming algae polysaccharides: from seaweed to biomedical applications, Biomacromolecules 22 (3) (Mar. 2021) 1027–1052, https://doi.org/10.1021/acs.biomac.0c01406.

[33] M. Bahram, N. Mohseni, M. Moghtader, An introduction to hydrogels and some recent applications, in: Emerging Concepts in Analysis and Applications of Hydrogels, InTech, 2016, https://doi.org/10.5772/64301.

[34] T.C. Mokhena, V.C. Agbakoba, A. Mtibe, M.J. John, An overview on additive manufacturing of biopolymer nanocomposites, in: Handbook of Polymer Nanocomposites for Industrial Applications, Elsevier, 2021, pp. 687–708, https://doi.org/10.1016/B978-0-12-821497-8.00026-5.

[35] A.E. Alexander, N. Wake, L. Chepelev, P. Brantner, J. Ryan, K.C. Wang, A guideline for 3D printing terminology in biomedical research utilizing ISO/ASTM standards, 3D Print Med 7 (1) (Dec. 2021) 8, https://doi.org/10.1186/s41205-021-00098-5.

[36] R.A. Pradhan, S.S. Rahman, A. Qureshi, A. Ullah, Biopolymers," in *Biopolymers And Their Industrial Applications*, Elsevier, 2021, pp. 281–303, https://doi.org/10.1016/B978-0-12-819240-5.00012-2.

[37] S. Wang, Y. Ma, Z. Deng, S. Zhang, J. Cai, Effects of fused deposition modeling process parameters on tensile, dynamic mechanical properties of 3D printed polylactic acid materials, Polym. Test. 86 (Jun. 2020), 106483, https://doi.org/10.1016/j.polymertesting.2020.106483.

[38] W. Aljohani, M.W. Ullah, X. Zhang, G. Yang, Bioprinting and its applications in tissue engineering and regenerative medicine, Int. J. Biol. Macromol. 107 (Feb. 2018) 261–275, https://doi.org/10.1016/j.ijbiomac.2017.08.171.

[39] B. Mahendiran, et al., Recent trends in natural polysaccharide based bioinks for multiscale 3D printing in tissue regeneration: a review, Int. J. Biol. Macromol. 183 (Jul. 2021) 564–588, https://doi.org/10.1016/j.ijbiomac.2021.04.179.

[40] Y. Zhang, et al., Biomaterials based on marine resources for 3D bioprinting applications, Mar. Drugs 17 (10) (Sep. 2019) 555, https://doi.org/10.3390/md17100555.

[41] Y. Guo, H.S. Patanwala, B. Bognet, A.W.K. Ma, Inkjet and inkjet-based 3D printing: connecting fluid properties and printing performance, Rapid Prototyp. J. 23 (3) (Apr. 2017) 562–576, https://doi.org/10.1108/RPJ-05-2016-0076.

[42] L. del-Mazo-Barbara, M.-P. Ginebra, Rheological characterisation of ceramic inks for 3D direct ink writing: a review, J. Eur. Ceram. Soc. 41 (16) (Dec. 2021) 18–33, https://doi.org/10.1016/j.jeurceramsoc.2021.08.031.

[43] M. Bhuvanesh Kumar, P. Sathiya, Methods and materials for additive manufacturing: a critical review on advancements and challenges, Thin-Walled Struct. 159 (Feb. 2021), 107228, https://doi.org/10.1016/j.tws.2020.107228.

[44] J. Liu, L. Sun, W. Xu, Q. Wang, S. Yu, J. Sun, Current advances and future perspectives of 3D printing natural-derived biopolymers, Carbohydr. Polym. 207 (Mar. 2019) 297–316, https://doi.org/10.1016/j.carbpol.2018.11.077.

[45] M. Mehrpouya, H. Vahabi, M. Barletta, P. Laheurte, V. Langlois, Additive manufacturing of polyhydroxyalkanoates (PHAs) biopolymers: materials, printing techniques, and applications, Mater. Sci. Eng. C 127 (Aug. 2021), 112216, https://doi.org/10.1016/j.msec.2021.112216.

[46] W.Y. Chia, D.Y. Ying Tang, K.S. Khoo, A.N. Kay Lup, K.W. Chew, Nature's fight against plastic pollution: algae for plastic biodegradation and bioplastics production, Environmental Science and Ecotechnology 4 (Oct. 2020), 100065, https://doi.org/10.1016/j.ese.2020.100065.

[47] G. Ross, S. Ross, B.J. Tighe, Bioplastics: New Routes, New Products," *Brydson's Plastics Materials*, Eighth Edition, 2017, pp. 631–652, https://doi.org/10.1016/B978-0-323-35824-8.00023-2.

[48] S.S. Sawant, B.K. Salunke, B.S. Kim, Consolidated bioprocessing for production of polyhydroxyalkanotes from red algae Gelidium amansii, Int. J. Biol. Macromol. 109 (Apr. 2018) 1012–1018, https://doi.org/10.1016/j.ijbiomac.2017.11.084.

[49] B. Alkotaini, H. Koo, B.S. Kim, Production of polyhydroxyalkanoates by batch and fed-batch cultivations of Bacillus megaterium from acid-treated red algae, Kor. J. Chem. Eng. 33 (5) (May 2016) 1669–1673, https://doi.org/10.1007/s11814-015-0293-6.

[50] F.A. El-malek, M. Rofeal, A. Farag, S. Omar, H. Khairy, Polyhydroxyalkanoate nanoparticles produced by marine bacteria cultivated on cost effective Mediterranean algal hydrolysate media, J. Biotechnol. 328 (Feb. 2021) 95–105, https://doi.org/10.1016/j.jbiotec.2021.01.008.

[51] A.P.A. Cassuriaga, B.C.B. Freitas, M.G. Morais, J.A.V. Costa, Innovative polyhydroxybutyrate production by Chlorella fusca grown with pentoses, Bioresour. Technol. 265 (Oct. 2018) 456–463, https://doi.org/10.1016/j.biortech.2018.06.026.

[52] K. Roja, D. Ruben Sudhakar, S. Anto, T. Mathimani, Extraction and characterization of polyhydroxyalkanoates from marine green alga and cyanobacteria, Biocatal. Agric. Biotechnol. 22 (Nov. 2019), 101358, https://doi.org/10.1016/j.bcab.2019.101358.

[53] X. Han, et al., Polyhydroxyalkanoate production by a novel bacterium Massilia sp. UMI-21 isolated from seaweed, and molecular cloning of its polyhydroxyalkanoate synthase gene, J. Biosci. Bioeng. 118 (5) (Nov. 2014) 514–519, https://doi.org/10.1016/j.jbiosc.2014.04.022.

[54] G. Kavitha, C. Kurinjimalar, K. Sivakumar, P. Palani, R. Rengasamy, Biosynthesis, purification and characterization of polyhydroxybutyrate from Botryococcus braunii kütz, Int. J. Biol. Macromol. 89 (Aug. 2016) 700–706, https://doi.org/10.1016/J.IJBIOMAC.2016.04.086.

[55] M. Muhammad, H. Aloui, C. Khomlaem, C.T. Hou, B.S. Kim, Production of polyhydroxyalkanoates and carotenoids through cultivation of different bacterial strains using brown algae hydrolysate as a carbon source, Biocatal. Agric. Biotechnol. 30 (Nov. 2020), 101852, https://doi.org/10.1016/j.bcab.2020.101852.

[56] D.M. Arias, J. García, E. Uggetti, Production of polymers by cyanobacteria grown in wastewater: current status, challenges and future perspectives, N. Biotech. 55 (Mar. 2020) 46–57, https://doi.org/10.1016/j.nbt.2019.09.001.

[57] M. Koller, 'Bioplastics from microalgae'—polyhydroxyalkanoate production by cyanobacteria, in: Handbook of Microalgae-Based Processes and Products, Elsevier, 2020, pp. 597–645, https://doi.org/10.1016/B978-0-12-818536-0.00022-1.

[58] J.C. Fradinho, J.M.B. Domingos, G. Carvalho, A. Oehmen, M.A.M. Reis, Polyhydroxyalkanoates production by a mixed photosynthetic consortium of bacteria and algae, Bioresour. Technol. 132 (Mar. 2013) 146–153, https://doi.org/10.1016/j.biortech.2013.01.050.

[59] S.S. Costa, et al., Influence of nitrogen on growth, biomass composition, production, and properties of polyhydroxyalkanoates (PHAs) by microalgae, Int. J. Biol. Macromol. 116 (Sep. 2018) 552–562, https://doi.org/10.1016/j.ijbiomac.2018.05.064.

[60] M. Akdoğan, E. Çelik, Enhanced production of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) biopolymer by recombinant Bacillus megaterium in fed-batch bioreactors, Bioproc. Biosyst. Eng. 44 (2) (Feb. 2021) 403–416, https://doi.org/10.1007/s00449-020-02452-z.

[61] H.-M. Müller, D. Seebach, Poly(hydroxyalkanoates): a fifth class of physiologically important organic biopolymers? Angew Chem. Int. Ed. Engl. 32 (4) (Apr. 1993) 477–502, https://doi.org/10.1002/anie.199304771.

[62] S. Gogolewski, M. Jovanovic, S.M. Perren, J.G. Dillon, M.K. Hughes, Tissue response andin vivo degradation of selected polyhydroxyacids: polylactides (PLA), poly(3-hydroxybutyrate) (PHB), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB/VA), J. Biomed. Mater. Res. 27 (9) (Sep. 1993) 1135–1148, https://doi.org/10.1002/jbm.820270904.

[63] A. Kartik, et al., A critical review on production of biopolymers from algae biomass and their applications, Bioresour. Technol. 329 (Jun. 2021), 124868, https://doi.org/10.1016/j.biortech.2021.124868.

[64] B. Duan, M. Wang, Encapsulation and release of biomolecules from Ca–P/PHBV nanocomposite microspheres and three-dimensional scaffolds fabricated by selective laser sintering, Polym. Degrad. Stabil. 95 (9) (Sep. 2010) 1655–1664, https://doi.org/10.1016/j.polymdegradstab.2010.05.022.

[65] K.W. Meereboer, M. Misra, A.K. Mohanty, Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites, Green Chem. 22 (17) (2020) 5519–5558, https://doi.org/10.1039/D0GC01647K.

[66] C.-S. Wu, H.-T. Liao, Y.-X. Cai, Characterisation, biodegradability and application of palm fibre-reinforced polyhydroxyalkanoate composites, Polym. Degrad. Stabil. 140 (Jun. 2017) 55–63, https://doi.org/10.1016/j.polymdegradstab.2017.04.016.

[67] J. Tian, R. Zhang, Y. Wu, P. Xue, Additive manufacturing of wood flour/polyhydroxyalkanoates (PHA) fully bio-based composites based on micro-screw extrusion system, Mater. Des. 199 (Feb. 2021), 109418, https://doi.org/10.1016/j.matdes.2020.109418.

[68] A.A. Vaidya, C. Collet, M. Gaugler, G. Lloyd-Jones, Integrating softwood biorefinery lignin into polyhydroxybutyrate composites and application in 3D printing, Mater. Today Commun. 19 (Jun. 2019) 286–296, https://doi.org/10.1016/j.mtcomm.2019.02.008.

[69] S. Kontárová, et al., Printability, mechanical and thermal properties of poly(3-hydroxybutyrate)-poly(lactic acid)-plasticizer blends for three-dimensional (3D) printing, Materials 13 (21) (Oct. 2020) 4736, https://doi.org/10.3390/ma13214736.

[70] F. Valentini, A. Dorigato, D. Rigotti, A. Pegoretti, Polyhydroxyalkanoates/fibrillated nanocellulose composites for additive manufacturing, J. Polym. Environ. 27 (6) (Jun. 2019) 1333–1341, https://doi.org/10.1007/s10924-019-01429-8.

[71] A.N. Frone, et al., Morpho-structural, thermal and mechanical properties of PLA/PHB/cellulose biodegradable nanocomposites obtained by compression molding, extrusion, and 3D printing, Nanomaterials 10 (1) (Dec. 2019) 51, https://doi.org/10.3390/nano10010051.

[72] T.F. Pereira, M.F. Oliveira, I.A. Maia, J.V.L. Silva, M.F. Costa, R.M.S.M. Thiré, 3D printing of poly(3-hydroxybutyrate) porous structures using selective laser sintering, Macromol. Symp. 319 (1) (Sep. 2012) 64–73, https://doi.org/10.1002/masy.201100237.

[73] T.F. Pereira, et al., Effect of process parameters on the properties of selective laser sintered Poly(3-hydroxybutyrate) scaffolds for bone tissue engineering, Virtual Phys. Prototyp. 7 (4) (Dec. 2012) 275–285, https://doi.org/10.1080/17452759.2012.738551.

[74] L. Chaunier, S. Guessasma, S. Belhabib, G. della Valle, D. Lourdin, E. Leroy, Material extrusion of plant biopolymers: opportunities & challenges for 3D printing, Addit. Manuf. 21 (May 2018) 220–233, https://doi.org/10.1016/J.ADDMA.2018.03.016.

[75] A. Sreenikethanam, A. Bajhaiya, Algae Based Bio-Plastics: Future of Green Economy, Biorefineries - Selected Processes, IntechOpen, 2022, https://doi.org/10.5772/intechopen.100981.

[76] B. Ahmed, S. Sultana, A critical review on PLA-algae composite: chemistry, mechanical, and thermal properties, J. Textil. Sci. Eng. 10 (7) (2020), https://doi.org/10.37421/jtese.2020.10.425.

[77] M. Bulota, T. Budtova, PLA/algae composites: morphology and mechanical properties, Composer Part A Appl Sci Manuf 73 (Jun. 2015) 109–115, https://doi.org/10.1016/j.compositesa.2015.03.001.

[78] N.K. Kalita, N.A. Damare, D. Hazarika, P. Bhagabati, A. Kalamdhad, V. Katiyar, Biodegradation and characterization study of compostable PLA bioplastic containing algae biomass as potential degradation accelerator, Environmental Challenges 3 (Apr. 2021), 100067, https://doi.org/10.1016/j.envc.2021.100067.

[79] S. Sayin, et al., Marine Algae-PLA composites as de novo alternative to porcine derived collagen membranes, Mater. Today Chem. 17 (Sep. 2020), 100276, https://doi.org/10.1016/j.mtchem.2020.100276.

[80] T. Ozyhar, F. Baradel, J. Zoppe, Effect of functional mineral additive on processability and material properties of wood-fiber reinforced poly(lactic acid) (PLA) composites, Composer Part A Appl Sci Manuf 132 (May 2020), 105827, https://doi.org/10.1016/J.COMPOSITESA.2020.105827.

[81] S.A. Adli, F. Ali, A.S. Azmi, Preparation and characterization of PLA/algae nanocomposite for packaging industry, Journal of Advanced Research in Materials Science 50 (1) (2018) 19–25.

[82] K.Y. Lee, D.J. Mooney, Alginate: properties and biomedical applications, Prog. Polym. Sci. 37 (1) (Jan. 2012) 106–126, https://doi.org/10.1016/j.progpolymsci.2011.06.003.

[83] E. Axpe, M. Oyen, Applications of alginate-based bioinks in 3D bioprinting, Int. J. Mol. Sci. 17 (12) (Nov. 2016) 1976, https://doi.org/10.3390/ijms17121976.

[84] X. Guo, Y. Wang, Y. Qin, P. Shen, Q. Peng, Structures, properties and application of alginic acid: a review, Int. J. Biol. Macromol. 162 (Nov. 2020) 618–628, https://doi.org/10.1016/J.IJBIOMAC.2020.06.180.

[85] S. Naghieh, M.R. Karamooz-Ravari, M. Sarker, E. Karki, X. Chen, Influence of crosslinking on the mechanical behavior of 3D printed alginate scaffolds: experimental and numerical approaches, J. Mech. Behav. Biomed. Mater. 80 (Apr. 2018) 111–118, https://doi.org/10.1016/j.jmbbm.2018.01.034.

[86] C.K. Kuo, P.X. Ma, Ionically crosslinked alginate hydrogels as scaffolds for tissue engineering: Part 1. Structure, gelation rate and mechanical properties, Biomaterials 22 (6) (Mar. 2001) 511–521, https://doi.org/10.1016/S0142-9612(00)00201-5.

[87] G.A. Paredes JuÃ¡rez, M. Spasojevic, M.M. Faas, P. de Vos, Immunological and technical considerations in application of alginate-based microencapsulation systems, Front. Bioeng. Biotechnol. 2 (Aug. 2014), https://doi.org/10.3389/fbioe.2014.00026.

[88] M. Zanon, et al., Photocurable thiol–yne alginate hydrogels for regenerative medicine purposes, Polymers 14 (21) (Nov. 2022) 4709, https://doi.org/10.3390/polym14214709.

[89] R. Ahmad Raus, W.M.F. Wan Nawawi, R.R. Nasaruddin, Alginate and alginate composites for biomedical applications, Asian J. Pharm. Sci. 16 (3) (May 2021) 280–306, https://doi.org/10.1016/j.ajps.2020.10.001.

[90] F.E. Freeman, D.J. Kelly, Tuning alginate bioink stiffness and composition for controlled growth factor delivery and to spatially direct MSC fate within bioprinted tissues, Sci. Rep. 7 (1) (Dec. 2017) 17042, https://doi.org/10.1038/s41598-017-17286-1.

[91] M. Leonardo, E. Prajatelistia, H. Judawisastra, Alginate-based bioink for organoid 3D bioprinting: a review, Bioprinting 28 (Dec. 2022), e00246, https://doi.org/10.1016/j.bprint.2022.e00246.

[92] I.P.S. Fernando, W. Lee, E.J. Han, G. Ahn, Alginate-based nanomaterials: fabrication techniques, properties, and applications, Chem. Eng. J. 391 (Jul. 2020), 123823, https://doi.org/10.1016/j.cej.2019.123823.

[93] A.H. King, Brown Seaweed Extracts (Alginates), first ed., Food Hydrocolloids, 1983.

[94] S.-Y. Chee, P.-K. Wong, C.-L. Wong, Extraction and characterisation of alginate from brown seaweeds (fucales, phaeophyceae) collected from port dickson, peninsular Malaysia, J. Appl. Phycol. 23 (2) (Apr. 2011) 191–196, https://doi.org/10.1007/s10811-010-9533-7.

[95] G.D.T.M. Jayasinghe, B.K.K.K. Jinadasa, N.A.G. Sadaruwan, Pathway of sodium alginate synthesis from marine brown algae, Sargassum wightii from Sri Lanka, Discover Food 2 (1) (Dec. 2022) 2, https://doi.org/10.1007/s44187-021-00001-5.

[96] A.R. Lucaci, D. Bulgariu, I. Ahmad, L. Bulgariu, Equilibrium and kinetics studies of metal ions biosorption on alginate extracted from marine red algae biomass (callithamnion corymbosum sp.), Polymers 12 (9) (Aug. 2020) 1888, https://doi.org/10.3390/polym12091888.

[97] B. Deepa, E. Abraham, L. Pothan, N. Cordeiro, M. Faria, S. Thomas, Biodegradable nanocomposite films based on sodium alginate and cellulose nanofibrils, Materials 9 (1) (Jan. 2016) 50, https://doi.org/10.3390/ma9010050.

[98] S.K. Tam, J. Dusseault, S. Bilodeau, G. Langlois, J.-P. Hallé, L. Yahia, Factors influencing alginate gel biocompatibility, J. Biomed. Mater. Res. 98A (1) (Jul. 2011) 40–52, https://doi.org/10.1002/jbm.a.33047.

[99] S.Y. Sonaye, E.G. Ertugral, C.R. Kothapalli, P. Sikder, Extrusion 3D (Bio)Printing of alginate-gelatin-based composite scaffolds for skeletal muscle tissue engineering, Materials 15 (22) (Nov. 2022) 7945, https://doi.org/10.3390/ma15227945.

[100] P.P. Shah, H.B. Shah, K.K. Maniar, T. Özel, Extrusion-based 3D bioprinting of alginate-based tissue constructs, Procedia CIRP 95 (2020) 143–148, https://doi.org/10.1016/j.procir.2020.06.007.

[101] K. Christensen, C. Xu, W. Chai, Z. Zhang, J. Fu, Y. Huang, Freeform inkjet printing of cellular structures with bifurcations, Biotechnol. Bioeng. 112 (5) (May 2015) 1047–1055, https://doi.org/10.1002/bit.25501.

[102] R. Xiong, Z. Zhang, Y. Huang, Identification of optimal printing conditions for laser printing of alginate tubular constructs, J. Manuf. Process. 20 (Oct. 2015) 450–455, https://doi.org/10.1016/j.jmapro.2015.06.023.

[103] J. Yan, Y. Huang, D.B. Chrisey, Laser-assisted printing of alginate long tubes and annular constructs, Biofabrication 5 (1) (Nov. 2012), 015002, https://doi.org/10.1088/1758-5082/5/1/015002.

[104] M. Ghebremedhin, S. Seiffert, T.A. Vilgis, Physics of agarose fluid gels: rheological properties and microstructure, Curr. Res. Food Sci. 4 (2021) 436–448, https://doi.org/10.1016/j.crfs.2021.06.003.

[105] J.J. Roberts, P.J. Martens, Engineering biosynthetic cell encapsulation systems, in: Biosynthetic Polymers for Medical Applications, Elsevier, 2016, pp. 205–239, https://doi.org/10.1016/B978-1-78242-105-4.00009-2.

[106] S. Datta, L.R. Christena, Y.R.S. Rajaram, Enzyme immobilization: an overview on techniques and support materials, 3 Biotech 3 (1) (Feb. 2013) 1–9, https://doi.org/10.1007/s13205-012-0071-7.

[107] M. Rayung, et al., Bio-based polymer electrolytes for electrochemical devices: insight into the ionic conductivity performance, Materials 13 (4) (Feb. 2020) 838, https://doi.org/10.3390/ma13040838.

[108] Y. Hu, Y. Kim, I. Hong, M. Kim, S. Jung, Fabrication of flexible pH-responsive agarose/succinoglycan hydrogels for controlled drug release, Polymers 13 (13) (Jun. 2021) 2049, https://doi.org/10.3390/polym13132049.

[109] W.Y. Seow, K. Kandasamy, G.S.L. Peh, J.S. Mehta, W. Sun, Ultrathin, strong, and cell-adhesive agarose-based membranes engineered as substrates for corneal endothelial cells, ACS Biomater. Sci. Eng. 5 (8) (Aug. 2019) 4067–4076, https://doi.org/10.1021/acsbiomaterials.9b00610.

[110] C. Jiang, Z. Liu, D. Cheng, X. Mao, Agarose degradation for utilization: enzymes, pathways, metabolic engineering methods and products, Biotechnol. Adv. 45 (Dec. 2020), 107641, https://doi.org/10.1016/j.biotechadv.2020.107641.

[111] X.T. Fu, S.M. Kim, Agarase: review of major sources, categories, purification method, enzyme characteristics and applications, Mar. Drugs 8 (1) (Jan. 2010) 200–218, https://doi.org/10.3390/md8010200.

[112] L.-M. Zhang, C.-X. Wu, J.-Y. Huang, X.-H. Peng, P. Chen, S.-Q. Tang, Synthesis and characterization of a degradable composite agarose/HA hydrogel, Carbohydr. Polym. 88 (4) (May 2012) 1445–1452, https://doi.org/10.1016/j.carbpol.2012.02.050.

[113] V. Muşat, et al., A chitosan–agarose polysaccharide-based hydrogel for biomimetic remineralization of dental enamel, Biomolecules 11 (8) (Aug. 2021) 1137, https://doi.org/10.3390/biom11081137.

[114] L. Ning, C. You, Y. Zhang, X. Li, F. Wang, Polydopamine loaded fluorescent nanocellulose–agarose hydrogel: a pH-responsive drug delivery carrier for cancer therapy, Compos. Commun. 26 (Aug. 2021), 100739, https://doi.org/10.1016/j.coco.2021.100739.

[115] A. Forget, et al., Mechanically tunable bioink for 3D bioprinting of human cells, Adv Healthc Mater 6 (20) (Oct. 2017), 1700255, https://doi.org/10.1002/adhm.201700255.

[116] N. Arya, A. Forget, M. Sarem, V.P. Shastri, RGDSP functionalized carboxylated agarose as extrudable carriers for chondrocyte delivery, Mater. Sci. Eng. C 99 (Jun. 2019) 103–111, https://doi.org/10.1016/j.msec.2019.01.080.

[117] C. Gong, Z. Kong, X. Wang, The effect of agarose on 3D bioprinting, Polymers 13 (22) (Nov. 2021) 4028, https://doi.org/10.3390/polym13224028.

[118] G.R. López-Marcial, A.Y. Zeng, C. Osuna, J. Dennis, J.M. García, G.D. O'Connell, Agarose-based hydrogels as suitable bioprinting materials for tissue engineering, ACS Biomater. Sci. Eng. 4 (10) (Oct. 2018) 3610–3616, https://doi.org/10.1021/acsbiomaterials.8b00903.

[119] Z. Teng, et al., Agarose hydrogel composite supports microgreen cultivation with enhanced porosity and continuous water supply under terrestrial and microgravitational conditions, Int. J. Biol. Macromol. 220 (Nov. 2022) 135–146, https://doi.org/10.1016/j.ijbiomac.2022.08.046.

[120] A.B.A. Ahmed, M. Adel, P. Karimi, M. Peidayesh, Pharmaceutical, cosmeceutical, and traditional applications of marine carbohydrates, Adv. Food Nutr. Res. 73 (Jan. 2014) 197–220, https://doi.org/10.1016/B978-0-12-800268-1.00010-X.

[121] T.A. Kuznetsova, B.G. Andryukov, N.N. Besednova, T.S. Zaporozhets, A.v. Kalinin, Marine algae polysaccharides as basis for wound dressings, drug delivery, and tissue engineering: a review, J. Mar. Sci. Eng. 8 (7) (Jun. 2020) 481, https://doi.org/10.3390/jmse8070481.

[122] L. Cunha, A. Grenha, Sulfated seaweed polysaccharides as multifunctional materials in drug delivery applications, Mar. Drugs 14 (3) (Feb. 2016) 42, https://doi.org/10.3390/md14030042.

[123] K.M. Zia, et al., A review on synthesis, properties and applications of natural polymer based carrageenan blends and composites, Int. J. Biol. Macromol. 96 (Mar. 2017) 282–301, https://doi.org/10.1016/j.ijbiomac.2016.11.095.

[124] E.-M. Pacheco-Quito, R. Ruiz-Caro, M.-D. Veiga, Carrageenan: drug delivery systems and other biomedical applications, Mar. Drugs 18 (11) (Nov. 2020) 583, https://doi.org/10.3390/md18110583.

[125] S.M. Mihaila, A.K. Gaharwar, R.L. Reis, A.P. Marques, M.E. Gomes, A. Khademhosseini, Photocrosslinkable *kappa* -carrageenan hydrogels for tissue engineering applications, Adv Healthc Mater 2 (6) (Jun. 2013) 895–907, https://doi.org/10.1002/adhm.201200317.

[126] T.R. Martiny, et al., A novel biodegradable film based on κ-carrageenan activated with olive leaves extract, Food Sci. Nutr. 8 (7) (Jul. 2020) 3147–3156, https://doi.org/10.1002/fsn3.1554.

[127] J. Li, et al., *Iota* -carrageenan/chitosan/gelatin scaffold for the osteogenic differentiation of adipose-derived MSCs *in vitro*, J. Biomed. Mater. Res. B Appl. Biomater. 103 (7) (Oct. 2015) 1498–1510, https://doi.org/10.1002/jbm.b.33339.

[128] J.S. Varghese, N. Chellappa, N.N. Fathima, Gelatin–carrageenan hydrogels: role of pore size distribution on drug delivery process, Colloids Surf. B Biointerfaces 113 (Jan. 2014) 346–351, https://doi.org/10.1016/j.colsurfb.2013.08.049.

[129] S.A. Wilson, L.M. Cross, C.W. Peak, A.K. Gaharwar, Shear-thinning and thermo-reversible nanoengineered inks for 3D bioprinting, ACS Appl. Mater. Interfaces 9 (50) (Dec. 2017) 43449–43458, https://doi.org/10.1021/acsami.7b13602.

[130] H. Li, Y.J. Tan, L. Li, A strategy for strong interface bonding by 3D bioprinting of oppositely charged κ-carrageenan and gelatin hydrogels, Carbohydr. Polym. 198 (Oct. 2018) 261–269, https://doi.org/10.1016/j.carbpol.2018.06.081.

[131] C. Kelder, A. Bakker, J. Klein-Nulend, D. Wismeijer, The 3D printing of calcium phosphate with K-carrageenan under conditions permitting the incorporation of biological components—a method, J. Funct. Biomater. 9 (4) (Oct. 2018) 57, https://doi.org/10.3390/jfb9040057.
[132] R. Joy, P.N. Vigneshkumar, F. John, J. George, Hydrogels based on carrageenan, in: Plant and Algal Hydrogels for Drug Delivery and Regenerative Medicine, Elsevier, 2021, pp. 293–325, https://doi.org/10.1016/B978-0-12-821649-1.00003-9.
[133] H. Mokhtari, et al., Recent advances in chemically-modified and hybrid carrageenan-based platforms for drug delivery, wound healing, and tissue engineering, Polymers 13 (11) (May 2021) 1744, https://doi.org/10.3390/polym13111744.
[134] M.-A. Kamlow, F. Spyropoulos, T. Mills, 3D printing of kappa-carrageenan emulsion gels, Food Hydrocolloids for Health 1 (2021), 100044, https://doi.org/10.1016/j.fhfh.2021.100044.
[135] S. Luthuli, S. Wu, Y. Cheng, X. Zheng, M. Wu, H. Tong, Therapeutic effects of fucoidan: a review on recent studies, Mar. Drugs 17 (9) (Aug. 2019) 487, https://doi.org/10.3390/md17090487.
[136] S. Giri, P. Dutta, D. Kumarasamy, T.K. Giri, Natural polysaccharides: types, basic structure and suitability for forming hydrogels, in: Plant and Algal Hydrogels for Drug Delivery and Regenerative Medicine, Elsevier, 2021, pp. 1–35, https://doi.org/10.1016/B978-0-12-821649-1.00007-6.
[137] J. Venkatesan, I. Bhatnagar, S.-K. Kim, Chitosan-alginate biocomposite containing fucoidan for bone tissue engineering, Mar. Drugs 12 (1) (Jan. 2014) 300–316, https://doi.org/10.3390/md12010300.
[138] D.-H. Ngo, S.-K. Kim, Sulfated polysaccharides as bioactive agents from marine algae, Int. J. Biol. Macromol. 62 (Nov. 2013) 70–75, https://doi.org/10.1016/j.ijbiomac.2013.08.036.
[139] T.-S. Vo, S.-K. Kim, Fucoidans as a natural bioactive ingredient for functional foods, J. Funct.Foods 5 (1) (Jan. 2013) 16–27, https://doi.org/10.1016/j.jff.2012.08.007.
[140] H. Hsu, P. Hwang, Clinical applications of fucoidan in translational medicine for adjuvant cancer therapy, Clin. Transl. Med. 8 (1) (Dec. 2019), https://doi.org/10.1186/s40169-019-0234-9.
[141] S.M. Etman, Y.S.R. Elnaggar, O.Y. Abdallah, Fucoidan, a natural biopolymer in cancer combating: from edible algae to nanocarrier tailoring, Int. J. Biol. Macromol. 147 (Mar. 2020) 799–808, https://doi.org/10.1016/j.ijbiomac.2019.11.191.
[142] Lu, Chang, Tsai, Chen, Chen, Mi, Development of injectable fucoidan and biological macromolecules hybrid hydrogels for intra-articular delivery of platelet-rich plasma, Mar. Drugs 17 (4) (Apr. 2019) 236, https://doi.org/10.3390/md17040236.
[143] B.M. Sutapa, A. Dhruti, R.B. Gopa, Pharmacological, pharmaceutical, cosmetic and diagnostic applications of sulfated polysaccharides from marine algae and bacteria, Afr J Pharm Pharmacol 11 (5) (Feb. 2017) 68–77, https://doi.org/10.5897/AJPP2016.4695.
[144] G.S. Anisha, S. Padmakumari, A.K. Patel, A. Pandey, R.R. Singhania, Fucoidan from marine macroalgae: biological actions and applications in regenerative medicine, drug delivery systems and food industry, Bioengineering 9 (9) (Sep. 2022) 472, https://doi.org/10.3390/bioengineering9090472.
[145] M. Tako, Rheological characteristics of fucoidan isolated from commercially cultured cladosiphon okamuranus, Bot. Mar. 46 (5) (Jan. 2003), https://doi.org/10.1515/BOT.2003.047.
[146] S.-H. Wang, et al., Isolation and purification of brown algae fucoidan from Sargassum siliquosum and the analysis of anti-lipogenesis activity, Biochem. Eng. J. 165 (Jan. 2021), 107798, https://doi.org/10.1016/j.bej.2020.107798.
[147] R.v. Menshova, et al., Fucoidans from Brown alga Fucus evanescens: structure and biological activity, Front. Mar. Sci. 3 (Aug. 2016), https://doi.org/10.3389/fmars.2016.00129.
[148] N.M.A. Ponce, C.A. Stortz, A comprehensive and comparative analysis of the fucoidan compositional data across the phaeophyceae, Front. Plant Sci. 11 (Nov. 2020), https://doi.org/10.3389/fpls.2020.556312.
[149] M.A. Rahman, J. Halfar, First evidence of chitin in calcified coralline algae: new insights into the calcification process of Clathromorphum compactum, Sci. Rep. 4 (1) (May 2015) 6162, https://doi.org/10.1038/srep06162.
[150] C.A. Durkin, T. Mock, E.V. Armbrust, Chitin in diatoms and its association with the cell wall, Eukaryot. Cell 8 (7) (Jul. 2009) 1038–1050, https://doi.org/10.1128/EC.00079-09.
[151] M. Rinaudo, Chitin and chitosan: properties and applications, Prog. Polym. Sci. 31 (7) (Jul. 2006) 603–632, https://doi.org/10.1016/j.progpolymsci.2006.06.001.
[152] A. Pellis, G.M. Guebitz, G.S. Nyanhongo, Chitosan: sources, processing and modification techniques, Gels 8 (7) (Jun. 2022) 393, https://doi.org/10.3390/gels8070393.
[153] J. Nilsen-Nygaard, S. Strand, K. Vårum, K. Draget, C. Nordgård, Chitosan: gels and interfacial properties, Polymers 7 (3) (Mar. 2015) 552–579, https://doi.org/10.3390/polym7030552.
[154] M. Rajabi, M. McConnell, J. Cabral, M.A. Ali, Chitosan hydrogels in 3D printing for biomedical applications, Carbohydr. Polym. 260 (May 2021), 117768, https://doi.org/10.1016/j.carbpol.2021.117768.
[155] J. Fu, F. Yang, Z. Guo, The chitosan hydrogels: from structure to function, New J. Chem. 42 (21) (2018) 17162–17180, https://doi.org/10.1039/C8NJ03482F.
[156] S. Rodrigues, M. Dionísio, C.R. López, A. Grenha, Biocompatibility of chitosan carriers with application in drug delivery, J. Funct. Biomater. 3 (3) (Sep. 2012) 615–641, https://doi.org/10.3390/jfb3030615.
[157] M. Zubair, M. Arshad, R.A. Pradhan, A. Ullah, Chitosan/chitin-based composites for food packaging applications, in: Handbook of Chitin and Chitosan, Elsevier, 2020, pp. 641–670, https://doi.org/10.1016/B978-0-12-817966-6.00020-0.
[158] R. Priyadarshi, J.-W. Rhim, Chitosan-based biodegradable functional films for food packaging applications, Innovat. Food Sci. Emerg. Technol. 62 (Jun. 2020), 102346, https://doi.org/10.1016/j.ifset.2020.102346.
[159] P. Mohammadzadeh Pakdel, S.J. Peighambardoust, Review on recent progress in chitosan-based hydrogels for wastewater treatment application, Carbohydr. Polym. 201 (Dec. 2018) 264–279, https://doi.org/10.1016/j.carbpol.2018.08.070.
[160] M. Sahranavard, A. Zamanian, F. Ghorbani, M.H. Shahrezaee, A critical review on three dimensional-printed chitosan hydrogels for development of tissue engineering, Bioprinting 17 (Mar. 2020), e00063, https://doi.org/10.1016/j.bprint.2019.e00063.
[161] K. Pal, et al., Selected applications of chitosan composites, Int. J. Mol. Sci. 22 (20) (Oct. 2021), 10968, https://doi.org/10.3390/ijms222010968.
[162] J. Venkatesan, S.-K. Kim, Chitosan composites for bone tissue engineering—an overview, Mar. Drugs 8 (8) (Aug. 2010) 2252–2266, https://doi.org/10.3390/md8082252.
[163] M.A. Elgadir, Md S. Uddin, S. Ferdosh, A. Adam, A.J.K. Chowdhury, Md Z. I. Sarker, Impact of chitosan composites and chitosan nanoparticle composites on various drug delivery systems: a review, J. Food Drug Anal. 23 (4) (Dec. 2015) 619–629, https://doi.org/10.1016/j.jfda.2014.10.008.
[164] W.S. Wan Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: a review, Carbohydr. Polym. 83 (4) (Feb. 2011) 1446–1456, https://doi.org/10.1016/j.carbpol.2010.11.004.
[165] Q. Wu, M. Maire, S. Lerouge, D. Therriault, M.-C. Heuzey, 3D printing of microstructured and stretchable chitosan hydrogel for guided cell growth, Adv Biosyst 1 (6) (Jun. 2017), 1700058, https://doi.org/10.1002/adbi.201700058.
[166] Shengjie Li, Zhuo Xiong, Xiaohong Wang, Yongnian Yan, Haixia Liu, Renji Zhang, Direct fabrication of a hybrid cell/hydrogel construct by a double-nozzle assembling technology, J. Bioact. Compat Polym. 24 (3) (May 2009) 249–265, https://doi.org/10.1177/0883911509104094.
[167] Y. Sun, et al., 3D printing collagen/chitosan scaffold ameliorated axon regeneration and neurological recovery after spinal cord injury, J. Biomed. Mater. Res. 107 (9) (Sep. 2019) 1898–1908, https://doi.org/10.1002/jbm.a.36675.
[168] W.L. Ng, W.Y. Yeong, M.W. Naing, Polyelectrolyte gelatin-chitosan hydrogel optimized for 3D bioprinting in skin tissue engineering, Int J Bioprint 2 (0) (Jan. 2016), https://doi.org/10.18063/IJB.2016.01.009.
[169] C. Tonda-Turo, et al., Photocurable chitosan as bioink for cellularized therapies towards personalized scaffold architecture, Bioprinting 18 (Jun. 2020), e00082, https://doi.org/10.1016/j.bprint.2020.e00082.
[170] S. Nganga, et al., Inkjet printing of Chitlac-nanosilver—a method to create functional coatings for non-metallic bone implants, Biofabrication 6 (4) (Oct. 2014), 041001, https://doi.org/10.1088/1758-5082/6/4/041001.
[171] F. Fu, et al., Magnetic resonance imaging-three-dimensional printing technology fabricates customized scaffolds for brain tissue engineering, Neural Regen Res 12 (4) (2017) 614, https://doi.org/10.4103/1673-5374.205101.
[172] V.B. Morris, S. Nimbalkar, M. Younesi, P. McClellan, O. Akkus, Mechanical properties, cytocompatibility and manufacturability of chitosan:PEGDA hybrid-gel scaffolds by stereolithography, Ann. Biomed. Eng. 45 (1) (Jan. 2017) 286–296, https://doi.org/10.1007/s10439-016-1643-1.
[173] Y.-L. Cheng, F. Chen, Preparation and characterization of photocured poly (ε-caprolactone) diacrylate/poly (ethylene glycol) diacrylate/chitosan for photopolymerization-type 3D printing tissue engineering scaffold application, Mater. Sci. Eng. C 81 (Dec. 2017) 66–73, https://doi.org/10.1016/j.msec.2017.07.025.
[174] K.N. Bardakova, et al., 3D printing biodegradable scaffolds with chitosan materials for tissue engineering, IOP Conf. Ser. Mater. Sci. Eng. 347 (Apr. 2018), 012009, https://doi.org/10.1088/1757-899X/347/1/012009.
[175] D. Fan, U. Staufer, A. Accardo, Engineered 3D polymer and hydrogel microenvironments for cell culture applications, Bioengineering 6 (4) (Dec. 2019) 113, https://doi.org/10.3390/bioengineering6040113.
[176] M. Zanon, et al., Bioderived dyes-mediated vat photopolymerization 3D printing of chitosan hydrogels for tissue engineering, Addit. Manuf. 69 (May 2023), 103553, https://doi.org/10.1016/j.addma.2023.103553.
[177] S.A. Binti Mohd Isa, R. Mohamed, Physical and mechanical properties of chitosan and polyethylene blend for food packaging film, International Journal of Mechanical and Production Engineering (IJMPE)-IJMPE 3 (10) (Oct. 2015) 51–55.
[178] M.Z. Albanna, T.H. Bou-Akl, H.L. Walters, H.W.T. Matthew, Improving the mechanical properties of chitosan-based heart valve scaffolds using chitosan fibers, J. Mech. Behav. Biomed. Mater. 5 (1) (Jan. 2012) 171–180, https://doi.org/10.1016/j.jmbbm.2011.08.021.
[179] M.I. Wahba, Enhancement of the mechanical properties of chitosan, J. Biomater. Sci. Polym. Ed. 31 (3) (Feb. 2020) 350–375, https://doi.org/10.1080/09205063.2019.1692641.
[180] K. Agarwal, V. Srinivasan, V. Lather, D. Pandita, K.S. Vasanthan, Insights of 3D bioprinting and focusing the paradigm shift towards 4D printing for biomedical applications, J. Mater. Res. 38 (1) (Jan. 2023) 112–141, https://doi.org/10.1557/s43578-022-00524-2.
[181] R. Ajdary, et al., Direct ink writing of biocompatible nanocellulose and chitosan hydrogels for implant mesh matrices, ACS Polymers Au 2 (2) (Apr. 2022) 97–107, https://doi.org/10.1021/acspolymersau.1c00045.

[182] R.S. Baghel, C.R.K. Reddy, R.P. Singh, Seaweed-based cellulose: applications, and future perspectives, Carbohydr. Polym. 267 (Sep. 2021), 118241, https://doi.org/10.1016/j.carbpol.2021.118241.

[183] H. Gao, et al., Fabrication of cellulose nanofibers from waste brown algae and their potential application as milk thickeners, Food Hydrocolloids 79 (Jun. 2018) 473–481, https://doi.org/10.1016/j.foodhyd.2018.01.023.

[184] D. Trache, et al., Nanocellulose: from fundamentals to advanced applications, Front. Chem. 8 (May 2020), https://doi.org/10.3389/fchem.2020.00392.

[185] G. Chinga-Carrasco, Potential and limitations of nanocelluloses as components in biocomposite inks for three-dimensional bioprinting and for biomedical devices, Biomacromolecules 19 (3) (Mar. 2018) 701–711, https://doi.org/10.1021/acs.biomac.8b00053.

[186] M. Zaki, et al., Microbial treatment for nanocellulose extraction from marine algae and its applications as sustainable functional material, Bioresour Technol Rep 16 (Dec. 2021), 100811, https://doi.org/10.1016/j.biteb.2021.100811.

[187] I.L. Ross, S. Shah, B. Hankamer, N. Amiralian, Microalgal nanocellulose – opportunities for a circular bioeconomy, Trends Plant Sci. 26 (9) (Sep. 2021) 924–939, https://doi.org/10.1016/j.tplants.2021.05.004.

[188] R. Ajdary, et al., Acetylated nanocellulose for single-component bioinks and cell proliferation on 3D-printed scaffolds, Biomacromolecules 20 (7) (Jul. 2019) 2770–2778, https://doi.org/10.1021/acs.biomac.9b00527.

[189] R. Curvello, V.S. Raghuwanshi, G. Garnier, Engineering nanocellulose hydrogels for biomedical applications, Adv. Colloid Interface Sci. 267 (May 2019) 47–61, https://doi.org/10.1016/j.cis.2019.03.002.

[190] M. Saric-Coric, K.H. Khayat, A. Tagnit-Hamou, Performance characteristics of cement grouts made with various combinations of high-range water reducer and cellulose-based viscosity modifier, Cement Concr. Res. 33 (12) (Dec. 2003) 1999–2008, https://doi.org/10.1016/S0008-8846(03)00214-X.

[191] P.G. Gan, S.T. Sam, M.F. bin Abdullah, M.F. Omar, Thermal properties of nanocellulose-reinforced composites: a review, J. Appl. Polym. Sci. 137 (11) (Mar. 2020), 48544, https://doi.org/10.1002/app.48544.

[192] S. Das, B. Ghosh, K. Sarkar, Nanocellulose as sustainable biomaterials for drug delivery, Sensors International 3 (2022), 100135, https://doi.org/10.1016/j.sintl.2021.100135.

[193] J. Jiang, H. Oguzlu, F. Jiang, 3D printing of lightweight, super-strong yet flexible all-cellulose structure, Chem. Eng. J. 405 (Feb. 2021), 126668, https://doi.org/10.1016/j.cej.2020.126668.

[194] J. Leppiniemi, et al., 3D-Printable bioactivated nanocellulose–alginate hydrogels, ACS Appl. Mater. Interfaces 9 (26) (Jul. 2017) 21959–21970, https://doi.org/10.1021/acsami.7b02756.

[195] A. Gumrah Dumanli, Nanocellulose and its composites for biomedical applications, Curr. Med. Chem. 24 (5) (2017) [Online]. Available: https://www.ingentaconnect.com/content/ben/cmc/2017/00000024/00000005/art00008. (Accessed 21 November 2022).

[196] B. Thomas, et al., Nanocellulose, a versatile green platform: from biosources to materials and their applications, Chem. Rev. 118 (24) (Dec. 2018) 11575–11625, https://doi.org/10.1021/acs.chemrev.7b00627.

[197] A.S. Finny, O. Popoola, S. Andreescu, 3D-Printable nanocellulose-based functional materials: fundamentals and applications, Nanomaterials 11 (9) (Sep. 2021) 2358, https://doi.org/10.3390/nano11092358.

[198] T. Xu, et al., Advanced nanocellulose-based composites for flexible functional energy storage devices, Adv. Mater. 33 (48) (Dec. 2021), 2101368, https://doi.org/10.1002/adma.202101368.

[199] A. Mautner, Nanocellulose water treatment membranes and filters: a review, Polym. Int. 69 (9) (Sep. 2020) 741–751, https://doi.org/10.1002/pi.5993.

[200] F.A.G.S. Silva, F. Dourado, M. Gama, F. Poças, Nanocellulose bio-based composites for food packaging, Nanomaterials 10 (10) (Oct. 2020) 2041, https://doi.org/10.3390/nano10102041.

[201] C. Amara, A. el Mahdi, R. Medimagh, K. Khwaldia, Nanocellulose-based composites for packaging applications, Curr Opin Green Sustain Chem 31 (Oct. 2021), 100512, https://doi.org/10.1016/j.cogsc.2021.100512.

[202] Q. Wang, et al., Kinetic thermal behavior of nanocellulose filled polylactic acid filament for fused filament fabrication 3D printing, J. Appl. Polym. Sci. 137 (7) (Feb. 2020) 48374, https://doi.org/10.1002/app.48374.

[203] T. Ambone, A. Torris, K. Shanmuganathan, Enhancing the mechanical properties of <scp>3D</scp> printed polylactic acid using nanocellulose, Polym. Eng. Sci. 60 (8) (Aug. 2020) 1842–1855, https://doi.org/10.1002/pen.25421.

[204] L.A.E. Müller, T. Zimmermann, G. Nyström, I. Burgert, G. Siqueira, Mechanical properties tailoring of 3D printed photoresponsive nanocellulose composites, Adv. Funct. Mater. 30 (35) (Aug. 2020), 2002914, https://doi.org/10.1002/adfm.202002914.

[205] Y. Teramoto, Material development using the inherent features of nano-cellulose and nano-chitin: necessity of simple processes and cross-disciplinary collaboration, Adv. Powder Technol. 31 (2) (Feb. 2020) 528–532, https://doi.org/10.1016/j.apt.2019.11.009.

[206] X. Sun, P. Tyagi, S. Agate, M.G. McCord, L.A. Lucia, L. Pal, Highly tunable bioadhesion and optics of 3D printable PNIPAm/cellulose nanofibrils hydrogels, Carbohydr. Polym. 234 (Apr. 2020), 115898, https://doi.org/10.1016/j.carbpol.2020.115898.

[207] L.Y. Ee, S.F. Yau Li, Recent advances in 3D printing of nanocellulose: structure, preparation, and application prospects, Nanoscale Adv. 3 (5) (2021) 1167–1208, https://doi.org/10.1039/D0NA00408A.

[208] D. Cafiso, et al., 3D printing of fully cellulose-based hydrogels by digital light processing, Sustainable Materials and Technologies 32 (Jul. 2022), e00444, https://doi.org/10.1016/j.susmat.2022.e00444.

[209] G. Melilli, et al., DLP 3D printing meets lignocellulosic biopolymers: carboxymethyl cellulose inks for 3D biocompatible hydrogels, Polymers 12 (8) (Jul. 2020) 1655, https://doi.org/10.3390/polym12081655.

[210] Y. Deng, et al., Stimuli-Responsive nanocellulose Hydrogels: an overview, Eur. Polym. J. 180 (Nov. 2022), 111591, https://doi.org/10.1016/j.eurpolymj.2022.111591.

[211] A. Lode, et al., Green bioprinting: fabrication of photosynthetic algae-laden hydrogel scaffolds for biotechnological and medical applications, Eng. Life Sci. 15 (2) (Mar. 2015) 177–183, https://doi.org/10.1002/elsc.201400205.

[212] S. Landerneau, L. Lemarié, C. Marquette, E. Petiot, Green 3D bioprinting of plant cells: a new scope for 3D bioprinting, Bioprinting 27 (Aug. 2022), e00216, https://doi.org/10.1016/j.bprint.2022.e00216.

[213] A. Indurkar, A. Pandit, R. Jain, P. Dandekar, Plant-based biomaterials in tissue engineering, Bioprinting 21 (Mar. 2021), e00127, https://doi.org/10.1016/j.bprint.2020.e00127.

[214] N.F.Y. Tam, Y.-S. Wong, C.G. Simpson, Removal of copper by free and immobilized microalga, chlorella vulgaris, in: Wastewater Treatment with Algae, Springer Berlin Heidelberg, Berlin, Heidelberg, 1998, pp. 17–36, https://doi.org/10.1007/978-3-662-10863-5_2.

[215] L. Singh, A.R. Pavankumar, R. Lakshmanan, G.K. Rajarao, Effective removal of Cu2+ ions from aqueous medium using alginate as biosorbent, Ecol. Eng. 38 (1) (Jan. 2012) 119–124, https://doi.org/10.1016/j.ecoleng.2011.10.007.

[216] S.K. Papageorgiou, E.P. Kouvelos, F.K. Katsaros, Calcium alginate beads from Laminaria digitata for the removal of Cu+2 and Cd+2 from dilute aqueous metal solutions, Desalination 224 (1–3) (Apr. 2008) 293–306, https://doi.org/10.1016/j.desal.2007.06.011.

[217] K. Thakare, L. Jerpseth, Z. Pei, B. Tomlin, H. Qin, Three-dimensional printing of hydrogel filters containing algae cells for copper removal from contaminated water, J. Manuf. Sci. Eng. 143 (10) (Oct. 2021), https://doi.org/10.1115/1.4050761.

[218] S. Malik, et al., Robotic extrusion of algae-laden hydrogels for large-scale applications, Global Challenges 4 (1) (Jan. 2020), 1900064, https://doi.org/10.1002/gch2.201900064.

[219] L.M. Kalossaka, G. Sena, L.M.C. Barter, C. Myant, Review: 3D printing hydrogels for the fabrication of soilless cultivation substrates, Appl. Mater. Today 24 (Sep. 2021), 101088, https://doi.org/10.1016/j.apmt.2021.101088.

[220] S. Zhao, C. Guo, A. Kumarasena, F.G. Omenetto, D.L. Kaplan, 3D printing of functional microalgal silk structures for environmental applications, ACS Biomater. Sci. Eng. 5 (9) (Sep. 2019) 4808–4816, https://doi.org/10.1021/acsbiomaterials.9b00554.

[221] T.G. Johnston, et al., Cell-laden hydrogels for multikingdom 3D printing, Macromol. Biosci. 20 (8) (Aug. 2020), 2000121, https://doi.org/10.1002/mabi.202000121.

[222] K. Thakare, L. Jerpseth, H. Qin, Z. Pei, Bioprinting using algae: effects of extrusion pressure and needle diameter on cell quantity in printed samples, J. Manuf. Sci. Eng. 143 (1) (Jan. 2021), https://doi.org/10.1115/1.4048853.

[223] P. Heidarian, et al., Dynamic plant-derived polysaccharide-based hydrogels, Carbohydr. Polym. 231 (Mar. 2020), 115743, https://doi.org/10.1016/j.carbpol.2019.115743.

[224] A. Zolfagharian, M. Denk, M. Bodaghi, A.Z. Kouzani, A. Kaynak, Topology-Optimized 4D printing of a soft actuator, Acta Mech. Solida Sin. 33 (3) (Jun. 2020) 418–430, https://doi.org/10.1007/s10338-019-00137-z.

[225] A. Zolfagharian, A.Z. Kouzani, S.Y. Khoo, I. Gibson, A. Kaynak, 3D printed hydrogel soft actuators, in: 2016 IEEE Region 10 Conference (TENCON), IEEE, Nov, 2016, pp. 2272–2277, https://doi.org/10.1109/TENCON.2016.7848433.

[226] M. Champeau, D.A. Heinze, T.N. Viana, E.R. de Souza, A.C. Chinellato, S. Titotto, 4D printing of hydrogels: a review, Adv. Funct. Mater. 30 (31) (Aug. 2020), 1910606, https://doi.org/10.1002/adfm.201910606.

[227] A. Halperin, M. Kröger, F.M. Winnik, Poly(*N* -isopropylacrylamide) phase diagrams: fifty years of research, Angew. Chem. Int. Ed. 54 (51) (Dec. 2015) 15342–15367, https://doi.org/10.1002/anie.201506663.

[228] C. Wu, X. Wang, Globule-to-Coil transition of a single homopolymer chain in solution, Phys. Rev. Lett. 80 (18) (May 1998) 4092–4094, https://doi.org/10.1103/PhysRevLett.80.4092.

[229] S.E. Bakarich, R. Gorkin, M. in het Panhuis, G.M. Spinks, 4D printing with mechanically robust, thermally actuating hydrogels, Macromol. Rapid Commun. 36 (12) (Jun. 2015) 1211–1217, https://doi.org/10.1002/marc.201500079.

[230] J. Guo, R. Zhang, L. Zhang, X. Cao, 4D printing of robust hydrogels consisted of agarose nanofibers and polyacrylamide, ACS Macro Lett. 7 (4) (Apr. 2018) 442–446, https://doi.org/10.1021/acsmacrolett.7b00957.

[231] P. Sabourian, et al., Stimuli-responsive chitosan as an advantageous platform for efficient delivery of bioactive agents, J. Contr. Release 317 (Jan. 2020) 216–231, https://doi.org/10.1016/j.jconrel.2019.11.029.

[232] A.L. Daniel-da-Silva, L. Ferreira, A.M. Gil, T. Trindade, Synthesis and swelling behavior of temperature responsive κ-carrageenan nanogels, J. Colloid Interface Sci. 355 (2) (Mar. 2011) 512–517, https://doi.org/10.1016/j.jcis.2010.12.071.

[233] Y. Deng, et al., Stimuli-Responsive nanocellulose Hydrogels: an overview, Eur. Polym. J. 180 (Nov. 2022), 111591, https://doi.org/10.1016/j.eurpolymj.2022.111591.

[234] P. Ilgin, H. Ozay, O. Ozay, Synthesis and characterization of pH responsive alginate based-hydrogels as oral drug delivery carrier, J. Polym. Res. 27 (9) (Sep. 2020) 251, https://doi.org/10.1007/s10965-020-02231-0.

[235] D.S. Lima, et al., pH-responsive alginate-based hydrogels for protein delivery, J. Mol. Liq. 262 (Jul. 2018) 29–36, https://doi.org/10.1016/j.molliq.2018.04.002.

[236] A. Kirillova, R. Maxson, G. Stoychev, C.T. Gomillion, L. Ionov, 4D biofabrication using shape-morphing hydrogels, Adv. Mater. 29 (46) (Dec. 2017), 1703443, https://doi.org/10.1002/adma.201703443.
[237] R.v. Kulkarni, R. Boppana, G. Krishna Mohan, S. Mutalik, N.v. Kalyane, pH-responsive interpenetrating network hydrogel beads of poly(acrylamide)-g-carrageenan and sodium alginate for intestinal targeted drug delivery: synthesis, in vitro and in vivo evaluation, J. Colloid Interface Sci. 367 (1) (Feb. 2012) 509–517, https://doi.org/10.1016/j.jcis.2011.10.025.
[238] K. Lavanya, S.V. Chandran, K. Balagangadharan, N. Selvamurugan, Temperature- and pH-responsive chitosan-based injectable hydrogels for bone tissue engineering, Mater. Sci. Eng. C 111 (Jun. 2020), 110862, https://doi.org/10.1016/j.msec.2020.110862.
[239] Y. Hu, Y. Kim, I. Hong, M. Kim, S. Jung, Fabrication of flexible pH-responsive agarose/succinoglycan hydrogels for controlled drug release, Polymers 13 (13) (Jun. 2021) 2049, https://doi.org/10.3390/polym13132049.
[240] J. Lai, et al., 4D printing of highly printable and shape morphing hydrogels composed of alginate and methylcellulose, Mater. Des. 205 (Jul. 2021), 109699, https://doi.org/10.1016/j.matdes.2021.109699.
[241] Z.J. Wang, C.Y. Li, X.Y. Zhao, Z.L. Wu, Q. Zheng, Thermo- and photo-responsive composite hydrogels with programmed deformations, J. Mater. Chem. B 7 (10) (2019) 1674–1678, https://doi.org/10.1039/C8TB02896F.
[242] Q. Zhao, et al., Design and fabrication of nanofibrillated cellulose-containing bilayer hydrogel actuators with temperature and near infrared laser responses, J. Mater. Chem. B 6 (8) (2018) 1260–1271, https://doi.org/10.1039/C7TB02853A.
[243] A.C. Estrada, A.L. Daniel-da-Silva, T. Trindade, Photothermally enhanced drug release by κ-carrageenan hydrogels reinforced with multi-walled carbon nanotubes, RSC Adv. 3 (27) (2013) 10828, https://doi.org/10.1039/c3ra40662h.
[244] B.P. Nowak, B.J. Ravoo, Photoresponsive hybrid hydrogel with a dual network of agarose and a self-assembling peptide, Soft Matter 16 (31) (2020) 7299–7304, https://doi.org/10.1039/D0SM00835D.
[245] M. Hou, et al., Responsive agarose hydrogel incorporated with natural humic acid and MnO_2 nanoparticles for effective relief of tumor hypoxia and enhanced photo-induced tumor therapy, Biomater. Sci. 8 (1) (2020) 353–369, https://doi.org/10.1039/C9BM01472A.
[246] S. Yang, et al., Interfacial self-assembled behavior of pH/light-responsive host-guest alginate-based supra-amphiphiles for controlling emulsifying property, Carbohydr. Polym. 266 (Aug. 2021), 118121, https://doi.org/10.1016/j.carbpol.2021.118121.
[247] J. Lu, et al., CaCO3-assistant synthesis of pH/near-infrared light-responsive and injectable sodium alginate hydrogels for melanoma synergistic treatment, J. Colloid Interface Sci. (Nov. 2022), https://doi.org/10.1016/j.jcis.2022.11.137.
[248] D.S.B. Anugrah, K. Ramesh, M. Kim, K. Hyun, K.T. Lim, Near-infrared light-responsive alginate hydrogels based on diselenide-containing cross-linkage for on demand degradation and drug release, Carbohydr. Polym. 223 (Nov. 2019), 115070, https://doi.org/10.1016/j.carbpol.2019.115070.
[249] W. Sangwan, K. Petcharoen, N. Paradee, W. Lerdwijitjarud, A. Sirivat, Electrically responsive materials based on polycarbazole/sodium alginate hydrogel blend for soft and flexible actuator application, Carbohydr. Polym. 151 (Oct. 2016) 213–222, https://doi.org/10.1016/j.carbpol.2016.05.077.
[250] K. Rotjanasuworapong, N. Thummarungsan, W. Lerdwijitjarud, A. Sirivat, Facile formation of agarose hydrogel and electromechanical responses as electro-responsive hydrogel materials in actuator applications, Carbohydr. Polym. 247 (Nov. 2020), 116709, https://doi.org/10.1016/j.carbpol.2020.116709.
[251] N. Tanusorn, N. Thummarungsan, W. Sangwan, W. Lerdwijitjarud, A. Sirivat, Influence of carrageenan molecular structures on electromechanical behaviours of poly(3-hexylthiophene)/carrageenan conductive hydrogels, Int. J. Biol. Macromol. 118 (Oct. 2018) 2098–2107, https://doi.org/10.1016/j.ijbiomac.2018.07.066.
[252] J.M. McCracken, B.M. Rauzan, J.C.E. Kjellman, H. Su, S.A. Rogers, R.G. Nuzzo, Ionic hydrogels with biomimetic 4D-printed mechanical gradients: models for soft-bodied aquatic organisms, Adv. Funct. Mater. 29 (28) (Jul. 2019), 1806723, https://doi.org/10.1002/adfm.201806723.
[253] N. Zohreh, et al., Natural salep/PEGylated chitosan double layer toward a more sustainable pH-responsive magnetite nanocarrier for targeted delivery of DOX and hyperthermia application, ACS Appl. Nano Mater. 2 (2) (Feb. 2019) 853–866, https://doi.org/10.1021/acsanm.8b02076.
[254] V. Mironov, R.P. Visconti, V. Kasyanov, G. Forgacs, C.J. Drake, R.R. Markwald, Organ printing: tissue spheroids as building blocks, Biomaterials 30 (12) (Apr. 2009) 2164–2174, https://doi.org/10.1016/j.biomaterials.2008.12.084.
[255] B. Gao, Q. Yang, X. Zhao, G. Jin, Y. Ma, F. Xu, 4D bioprinting for biomedical applications, Trends Biotechnol. 34 (9) (Sep. 2016) 746–756, https://doi.org/10.1016/j.tibtech.2016.03.004.
[256] C. Norotte, F.S. Marga, L.E. Niklason, G. Forgacs, Scaffold-free vascular tissue engineering using bioprinting, Biomaterials 30 (30) (Oct. 2009) 5910–5917, https://doi.org/10.1016/j.biomaterials.2009.06.034.