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Seaweed-based polysaccharides – review of extraction, characterization, and bioplastic application

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Seaweed biomass is gaining industrial and economic momentum as a renewable feedstock for high-value products, including nutraceuticals, value-added chemicals and bioplastics. These organisms can be sustainably cultivated on an industrial scale, provide new opportunities for decreasing our dependency on fossil feedstocks, and potentially contribute to climate mitigation while reducing pressure on land resources. Seaweed generally possesses a high polysaccharide content, making it an alternative source to crop plants for bioplastic production. Polysaccharides like alginate, carrageenan, ulvan, fucoidan and laminarin are good candidates as bioplastic components due to their compatibility with various matrices and film-forming abilities. A wide range of applications are already demonstrated for these polysaccharides in biomedical areas, food packaging, functional foods, nutraceuticals and the pharmaceutical industry. Composites and blends of these polysaccharides with other polymers, additives, and fillers have been reported as a solution to improve the mechanical properties and, in some cases, to combine desired attributes strategically. This review examines seaweed-derived polysaccharides, their extraction and characterization techniques, application and performance as bioplastics, blends and composites, and material characteristics.

1. Introduction

Seaweeds are macroscopic marine algae. Seaweeds are broadly classified into red (Rhodophyta), brown (Phaeophyta), and green (Chlorophyta) algae.[1] The major macromolecular components of macroalgae/seaweed are polysaccharides, lipids, cellulose, proteins, minerals and polyphenols. The percentage of the components varies with the species. There have been extensive studies on the therapeutic properties of the seaweed-derived polysaccharides and many biomedical applications have been demonstrated.[2–6] Polysaccharides form a part of the structural component of the macroalgal cell wall and can be extracted using various techniques. The most critical polysaccharides derived from these seaweeds are alginate, carrageenan, ulvan, fucoidan and laminarin. Seaweed cultivation has gained interest as an industrial crop over the past decade.

Recently, there has been a growing emphasis on the circular bioeconomy, which centres around the sustainable enhancement and conversion of biomass within production chains. This involves turning agro-industrial wastes into high-value products and utilizing renewable resources to create products with significant added value. The exploration of versatile and eco-friendly photosynthetic organisms, such as algae, holds great promise in advancing the development of these closed-loop systems.[7]

Developing value-added products from seaweeds plays a crucial role in contributing to zero carbon emissions and UN sustainability goals. The extracted polysaccharides have functional groups like sulphate, carboxyl, and hydroxyl, which helps them bind with biological components. Many of these polysaccharides show good gelling behaviour, have excellent biocompatibility, and possess antimicrobial and hypoallergenic traits. The anionic polysaccharides are particularly interesting in wound dressing applications as they do not bind well with serum proteins and hence avoid forming aggregates.[3]

Plastic-based products have become inevitable in day-to-day life. Increasing plastic consumption leads to the bigger problem of white pollution from piling plastic debris, which is a grave environmental problem. Bioplastics made from bio-based renewable resources provide a more sustainable commercial plastic life cycle as part of a circular economy. Bioplastics derived from agro-polymers, such as starch and lignocellulosic waste, offer a renewable and cost-effective

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resource, forming odorless, colourless, and transparent biofilms. However, their limitations, including poor water and gas barrier properties, a low melting point, lower mechanical strength, and potential impacts on the human food chain, along with an extended production time, have spurred the search for alternative renewable sources.[8,9] Macroalgae (seaweeds) surpass the aforementioned sources due to their high biomass production, cost-effectiveness, non-competition for land and fertilizers, ease of cultivation in natural ocean environments, and year-round harvestability. Seaweeds find wide applications in food technology, biotechnology, microbiology, and medicine. Although these applications are beyond the scope of this review, readers can refer to other sources[10,11] for up-to-date information.

The use of seaweeds in the plastic industry is emerging as a potential renewable candidate, providing non-toxic, environmentally friendly, and cost-effective bioplastics with qualities comparable in terms of tensile strength and chemical resistance. These unique properties position seaweeds as a new and alternative source for bioplastics in today's world.[9] Beyond their biodegradability, seaweed-derived biofilms possess antimicrobial properties due to a variety of phenolic compounds. These biofilms are proposed for application in the food packaging industry to prolong the shelf life of products by inhibiting the growth of foodborne pathogens.

Investigating seaweed as a bioresource for plastics and materials alike is of great advantage for the following reasons: (i) replacing conventional plastics with biodegradable and compostable systems for short-lifespan applications reduces waste management stress; (ii) sustainably sourced biomaterials can replace non-replenishable fossil-based sourcing; (iii) seaweeds are known to be carbon sinks that help to reduce global warming; (iv) seaweed farming can bring additional income for marginal communities in coastal regions; (v) it provides an alternate source of biomass for making bioplastics and hence not competing with food sources like corn or potato; and (vi) the land, water and nutrient requirements for this cultivation are much less than for traditional methods.[1,12]

Polysaccharides present in seaweed can be in the form of stored mass, structural, or present as mucilage in intercellular locations.[1] The structural polysaccharides could be cellulose or hemicellulose found in the cell walls. Food storage in seaweeds is in the form of polysaccharides such as fucoidans, laminarin, and starch. The mucilage type are generally located between the plant cells. They are usually slimy in character with the function of storing water. Examples of these polysaccharides include xylan, porphyran, carrageenan, agar, fucans, and alginates. The capability of these polysaccharides to be used in the bio-plastics industry has been extensively demonstrated.[1] The different polysaccharides and the major molecules present in brown, green and red seaweed are provided in Table 1. Extracted polysaccharides generally have inferior mechanical and permeation characteristics compared with petroleum-based plastics.[3,4,6] This limitation is overcome by modification of the structure, blending with other polymers, and preparing composites with suitable fillers and additives.

The efficiency of any process is assessed using green metrics, which incorporated measurements of material efficiency, economic evaluation, total energy input, and land use. The environmental impact of chemical processes is commonly assessed using two widely accepted, straightforward metrics. The first is the *E* factor, which is the mass ratio of waste to the desired product. The second is the atom economy, also known as atom utilization, which is defined as the percentage ratio of the molecular weight of the desired product to the total molecular weights of all the substances produced.[13,14]

This review aims to collate the techniques used to extract and characterize high-value polysaccharides from macroalgae. A novel approach of this paper is that it covers the use of green solvents utilized for the extraction of seaweed polysaccharides. Another novelty is that the challenges faced by the bioplastics and the future perspective of these bioplastics have been illustrated in this paper. A wide range of applications of bioplastics obtained from a diverse variety of polysaccharides has been outlined. The techno-economic aspects and life cycle assessment of seaweed-based bioplastics have also been covered briefly in this review paper.

Table 1 Polysaccharides present in brown, green, and red seaweed

Seaweed	Polysaccharides	Major molecule
Brown	Laminaran	(1,3)-β-D-Glucose and (1,6)-β-D-glucose branch unit mannitol
	Fucoidan	β-(1,4)-D-Mannuronic acid and 3-D-xyosyl-L-fucose-4-sulfate (1,2)- α-L-Fucose-L-sulfate (1,4)-D-Galactose and L-fucosyl-3-sulfate branch units-D-xylose, D-galactose and D-mannose
	Alginate	β-(1,4)-D-Mannuronic acid and α-(1,4)-L-guluronic acid
Green	Ulvan	β-D-Glucuronosyl-(1,4)-α-L-rhamnose 3-sulfate
	Mannan	Mannose (C-2 epimer of glucose)
	Xylan	β(1,4)-D-Xylose
	Starch	α-D-Glucose 20% amylose, 80–90% amylopectin
Red	Carrageenans	α(1,3)-Galactose acid and β-(1,4,3,6)-anhydro-D-galactose
	Floridean starch	α-D-Glucose, amylopectin
	Xylan	β(1,4)-D-Xylose
	Agar	D-Galactose acid and (3,6)-anhydro-L-galactose
	Mannan	Mannose (C-2 epimer of glucose)

2. Extraction technologies of macroalgal polysaccharides

Macroalgal polysaccharides (MP) have attracted significant attention from the scientific community due to their unique properties such as biological activities, film-formation, high potential for functional food, and biotechnological and biomedical applications.[15] A general summary of processes to obtain high-purity MP from algal biomass is summarized in Fig. 1. The first step comprises the preparation of the macroalgal biomass, which includes washing to remove salt and impurities, drying or freeze-drying, and crushing to convert the biomass to a powder. The next step is pre-treatment to remove interfering compounds, such as pigments, lipids, and low molecular compounds.[16] In general, solvents or a combination of solvents with different polarities that do not affect MP's structural integrity are used for pre-treatment.[17] Lower-polarity solvents like chloroform are used to remove lipids; semi-polar solvents such as methanol, ethanol and acetone are used to remove pigments; whereas water is used to extract high-polarity molecules, such as minerals, monosaccharides and proteins.[16] Then, polysaccharides are extracted by using both conventional and advanced green techniques.

The amount, location and composition of MP are influenced by the raw materials and their harvesting conditions, including location, season and species. However, other factors, such as extraction methods and conditions, also need to be considered.[18]

2.1 Conventional techniques

Heat-assisted solvent extraction (HSE) and Soxhlet extraction are the most common conventional techniques used in laboratory research and industrial applications. Hot water is generally used as a solvent to extract polysaccharides from macroalgae.[19] Tiwari *et al.* used the HSE technique, which involves temperature and agitation to increase the solubility of the targeted compounds in the solvent.[20] According to Huang's group, the pre-treated sample was mixed with 95% ethanol (w/v = 1 : 10) to remove unwanted materials, then centrifuged and washed with water and kept in the water bath at 85 °C to extract the polysaccharides.[21] Other literature described the use of a mixture of solvents, such as methanol and dichloromethane (1 : 1, v/v), and hydrochloric solutions (PH: 1.5) for the extraction.[22,23] The extraction time varies from several hours to 48 h, while the temperature ranges from ambient temperature to ≥100 °C. In contrast, the Soxhlet extraction technique is categorized by a continuous flow over the biomass, which increases the amount of product compared with HSE.[20] In this technique, hot water is the most used solvent, similar to HSE. However, to precipitate the polysaccharides, calcium chloride can be used.[24] Due to the continuous flow of solvents, the extraction time is significantly reduced in Soxhlet extraction.

Besides HSE and Soxhlet extraction, alkali and acid extraction techniques have also been employed to extract MP. In alkali and acid extraction techniques, HCl and NaOH are generally used to isolate polysaccharides from the macroalgae. The H^+ and OH^- of the acid and base interfere with the hydrogen linkage of the polysaccharides, releasing polysaccharides into the solvent.[25,26] Zhao *et al.* reported alkali extraction, where the dried macroalgae were treated with 0.3 mol L^{-1} NaOH solution for 3 h at ambient temperature with the algae and a solvent ratio of 1 : 10 (w/v).[27] However, Chi *et al.* reported

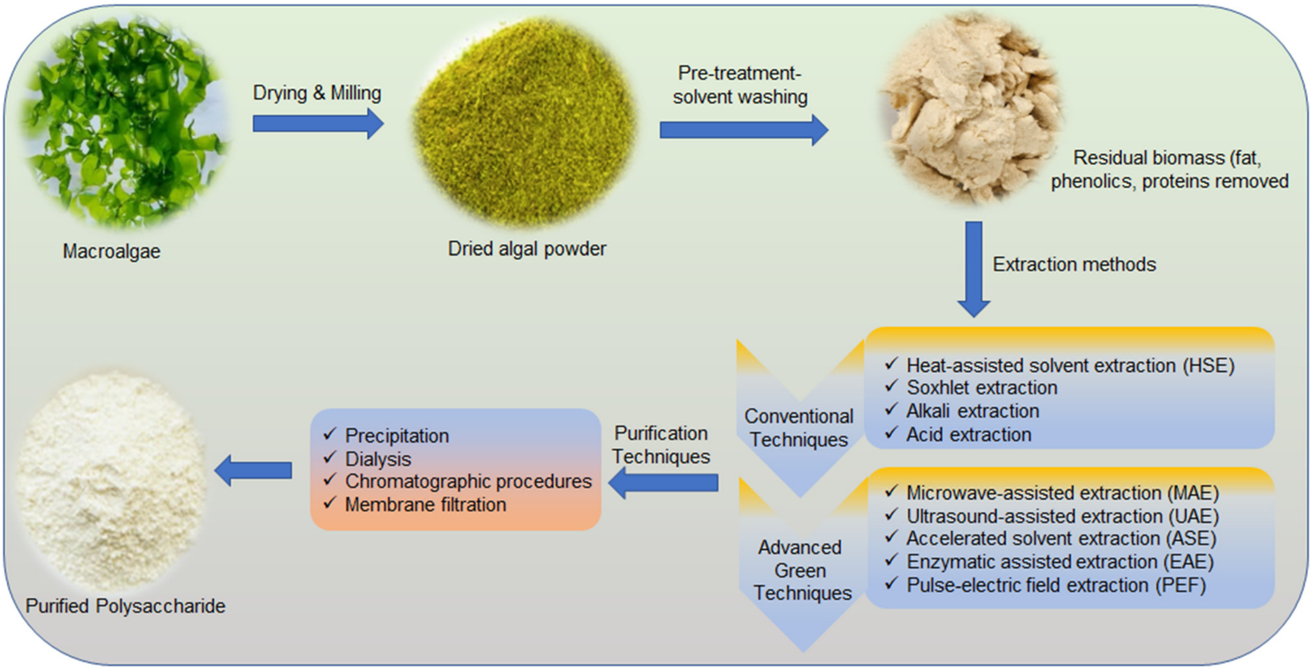


Fig. 1 Extraction of polysaccharides from seaweeds.

0.5 M NaOH with a ratio of 1 : 40 for 3 h at 60 °C.[28] The residue was filtered and neutralised with 0.1 M HCl. Many researchers employed acid extraction methods combining different times and temperatures to isolate polysaccharides. Liu *et al.* treated macroalgae using 0.1 N HCl in a 1 : 30 (w/v) algae:solvent ratio at room temperature for 4 h to extract the polysaccharide.[26] Chi *et al.* also isolated polysaccharides from macroalgae with 0.1 M HCl in the ratio of 1 : 20 (w/v) at 80 °C for 1 h. After filtration, the polysaccharide was treated with 6 N NaOH to neutralize the acid.[28] It was found that the alkali method is less effective and has a lower yield than the acid method.[28]

There are several disadvantages associated with the use of conventional techniques of extraction. A longer process time, large quantity of solvent consumption, and degradation of extracted compounds due to high-temperature operation are some of the few issues reported.

2.2 Advanced green techniques

Several advanced techniques have been employed to develop a more effective extraction process for MP. Microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), accelerated solvent extraction (ASE), enzymatic-assisted extraction (EAE) and pulse-electric field extraction (PEF) are some of the advanced green extraction techniques used as described below.

2.2.1 Microwave-assisted extraction (MAE). Microwave-assisted extraction is considered one of the most effective advanced techniques to extract bioactive compounds from various seaweeds. This technique employs microwaves to heat samples, which causes the evaporation of intracellular fluids, resulting in the breakdown of the cell walls and the liberation of intracellular compounds into the solvent.[29] MAE is an energy-assisted technique that requires less solvent and increases yield compared with conventional methods. The main disadvantage of this technique is that thermally sensitive compounds may degrade during the extraction process. Generally, water and acidic solutions (0.01 M HCl) are used for this type of extraction,[30,31] but other solvents such as deep eutectic solvent (choline chloride and 1,4-butanediol with a molar ratio of 1 : 5) have also been reported.[32] Carrageenan from *Solieria chordalis* (Rhodophyceae) has been successfully extracted by using MAE technique with a maximum yield of 29.3% at 90 °C for 10 minutes.[33] Yuan *et al.* reported polysaccharides from *Ulva prolifera* by MAE using HCl in 15 min. The highest yield of 36.4% was achieved with 0.01 M HCl at 120 °C.[34]

2.2.2 Ultrasound-assisted extraction (UAE). Ultrasound-assisted extraction is another innovative non-thermal technique, where ultrasound waves are applied above 20 kHz (range: 20 kHz to 100 kHz) in the solvent to create bubbles and zones, inducing low- and high-pressure zones. Due to the growth and collapse of these bubbles, sound waves are transformed into mechanical energy, which induces damage of the cell walls, reducing the particle size and increasing the mass transfer of the targeted compounds into the solvents.[35] An ultrasonic bath (frequency 40–50 kHz) or ultrasonic probe (20 kHz) can be used to perform UAE. The two methods differ in the way the ultrasound wave interacts with the samples.[36] Despite the energy input of this extraction method, it has many advantages, including low solvent consumption, time efficiency, the preservation of compounds from thermal degradation and feasibility to combine with other techniques (*e.g.* MAE).[37] Most employed solvents are water or acidic solutions; however, other solvents such as methanol have also been explored.[38–40] Youssouf *et al.*, using the ultrasound method, extracted carrageenans from *Kappaphycus alvarezii* and alginates from *Sargassum binderi.*[39] Kadam's group extracted laminarin from the brown seaweeds *Laminarina hyperborea* and *Ascophyllum nodosum* by using the UAE technique.[41]

2.2.3 Accelerated solvent extraction (ASE). Another promising green extraction technique is pressurized liquid extraction (PSE) or subcritical water extraction (SWE) for polar compounds. ASE is a solid–liquid extraction process based on the use of water as a solvent and performed at high pressures (5–15 MPa) and high temperatures (50–300 °C).[42] With high pressure and temperature assistance, the solvents are consistently below their boiling point to maintain a liquid state.[43] Compared with the traditional method, ASE has several advantages, including high efficiency, less solvent consumption, short times (5–10 min) and higher extraction yield.[44] According to the literature, water is the most used solvent in ASE for the extraction of MP; both alone or in combination with acids, alkali or ionic liquids in different concentrations have also been reported.[45] ASE was used to extract fucoidans from *Saccharina japonica* using different temperatures, pressures and solvents.[44] Gereniu *et al.* conducted a series of extractions of κ-carrageenan from *Kappaphycus alvarezii* using different conditions with different ionic liquids (ILs).[45] The main drawbacks of ASE are high temperature, which causes a degradation of compounds and unwanted side reactions; ASE also requires expensive equipment, and a large amount of energy also restricts industrial application.[46]

2.2.4 Enzymatic-assisted extraction (EAE). The principle of this green technique is using enzymes as a catalyst with high selectivity and specificity and the capability to break down the macroalgae's cell wall and liberate intracellular compounds in an aqueous solution.[47] Several factors, such as the ratio of enzymes to biomass, pH, temperature and solvent, should be optimized to increase the efficacy of extraction and yield.[48] Chi *et al.* reported an EAE method to extract polysaccharides from *Enteromorpha prolifera* using cellulase as an enzyme.[28] In another study, Michalak *et al.* extracted polysaccharides (yield: 36%) from the same species by EAE.[49] The optimum temperature, time and pH requirements of various enzymes have been summarized earlier.[50] This technique offers fast extraction, high selectivity, less energy consumption, and a green process. However, the higher cost of some enzymes restricts its industrial applications.[51]

2.2.5 Pulse-electric field extraction (PEF). In this method, biological samples are placed between two electrodes in a compartment and intense electric pulses (electric field: 10–50 kV

cm^{-1}) are applied to disrupt the linkage of the cell membranes and MP, which results in the subsequent release of intracellular compounds.[52] The main advantages of PFE are the higher yield, short extraction time, higher purity of product and low extraction temperature.[53] Although it is considered a green method, very few studies have used this technique to extract MP.[54]

After the initial extraction, the crude polysaccharide solution is treated with ethanol or calcium chloride at different temperatures and concentrations to precipitate the polysaccharides.[55,56] Then, the polysaccharides are purified using various techniques, including further precipitation, dialysis, chromatographic procedures and membrane filtration.[57,58]

3. Comparison of extraction techniques

Because of the variations in experimental conditions (different instrumental parameters, time, solvents) and the variety of targeted MP in the published literature (as summarized in Table 2), it is difficult to make a direct comparison among extraction techniques. Wang *et al.* employed MAE and UAE to extract fucoidan from *S. siliquosum* using water as a solvent. MAE showed an extraction yield of 6.94%, while UAE is less effective with a rate of 4.78%.[38] Yaich *et al.* utilized an acidic solution (pH 1.5–2) to extract ulvan from *U. lactuca* using EAE and conventional HAE. EAE achieved a significantly higher extraction yield of 17.15%, while the range of yield was between 3.04% and 13.04% in conventional HAE.[23] A recent study compared different techniques to recover fucoidan from *A. nodosum*. The conventional HAE showed a much higher extraction yield of 11.9%, while MAE, UAE and EAE showed 5.71, 4.56 and 3.89%, respectively.[31] Alboofetileh *et al.* employed water as a solvent to compare the recovery of fucoidans from *N. zanardinii* using HAE, ASE, MAE, UAE and EAE. Conventional HAE showed a yield of 5.2%, while ASE and MAE presented higher yields of 13.1 and 6.17%, respectively. Depending on the applied enzyme in EAE, the rate was between 5.58 to 4.36% and UAE was less effective, with a rate of 3.51%.[30]

Published reports have shown that advanced techniques are more effective, achieving higher yields than conventional extraction. However, the optimization of different operating parameters (time, temperature and solvent) and selection of extraction techniques are vital to achieve maximum output.

4. Green solvents for seaweed polysaccharide extraction

In the realm of seaweed biomass processing, conventional organic solvents pose challenges such as low extraction and processing efficiency, inadequate selectivity for target compounds, extended processing time, variable operational requisites, and substantial demands for both water and solvent volumes. Additionally, these solvents are volatile, toxic, and non-recyclable, raising environmental and health risks. Such concerns highlight sustainability, safety, and product integrity issues. In response, the surge in eco-friendly practices has spotlighted green solvents like ionic liquids (ILs) and deep eutectic solvents (DES), offering a fresh avenue for sustainable chemistry. These innovative solvents enhance efficiency, reduce resource usage, and align with environmentally conscious processes, heralding a transformative paradigm in seaweed biomass processing. Moreover, the physiochemical properties of both bio-solvents are highly tunable, which makes them "designer solvents" adaptable to a plethora of techniques and technologies.[68]

4.1 Ionic liquids

Ionic liquids (ILs) are composed of ions and exhibit a melting point lower than room temperature or even below the boiling point. These substances possess attributes like non-flammability, low vapor pressure, excellent thermal and electrochemical stability, along with features such as high conductivity, remarkable solute stabilization, and recyclability. Over time, numerous strategies have been investigated for the extraction of various biomolecules, including proteins, pigments, and phenolics from diverse seaweed sources using ILs.[69] However, the application of ILs for the extraction and purification of polysaccharides has seen limited exploration in a few select studies.

For the establishment of an eco-friendly polysaccharide industry derived from seaweed, meticulous operational control is essential. This entails minimizing chemical usage and optimizing chemical and solvent recycling during the polysaccharide isolation process, signifying a firm commitment to sustainable and responsible resource management. The idea of extracting seaweed polysaccharides using green solvents such as ILs was not considered until Prasad *et al.* (2009) showcased the capacity of 1-butyl-3-methylimidazolium chloride (BMIMCl) to create robust ion gels with diverse carrageenans and their cellulose composites. This pivotal demonstration foresaw the potential of ILs in extracting polysaccharides from seaweed sources; however their biocompatibility remained questionable. Hence, in many applications bio-based nontoxic ionic liquids (bio-ILs) are preferred considering their inherit properties of biodegradability, non-toxicity and biocompatibility.[70,71]

Trivedi and Kumar (2014) extracted agarose from *Gracilaria dura*, a red seaweed, by subjecting the biomass to 1-ethyl-3-methylimidazolium acetate treatment under microwave conditions followed by agarose precipitation in methanol. However, this process involved multiple processing and purification stages.[72] Subsequently, Sharma *et al.* (2015) introduced a more streamlined approach: a single-step selective precipitation of agarose using choline laurate-based bio-ILs (4.0% w/w). This method in an energy-efficient process directly extracted agarose from the hot seaweed extract of *G. dura*, yielding 14% w/w without purifying agar and freeze thawing. A

Table 2 Conventional and advanced green techniques for the extraction of macroalgal polysaccharides

Name of organisms and method	Pre-treatment	Extraction condition	Purification	Percentage of recovery	Ref.
Heat-assisted extraction (HAE)					
T. ornata	95% EtOH	H_2O, 95 °C, 3 h	EtOH pr.	TP	19
U. lactuca	—	H_2O-HCl (pH 1.5, 2), 80 and 90 °C, 1 h	EtOH pr.	Ulv. (3.04–13.06%)	23
N. zanardinii	85% EtOH, RT, overnight	H_2O, 65 °C, 3 h (×2)	$CaCl_2$ pr., EtOH pr.	Fuc. (5.2%)	30
A. nodosum	80% EtOH, RT, 20 h; 70 °C, 5 h	0.01 M HCl, 70 °C, 3 h	$CaCl_2$ pr., EtOH pr., filtration	Fuc. (11.9%)	31
A. nodosum, *L. hyperborea*	—	0.1 M HCl, 70 °C 150 min; H_2O, 70 °C 150 min	EtOH pr., dialysis	Lam. (4.3%; 4.6%)	55
G. persica, *E. intestinalis*	85% EtOH, RT, overnight	H_2O, 65 °C, 2 h	EtOH pr., filtration	TP	59
C. langsdorfii	96% EtOH, 40 °C, 24 h	0.1 M HCl, RT, 3 h	EtOH pr., dialysis, IEC	Alg. (13.3% d-DW); Lam. (0.4% d-DW); Fuc. (3.0–46.0% d-DW)	60
Soxhlet extraction					
F. evanescens, *F. serratus*, *D. foeniculaceus*, *S. latissimi*, *F. vesiculosus*, *L. digitata*	99% EtOH	2% $CaCl_2$, 85 °C, 2 h	EtOH pr., dialysis	Fuc. (10.9–31.7% DW)	24
H. cornea, *S. fluitans*, *R. pseudopalmata*, *S. filiformis*	AcO, MeOH	H_2O, 90 °C, 2 h	EtOH pr.	TP	61
T. ornata	—	Hot H_2O	—	TP (12%)	62
Microwave-assisted extraction (MAE)					
N. zanardinii	85% EtOH, RT, overnight	H_2O, 90 °C, 700 W, 20 min (×2)	$CaCl_2$ pr., EtOH pr.	Fuc. (6.17%)	30
A. nodosum	80% EtOH, RT, 20 h; 70 °C, 5 h	0.01 M HCl, 90 °C, 15 min	$CaCl_2$ pr., EtOH pr.	Fuc. (5.71%)	31
U. prolifera	—	0.01–0.1 M HCl, 90–120 °C, 500 W, 15 min	Neutralization with NaOH, EtOH pr.	TP	34
S. siliquosum	95% EtOH, 4 h	H_2O, 750 W, 10 min	Dialysis, EtOH pr., IEC	Fuc. (6.94%)	38
S. ceylonensis, *U. lactuca*, *D. antarctica*, *G. lemaneiformis*		H_2O, 70 °C, 500 W, 50 min	EtOH pr., IEC	TP (11.09; 13.32; 12.49; 14.21% DW)	63
Ultrasound-assisted extraction (UAE)					
N. zanardinii	85% EtOH, RT, overnight	H_2O, 55 °C, 20 kHz, 200 W (×2)	$CaCl_2$ pr., EtOH pr.	Fuc. (3.51%)	30
A. nodosum	80% EtOH, RT, 20 h//70 °C, 5 h	0.01M HCl, RT, 20 kHz; 35 min	$CaCl_2$ pr., EtOH pr.	Fuc. (4.56%)	31
S. siliquosum	95% EtOH, 4 h	H_2O, RT, 21–25 kHz, 950 W, 10 min	Dialysis, EtOH pr., IEC	Fuc. (4.78%)	38
K. alvarezii, *E. denticulatum*	80% EtOH, RT, overnight	H_2O, 90 °C, 25 kHz, 150 W, 15–30 min	Hot filtration	Carr. (50%; 55% DW)	39
A. nodosum, *L. hyperborea*	—	0.1 M HCl//H_2O, RT, 750 W, 15 min	EtOH pr.//dialysis (10 kDa)	Lam. (6.24%//5.97%)	55
U. intestinalis	80% EtOH, RT, overnight (×2)	H_2O, 66 °C, 53 kHz, 180 W, 40 min	EtOH pr.	Ulv. (8.30%)	64
Silvetia compressa	—	25% EtOH, 57.5 °C, 30 min	MeOH pr.	TP (25.13%)	65
Accelerated solvent extraction (ASE)					
N. zanardinii	85% EtOH, RT, overnight	H_2O, 150 °C, 10 min, ×2	$CaCl_2$ pr., EtOH pr.	Fuc. (13.1% DW)	30
K. alvarezii	—	H_2O, (60–180 °C), 50 bar, 5 min	2-Propanol pr.	k-Carr. (55–70%)	45
S. japonica	—	H_2O-DES (50–70%), 100–150 °C, 5–50 bar, 10–25 min	$CaCl_2$ pr., EtOH pr.	Alg. (5–27.2%) Fuc. (5–14.9%)	66
Enzyme-assisted extraction (EAE)					
U. lactuca	—	Protease, cellulase pH 7, 50 °C, 2 h	Dialysis, EtOH pr.	Ulv. (17.14%)	23
N. zanardinii	85% EtOH, RT, overnight	Alcalase, pH 8, 50 °C, 24 h, Flavourzyme, pH 7, 50 °C, 24 h	$CaCl_2$ pr., EtOH pr.	Fuc. (5.58%), (4.36%)	30
A. nodosum	80% EtOH, RT, 20 h; 70 °C, 5 h	Cellulase, pH 4.5, 50 °C, 24 h	$CaCl_2$ pr., EtOH pr.	Fuc. (3.89%)	31
C. fragile	—	Celluclast, pH 4.5, 50 °C, 24 h	EtOH pr.	TP (55.78%)	67

Abbreviations: TP: total polysaccharides; Ulv: ulvan; Fuc: fucoidan; Alg: alginate; Carr: carrageenan; Lam: laminarin; pr: precipitation; RT: room temperature; EtOH: ethanol; MeOH: methanol; AcO: Acetone; d-DW: defatted dry weight; DW: dry weight; DES: deep eutectic solvents; IEC: ion-exchange chromatography.

notable advantage of this method was the recycling and reuse of bio-ILs for successive rounds of agarose isolation, without compromising the yield or quality of the agarose.[73] In a similar strategy, Das *et al.* (2021) preferentially coagulated κ-carrageenan from the aqueous extract of *Kappaphycus alvarezii* by using the bio-ILs choline capriate and choline laurate.[74] In another work, coupling IL 1-butyl-3-methylimidazolium acetate (BMIMA) with subcritical water extraction (SWE) resulted in >78% yield of high purity κ-carrageenan from *K. alvarezii* when compared with conventional alkaline treatments (55.3%).[45]

A diverse array of ILs, spanning switchable, distillable, low-viscosity, and blended compositions, in addition to ILs enriched with oligo-ethylene glycol (EG) chains, have been explored comprehensively. These ILs have been rigorously evaluated for their effectiveness in hydrolysing and dissolving seaweed biomass, facilitating the extraction of carbohydrates and sugars from a variety of seaweed species across different genera.[75–78] These investigations involved subjecting seaweed biomass to direct treatment with ILs at elevated temperatures (90–160 °C) over extended operational periods (3–360 minutes). Notably, within the context of hydrolysis and dissolution employing ILs, a single study has successfully demonstrated a remarkable recovery of IL to 92% through precipitation.[75]

The application of ILs has further extended to the modification of silica particles for use in size exclusion chromatography, coupled with a refractive index detector. This innovative technique was employed to determine the presence of specific polysaccharides, including fucoidan, alginic acid, and laminarin, derived from *Undaria pinnatifida*.[79] In a more recent context, proteins and carbohydrates from *Ulva lactuca* were extracted under non-denaturing conditions using IL-ethyl methyl imidazolium dibutyl phosphate ([Emim][DBP]) by means of IL-assisted mechanical shear. This process was followed by two-phase partitioning or ultrafiltration, resulting in extraction yields of 80.4% for proteins and 30.7% for carbohydrates, with an impressive 85.7% recovery of the IL.[80]

4.2 Deep eutectic solvents

While ILs possess remarkable properties, their "green" credentials often come into question due to concerns over toxicity, poor biodegradability, biocompatibility, and sustainability. In 2003 Abbott and colleagues introduced a novel category of solvents termed deep eutectic solvents (DESs).[81] These solvents consist of hydrogen bond donors (HBDs) and acceptors (HBAs) which, when combined at precise ratios, yield a viscous liquid system at room temperature with a significantly lower melting point than that of each individual HBD and HBA species.[82] The formation of these eutectic systems is thought to be driven by hydrogen bonding interactions. Notably, certain researchers distinguish natural DESs (NADESs) from standard DESs when the constituent species are primary metabolites such as amino acids, organic acids, sugars, or choline derivatives.[83]

DESs are cousins of ILs, offering many shared benefits, including minimal vapor pressure, elevated boiling points, a broad electrochemical window, and the potential for efficient recycling. However, unlike traditional ILs, DESs do not solely consist of ionic species; rather, they can be derived from non-ionic components. Notably, DESs are often recognized for their cost-effectiveness and ease of preparation in contrast to ILs, as well as their marked biodegradability and low toxicity.[82] The synthesis of DESs relies on vacuum evaporation, freeze-drying, grinding and heating and stirring methods. Moreover, the manipulation of the ratio between the two components (HBD and HBA) enables the fine-tuning of thermodynamic attributes such as polarity and conductivity within the eutectic system. This distinctive ability renders DESs task-specific solvents, as highlighted by Yu *et al.* (2022).[84]

Type III DES comprising ChCl as an HBA is one of the simplest and highly biocompatible among the four DES categories,[85] most used in seaweed polysaccharide extraction studies. Das *et al.* (2016) explored diverse aqueous and non-aqueous ChC –urea/glycerol/ethylene glycol-based DESs for the extraction of κ-carrageenan. The highest yield of κ-carrageenan (60%) achieved using a 10% hydrated ChCl:glycerol DES surpassed the 36% yield obtained in conventional alkali methods. Nevertheless, it is worth noting that residual traces of the DES detected in the extracted carrageenan contributed to a slight softening of the resulting gels. Intriguingly, these gels exhibited greater viscoelastic properties, indicating potential advantages of this DES-based extraction approach.[74]

Researchers employed Box–Behnken response surface modelling to optimize alginate and fucoidan extraction from brown seaweeds using deep eutectic solvents (DESs) paired with subcritical water extraction (SWE) or microwave-assisted water extraction (MWE). Seven type III DESs, combined with SWE at 150 °C, 20 bar pressure, 70% water content, and a 1 : 36 S : L ratio, yielded high alginate (28% DW) and fucoidan (15% DW) from defatted *Saccharina japonica*.[86] Similarly, a DES (choline chloride : 1,4-butanediol; 1 : 5) with MWE at 168 °C and 32% water content produced potent fucoidan extracts from *Fucus vesiculosus*, exhibiting strong antioxidant and antiproliferative effects.[87] A DES consisting of choline chloride and 1.2-propanediol (1 : 2) with a 30% water content, a 1 : 30 S : L ratio, and ultrasonication (30 min, 40% amplitude) at 70 °C rapidly extracted polysaccharides with an 11% yield from *Sargassum horneri*.[88]

Deep eutectic solvents (DESs) offer a sustainable and cost-effective approach for creating functionalized graphene nano-polymeric sheets directly from seaweed through pyrolysis conditions.[89,90] Furthermore, DESs have gained attention for their utility in molecular imprinting (MIP) processes, enabling a selective recognition of seaweed polysaccharides and imprinting on specific sites with matching size, shape, and functional groups. Initially, Li and Row (2017) postulated the potential of hybrid magnetic imprinted polymers (HMIPs) modified by DESs, employing three templates for the swift purification of monosaccharides (fucose, galactose, and mannose) from seaweed.[91] Later, Li *et al.* (2019) prepared modified MIPs using DESs and ILs as packing materials for the solid-phase extraction (SPE) of fucoidan and laminarin. MIPs modified with DESs, specifically choline chloride and urea, exhibited outstanding extraction efficiencies for fucoidan (95.5%) and laminarin (87.6%) from marine kelp.[92] Similarly, Li *et al.* (2022) successfully synthesized MIPs based on 4-vinylbenzyltrimethylammonium chloride (VBTAC) and 4-vinylbenzoic acid (VBA) DESs as dual functional monomers, enabling the specific recognition and extraction of laminarin.[92]

These discoveries underscore the potential of DES-based extraction methods as eco-friendly and cost-efficient solvent alternatives within green chemistry. Nevertheless, our knowledge regarding their toxicological characteristics and biodegradability remains limited, especially concerning their impact on aquatic invertebrates.[93] Thus far, Type III DESs (used in a 1 : 2 molar ratio) have demonstrated biodegradability ranging from 75% to 91% within a four-week period.[94]

Recently, Sanches *et al.*, (2023) conducted an extensive ecotoxicological assessment of fifteen DESs, employing various marine and freshwater bioassays. Their findings indicated a general absence of toxicity in all the tested samples. However, it is essential to consider that natural ecosystems are complex, with both living (biotic) and non-living (abiotic) factors interacting. Chemical compounds like ionic liquids (ILs) and deep eutectic solvents (DESs) can exhibit synergistic effects. Therefore, continuous monitoring of their ecological impact remains crucial, especially given the rising predicted environmental concentrations (PECs) resulting from increased industrial use.[95]

5. Structural characterization methods

5.1 Structural characterization of algal polysaccharides

Structural characterization is performed after the extraction, purification, and isolation of algal polysaccharides from seaweeds. Structural characterization includes monomer composition analysis using chromatographic techniques, functional group identification by FTIR (Fourier transform infrared spectroscopy), and structure elucidation by NMR (nuclear magnetic resonance) spectroscopy. Yaich *et al.* reported that an extraction temperature below 160 °C caused moisture volatilization and resulted in yield loss during ulvan extraction from *Ulva lactuca.*[96] To analyse for the presence of sulphate content, a turbidimetric assay is performed. This colorimetric analysis combined with other spectroscopic methods (FTIR, Raman scattering, NMR) provides essential information on the structure of extracted algal polysaccharides.[97]

Another critical parameter for structural analysis is molecular weight determination. This analysis is done by size exclusion chromatography (SEC) equipped with a refractive index or UV-detector. SEC can measure the molecular weight of all algal polysaccharides-carrageenans, agar, ulvan, and alginate as well as particle size distribution.[98,99] For monomer composition analysis, several chromatographic techniques such as liquid chromatography (LC), high-performance liquid chromatography (HPLC), gas chromatography (GC) equipped with refractive index, and mass spectrometer detection are used.[100] GC is used to characterize volatile compounds (such as alditol) in polysaccharides, such as in ulvan.[63]

Complete structural analysis requires Fourier transform infrared spectroscopy (FTIR) coupled with nuclear magnetic resonance (NMR) spectroscopy. FTIR spectroscopy is performed within the 500–4000 cm^{-1} absorption band. Some characteristic bands for algal polysaccharides derived from seaweeds are 3200–3400 cm^{-1} representing O–H vibrations, 2927–2891 cm^{-1} corresponding to C–H stretching, 1638–1597 cm^{-1} representing C═O stretching, a 1247–1257 cm^{-1} absorption band suggesting S═O bond vibration and 1134–1150 cm^{-1} representing the stretching vibration of C–H bonds.[63] A characteristic band for agarose and carrageenan is found at 928–933 cm^{-1}, corresponding to 3,6-anhydro-galactose residues.[101] ^{1}H- and ^{13}C-NMR data provide information on the conformation of the individual components, molar ratios, and content of each component in the carrageenan mixture/blends.[177]

Sometimes it is challenging to analyse ^{1}H-NMR spectra due to extensive peaks overlapping, especially for heterogenous polysaccharides. On the other hand, ^{13}C-NMR spectra offer advantages because of the high quantum of information obtained. Anomeric carbons appear in the range of 90–110 ppm. Unlike ^{1}H-NMR spectrum, ^{13}C-NMR spectra show a wide range of displacement values and less overlapping of signals. The composition of the carrageenan blend can be determined quantitatively by the intensity of the anomeric carbon resonances of both monomeric units of carrageenan.[178] However, ^{13}C-NMR is a low-sensitivity technique. It requires a high-concentration sample (7–10%). For viscous polysaccharides like agar, and carrageenan, a ^{13}C experiment takes 12–18 h to achieve a rational signal-to-noise ratio.

Currently, some 2D NMR techniques, such as analysis of the seaweed polysaccharides' structural skeleton, heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC), are effective methods for investigating the structures of monomers and glycosidic linkage types.[102]

Analysis of the chain structure of polysaccharides includes periodate oxidation, enzymatic hydrolysis, and Smith degradation reactions. A modified methylation process, more straightforward than other reactions, is followed for monosaccharide linkage analysis.[103] The first step is the methylation of the polysaccharides; later, dialysis and freeze-drying are performed to recover the product. The next step is hydrolysis by TFA, followed by acetylation after reduction by borohydride to yield partially methylated monosaccharide derivatives (PMAA). Then the derivatives are analysed by GC-MS, and the composition and linkage pattern are analysed by comparing the spectral data with the Carbohydrate Research Centre Spectral Database-PMAA.[103,104,179] For example, the α, ι, and pyruvated carrageenan content and position of sulphate esters in the carrageenan from the red alga *Sarconema filiforme* were determined by linkage analysis by GC-MS.[105] Similarly, the nature of the glycosidic linkages and sulphate positions in the extracted sulphated polysaccharides from *Ulva pertusa* were elucidated by methylation analysis using GC-MS.[106]

5.2 Bioplastics from algal polysaccharides and structural characterization

Algal polysaccharides have been shown as a prospective renewable biomass source to produce bioplastic to combat the challenges posed by conventional plastic usage. Algae polysaccharides, such as carrageenan, ulvan, starch, and PHAs, have been extensively studied for bioplastic production. To achieve the best bioplastic quality, especially in the medical, food, and pharmaceutical industries, the structural features of the key ingredients, algal polysaccharides, must be customized. Standardizing the growth conditions of the algae, harvesting, environment-friendly extraction procedures, and a complete characterization including structural, physicochemical, thermal, and rheological properties characterization using cutting-edge technologies would be a promising strategy for achieving higher quality bioplastic production and hence reduce the pollution from petroleum-based plastics.

5.3 Characterization by molecular techniques and morphology analysis

5.3.1 FTIR (Fourier transform infrared) spectroscopy. FTIR provides information related to the chemical bonds in the composites and helps to understand bond changes after adding plasticizers at different concentrations. FTIR spectra reveal essential information on the intrinsic properties of polymer–plasticizer blends. Sudhakar *et al.* confirm the presence of 3,6-anhydro-galactose unit in the K-carrageenan polymer chains after PEG addition and heating by FTIR analysis.[107] According to the report of Moustafa *et al.*, interactions of the k-carrageenan and starch blend were confirmed by the shifting of the C–O stretching band and C–O–H group band from 1162 cm^{-1} to 1151 cm^{-1} (k-carrageenan : starch = 2 : 1).[108] This shifting explains that the –OH groups of starch interact with k-carrageenan ends and form hydrogen bridges. Davoodi *et al.* compared the FTIR spectra of *Ulva intestinalis* sulphated polysaccharide films after adding different plasticizers at different concentrations.[109] The spectra reveal essential information about the interactions between the polymer and plasticizers, *i.e.*, glycerol as a plasticizer increases the hydrophilicity of the biofilms more than PEG, which can be confirmed by comparing the absorbance of –OH functional groups from the FTIR spectra. Moreover, the absorbance of –OH functional groups increases with increasing concentration of the plasticizers, indicating an increasing number of –OH groups and increasing the water absorption capacity of the polymer blend.

In a study by Zhang *et al.*, a sodium alginate–pullulan composite was blended with capsaicin, and the FTIR spectroscopy results showed that the addition of capsaicin shifted the stretching vibration of the –OH groups from 3340 cm^{-1} to 3369 cm^{-1}, meaning that the hydrogen bonds in Na alginate + pullulan + capsaicin are weaker than the bonds present in the Na-alginate + pullulan composite.[110] Also, the asymmetric and symmetric stretching vibrations of COO^- remained the same in the Na-alginate + pullulan and Na-alginate + pullulan + capsaicin composites. Therefore, capsaicin dispersed in the actual composite (Na-alginate + pullulan) without any chemical interaction. Table 3 describes the band assignments of the algal-based polymers and their composites from several studies.

5.3.2 Scanning electron microscopy. Scanning electron microscopy (SEM) provided detailed information on the morphology of the composites formed by algal polysaccharides and plasticizers and structural information across a broad range of magnifications at higher resolution. In SEM, the interactions between the components in algal composites are observed to understand the properties. Abdillah *et al.* reported that in arrowroot starch–iota carrageenan blended edible films, increasing the iota-carrageenan concentration enhances the roughness and irregularity of the film's surface compared with the texture of the surface of the starch film itself.[111]

Investigation of the feasibility of nanoparticle addition into algal polysaccharides to improve bio-nanocomposite film properties can be performed by SEM. For example, the addition of ZnO/CuO in carrageenan-based nanocomposites caused small pits on the surface.[112] This may trap air into the surface and make it hydrophobic. On the other hand, the addition of SiO_2 nanoparticles in carrageenan-based biofilms made the surface smoother.[113] Therefore, the distribution of suspension of nanoparticles within the matrix, interactions between the added components (nanoparticles/plasticizers) with the algal-based polymers, and properties like hydrophilicity, transparency/opacity can be investigated by SEM.

5.4 Mechanical properties

Mechanical properties are one of the most important indicators of the core performance of algae-based bioplastics. Physical properties frequently measured are tensile strength, elongation at break and Young's modulus to assess the stress/compression applied on a thin film and study the deformation mechanism.

5.4.1 Tensile strength and elongation at break (%). Tensile strength (TS) is the highest tensile stress experienced by a sample during a tension test. Elongation at break (EAB%) indicates a film's extensibility and is determined at a point when the film is broken under stress. Tensile strength and elongation at break (%) are evaluated based on the ASTM D-882 standard and depend on the type and concentration of polymer and plasticizers.[183] For example, incorporating glycerol into ulvan-based biopolymers increased the TS and EAB compared with sorbitol. This can be explained as glycerol having a small molecular size, containing many hydroxyl groups, and being hydrophilic in nature, causing uniform penetration into the ulvan polymer matrix.[114] Similarly, blending carrageenan into starch bioplastic increased the tensile strength and elastic modulus. Increasing the concentration of carrageenan resulted in an increment in the mechanical strength of the starch bioplastic films. The low molecular weight and lower charge of

Table 3 FTIR band assignments of the algal-based polymers and their composites

Algal-based polymer	Blending material	Band characteristics of blends	Ref.
Carrageenan	PEG	• Galactose-4-sulfate (840–896 cm^{-1}) • 3,6-Anhydrogalactose unit (900–930 cm^{-1}) • OH stretching (3200–3600 cm^{-1}) • CH stretching (2800–2900 cm^{-1})	107
	Starch	• OH stretching (3100–3500 cm^{-1}) • Carbohydrate characteristic region (750–1300 cm^{-1}) • C–O stretching band after interaction of carrageenan and starch (1200–1300 cm^{-1}) • C–O–H stretching at (1151–1162 cm^{-1}) • Ester sulphate groups in carrageenan (1220 cm^{-1})	108
	Ca-alginate	• Sulphate stretch of S–O from carrageenan (1228 cm^{-1}) • Asymmetric and symmetric vibrations of COO^{-1} from Ca-alginate at 1416 cm^{-1} and 1595 cm^{-1}	131
	ι/κ/λ at different concentrations	• Stretching (3500–3000 cm^{-1}) • O═S═O asymmetric stretching at 1250–1290 cm^{-1} • S═O symmetric stretching at 1190 cm^{-1} • C–O–C asymmetric stretching 11 501–1160 cm^{-1} • C–O–C stretching in 3,6 anhydro-galactose unit 920–930 cm^{-1} • C–O–S stretching in (1–3) D-galactose at 854 cm^{-1}	132
Agar	Chitosan, glycerol	• OH stretching (3000–3500 cm^{-1}) • Alkane CH groups from agar and glycerol (2900^{-1}) • Amide-I and amide-II stretching functional groups from chitosan (1640 cm^{-1} and 1562 cm^{-1}) • Bending of aliphatic C–O (1370 cm^{-1}) • Bending of alkane C–C (1150 cm^{-1})	116
Agar	Starch, maltodextrin	• Free, inter-, intramolecular –OH groups at 3000–3700 cm^{-1} • C–H stretching regarding CH_2 deformation due to increased agar concentration at 2930 cm^{-1} • Coupling of C–O, C–C and O–H stretching vibration and C–O–C glycosidic linkage asymmetric vibration attributes at 1080 and 1150 cm^{-1}, respectively	133
Agar	Glycerol	• 3,6-Anhydro-galactose unit at 930 and 1070 cm^{-1} • C–H stretching at 2850–3000 cm^{-1} • OH stretching at 3200–3500 cm^{-1}	134
Ulvan	PEG, glycerol	• Presence of OH groups at 3265.1 cm^{-1} • C–H stretching vibration at 2933.53 cm^{-1} • Stretching of C═O and COO^{-} groups shows peaks at 1500–1700 cm^{-1}	109
Alginate	Gelatine, tea polyphenol	• Stretching vibration of N–H/O–H present in amide shows band at 3301.67 cm^{-1} • Band of C–H and -NH_2 stretching in amide at 2939.59 cm^{-1} • C═O stretching vibration in amide at 1641.68 cm^{-1} • Stretching vibration of C–N and bending vibration of N–H present in amide shown at 1547.66 cm^{-1}	135
Alginate	Essential oils	• Asymmetric stretching vibration of COO^{-} at 1600–1602 cm^{-1} • Deformation vibration of C–OH at 1403–1415 cm^{-1} • Stretching vibration of C–O present in uronic acid at 929 cm^{-1} • Presence of α-L-guluronic acid at 869 cm^{-1} • Presence of mannuronic acid residue at 815 cm^{-1}	122
Alginate	Carboxymethyl cellulose, glycerol, collagen powder	The following bands were common for the films having blended materials at different concentrations: • OH, stretching peak at 3295 cm^{-1} • Asymmetric and symmetric vibrations of COO^{-1} at 1619 and 1420 cm^{-1} • Presence of 3,6-glycosidic bridge at 1400 cm^{-1} • C-4 absorption peak at 1070 cm^{-1} and COC absorption peak at 900 cm^{-1} confirm the presence of galactose	136

the carrageenan enhance the solubility and effect a higher adsorption level into the starch polymer matrix.[115]

However, some studies reported increased concentrations of plasticizing agents to decrease TS and EAB. Fransiska *et al.* reported that the TS and EAB were reduced by 10% with the increasing concentration of chitosan in agar bioplastic.[116]

In alginate-based bioplastic, castor oil's incorporation initially increased the alginate's tensile strength due to the formation of hydrogen bonds and electrostatic attraction between the castor oil and alginate. However, further increasing the concentration (beyond 1%) decreased the TS value due to the ionic interaction of the castor oil with the Ca^{2+} ions present in the alginate and the formation of the crosslinked network.[117]

5.5 Physical properties

5.5.1 Bioplastic thickness. The bioplastic thickness is another significant parameter for calculating the mechanical and barrier properties. The thickness depends on several factors, such as the nature of the bioplastic and its composition.[118] Also, the biofilm's preparation process and drying conditions are key factors to be considered.[119] For example, the addition of 20% PEG in carrageenan bioplastics resulted in an increase in thickness by 13.1%.[120] However, the largest increase in thickness occurred with the addition of sorbitol and glycerol. Since glycerol has a higher water-absorbing capacity, it increased the thickness after adding it to carrageenan.[121] Galus *et al.* reported that increasing the concentration of pectin in Na-alginate biofilm increases the thickness due to the unique colloidal properties of pectin.[119]

5.5.2 Optical property. Colour is one of the most significant parameters of biofilms that needs to be monitored. Edible biofilms that are used in the food and packaging industries need to be colourless so that the exterior of the algal-polymeric films can achieve consumer acceptability.

Optical property is also a function of the property and concentration of algal polymers and blending agents. The colour of films is measured by a colorimeter using the parameters L^* (between black to white), a^* (between red to green), and b^* (between yellow to blue). L^* indicates brightness. According to Mahcene *et al.*, a biofilm made of Na-alginate blended with essential oils showed a higher value of L^* than only Na-alginate biofilm, meaning that the colour of the biofilm is transparent.[122] This report indicates that the homogenization and proper incorporation of blending materials into the polymer matrix affect the optical properties, which can be confirmed by SEM analysis.

5.5.3 Moisture content and solubility. The presence of moisture in bioplastics is determined by dehydration. This property is a function of the properties and concentration of the additives. Low molecular size compounds have more hydroxyl groups than compounds having a large molecular size and they easily form bonds with a greater number of water molecules in the polymer matrix. Therefore, increasing the concentration of low molecular size compounds in bioplastics increases the attraction between the bioplastics and water and the hydrophilicity.[109]

5.6 Barrier properties characterization

Barrier properties refer to the material's ability to resist the absorption of light, moisture, and oxygen. These properties come from the accumulation of the individual films used in the construction of the packaging. Barrier properties – water and oxygen permeability – are significant if the material's intended use is packaging.

5.6.1 Water vapour permeability. Water vapor permeability solely depends on the additives' types and concentrations; according to Henry's and Fick's laws, it is a function of both diffusion rate and solubility. For example, with increasing concentrations of plasticizers, PEG and glycerol in ulvan, the water vapor permeability of the biofilm increased,[109] which can be explained by the hydrophilic nature of the biofilm.[123] Moreover, water vapor permeability also depends on the properties of the plasticizers. Since glycerol has a higher solubility than PEG, the water vapor permeability of glycerol-blended ulvan biofilms is higher than that of PEG blended biofilms.[124] Alginate is highly hydrophilic and has low water vapour properties.[125] Micro- and nano-cellulose fibres have lower permeability. Therefore, adding them into alginate films decreases the route for water vapor to pass through the films and water vapour permeability is reduced.[126,127] Ionic cross-linking also improves the water vapor permeability of the algal-based biofilms.[127]

5.6.2 Oxygen permeability. The physical and mechanical properties of the biofilms can be affected by the permeability to ambient gases. Oxygen permeability (OP) depends on the concentration of the plasticizing agents and the thickness of the films. In ulvan/glycerol blend film, greater OP was observed for the 50% glycerol blend than the 30% blend.[109] Increasing the concentration of plasticizers decreases the bioplastics' resistance to the transfer of oxygen as the mobility of the polymer increases. Hydrophilic biopolymers (polysaccharide-based biopolymers) are suitable barriers for oxygen transportation.[128] Table 4 summarises the physical and barrier property characteristics of bioplastic films derived from algal polysaccharides.

5.7 Thermal properties

5.7.1 Thermal gravimetric analysis and differential scanning calorimetry. Thermal property analysis, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are commonly used to provide information on the thermal stability of the prototypes with thermal degradation.

Table 4 Physical and barrier properties of bioplastic films derived from seaweed polysaccharides

Bioplastic film samples	Water solubility (%)	Oxygen permeability ($\times10^{-4}$ cm^3 mm m^{-2} d^{-1} kPa^{-1})	Water vapour permeability ($\times10^{-10}$ g H_2O per m s per Pa)	Light transmission, T600, %	Opacity (UA per mm)	Ref.
Semirefined K-carrageenan (SRC)	42.8	1.82	3.26	—	4.82	137
SRC with 20% glycerol	44.4	1.84	3.30	—	4.47	137
SRC with 20% sorbitol	42.6	0.89	3.26	—	3.83	137
Alginate with chitosan	89.53	5.53	6.1	21.45	6.28	138
Alginate with chitosan and fucoidan	76.15	8.56	9.22	12.05	6.44	138
Alginate with chitosan fucoidan and calcium ions[138]	68.65	8.18	8.92	12.50	6.65	138
Ulvan with 1% glycerol	97.36	—	2.41	7.05	0.12	114
Ulvan with 1% sorbitol	76.81	—	1.54	6.14	0.13	114

Aziz *et al.* analysed the thermogravimetric curves and reported that the thermal stability was enhanced after the addition of castor oil into calcium alginate films.[117] Mahcene *et al.* and Boonruang *et al.* measured and compared the degree of crystallization and crystalline temperatures (Tc) of Na-alginate systems with several types of essential oil as additives using DSC thermograms.[122,129] DSC curves were shown to help in interpreting the intermolecular interaction within ulvan and PVA blends.[130]

6. Alginate-based bioplastics

Alginate, being the most abundant marine polysaccharide, with its characteristic gelling properties is evidenced to be a likely ingredient for synthetically modified biomaterials. A combination of alginate with other natural and synthetic polymers can be looked upon to alter the structure and properties of the resulting alginate-based bioplastic. Zia *et al.* have elaborated the use of polysaccharides in numerous applications due to their unique characteristics, such as biodegradability, structural diversity, biocompatibility, non-toxicity, abundance, and specific bioactive properties. Polyurethanes/alginate hydrogels, elastomers, and nanocomposites systems showing uniqueness in their properties are proving alginates to be effective polymers worthy of further research and development.[139]

Sodium alginate is one such edible polysaccharide that could form films with the following properties: flexibility, gloss, water solubility, microbial resistance, low permeability to oxygen and vapours, and tasteless or odourless. Sodium alginate is an effective alternative for packaging in the food industry and also finds usage in medicine and pharmaceutics. Increased usage of plastics is causing an environmental problem in the form of waste disposal behaviour. Laboratory research has confirmed that one solution to this is using edible bio-based polymer packaging materials.[140] Gheorghita *et al.* (2019) have recommended that further research can be carried out in food packaging films or foils to improvise certain features, such as maintaining or increasing the shelf life of the packed food products.[140]

Alginate is a phycocolloid extracted from brown algae. It consists of two 1,4-linked uronic acids: α-L-guluronic acid and β-D-mannuronic acid. The water-insoluble property is one of the important characteristics of alginates, which occurs through the formation of water-insoluble gels in the presence of cations such as calcium ions (Ca^{2+}). This is attributed to the strong crosslinking interaction between the C=O groups of guluronic acid with Ca^{2+}.[141] Jost and Reinelt have discussed about the crosslinking of alginates done in two ways: by diffusion and by internal setting. In the diffusion method, the cast alginate films are immersed in a solution of polyvalent ions. The polyvalent ions diffuse into the alginate matrix and initiate crosslinking. In the internal method, the polyvalent ions are combined in the alginate matrix formulation in an inactive form. The crosslinking is then initiated by a release mechanism brought about by a pH shift before casting the films.[142]

6.1 Plasticization

Plasticization is defined as the softening and thereby improvement of the flexibility of a polymer by the addition of a plasticizer. Alginate films have great potential for food packaging use but exhibit highly moisture-sensitive, absorbing characteristics. Alginate is commonly extracted from species of brown algae; however, Lim *et al.* conducted a study on the extraction of alginate from *Sargassum siliquosum* J. Agardh. Extraction processes with and without formaldehyde pre-treatment were carried out. The casting of the polymer solution was done to produce the cast film. The films cast were subjected to calcium chloride immersion for 1 minute. The extraction yield was higher in the case of formaldehyde pre-treatment (33.75 ± 1.21%) than without formaldehyde pre-treatment (26.91 ± 1.59%). A statistical model was developed to determine the bioplastic film composition as 2 g of extracted alginate, 15% sorbitol, followed by 75% calcium chloride immersion treatment. This model predicted the optimised properties of the bioplastic film as: 33.9 MPa tensile strength, 3.58% elongation at break, 2.63×10^{-10} g Pa^{-1} s^{-1} m^{-1} water vapour permeability, and 33.73% water solubility.[141]

Plasticizers such as diethyl phthalate, triacetin, tributyl citrate, or triethyl citrate can reduce the alginate matrix's water permeability and susceptibility to moisture in environmental applications. Thin films plasticized with glycerol were compared with films plasticized with tributyl citrate (TC). Also, thin films plasticized with varying proportions of glycerol and tributyl citrate were studied.[143] When Paixão *et al.* performed the moisture absorption tests, the films plasticized with pure TC were found to be less water soluble and performed well in the protection against dissolution. In contrast, the films plasticized with glycerol exhibited a high degree of dissolution. The tensile strength of the films with pure glycerol and pure TC were 103.1 ± 19.3 MPa and 146.8 ± 20.0 MPa, respectively. This increase in tensile strength could result from a greater interaction between the chains in the form of secondary bonds. The tensile strength, however, decreased as the glycerol proportion increased. The elongation at break for the films plasticized with pure TC and pure glycerol was 3.3 ± 1.6% and 6.05 ± 2.4%, respectively.[143]

Crosslinking alginate can be done by two methods: internal method and diffusion. Jost and Reinelt chose the internal method of crosslinking alginate for the preparation of alginate films with the help of crosslinking agents: $CaCl_2$ + Na_2-ethylene diamine tetra-acetic acid (EDTA) complex, calcium hydrogen phosphate ($CaHPO_4$) and calcium carbonate ($CaCO_3$) being used in the formulation of alginate solution. Glucono δ-lactone (GDL) was used to lower the system's pH and thereby initiate a controlled release of Ca^{2+}.[142]

The process of film formation is found to influence the film performance due to the relaxation of the polymeric chains during the process. Yeom and Lee developed membranes of sodium alginate crosslinked with glutaraldehyde (GA) using the solution method, in which acetone (non-solvent of sodium alginate) is used. It is found that with a GA content above 5 vol%, stable membranes are obtained by this method. Crosslinking helps reduce both the solubility in water and the stability of the membrane toward water. The crosslinked membrane is validated for excellent performance during the pervaporation separation of ethanol–water mixtures containing 70–90 wt% ethanol content at temperatures between 40 to 80 °C.[144]

6.2 Composites of alginate

Alginate films when incorporated with certain materials, that is, either polymers or non-polymers, can exhibit enhanced properties. This enhancement in properties arises due to the formation of chemical and physical bonds between the different constituents in the composite. Hu *et al.* incorporated silver nanoparticles into alginate/polycaprolactone composite fibres which have been shown to have applications in wound dressings. Silver nanoparticles inhibited the growth of microorganisms, including Gram-positive and Gram-negative bacteria. Calcium chloride is also used to incorporate crosslinking in the composite fibres; in addition, calcium ions when released into the wound help to accelerate coagulation. Wound healing studies confirmed that composite fibres accelerate wound closure and assist in the formation of collagen.[145]

Extensive research is attempted on polyurethanes to make them a green and sustainable material. Polyurethanes are conventionally produced by polymerizing polyols with poly-isocyanates under controlled reaction conditions. Polyols provide heat resistance, spatial stability, and physical cross-linking properties, while poly-isocyanates provide elasticity in polyurethane chains. Fossil derivatives are mainly used as polyurethane raw materials.[146] To replace the fossil-based derivatives, renewable resources such as natural oils and cellulose are being looked upon as a substitute to obtain bio-based polyurethanes. Almost all vegetable oils, except castor oil, must be chemically modified to introduce hydroxyl groups that need to be present in polyols to synthesize polyurethanes. Additives such as graphene oxide are incorporated to introduce secondary polymer chains in the polyurethane matrix, thus improving the properties of the resulting polymer composite. When added to bio-based polyurethane dispersions, castor oil incorporates the waterborne property of the prepared polyurethane-based films. 2,2-Dimethylolbutanoic acid is used as a chain extender. The prepared composite films from polyurethane and sodium alginate showed an increase in tensile strength and storage moduli with increased sodium alginate content, whereas a decrease in elongation at break occurred with increased sodium alginate content. Wang *et al.* attributed the property enhancements to the increased crosslinking and the development of interpenetrating networks with sodium alginate molecules.[146]

The properties of fibre-reinforced composites can be improved by subjecting the fibres to surface treatment. Khan *et al.* subjected calcium alginate fibres to silane treatment by exposure to vinyl triethoxy silane. Reductions in the fibers' hydrophilic nature and improvements in the mechanical and interfacial properties of the fibre-reinforced composites are achieved by silane treatment of the fibres. These silane-treated and untreated calcium alginate fibres are reinforced in a polypropylene (PP) matrix by compression moulding. The mechanical properties of the silane-treated fibre-reinforced composites are improved relative to the untreated fibre-reinforced composites. Degradation tests of the composites in soil confirmed that the silane-treated fibre-reinforced composites retained 84% of their original strength. The interfacial shear strength of the silane-treated fibre-reinforced composites is twice that of the untreated fibre-reinforced composites, confirming enhanced compatibility between the silane-treated calcium alginate fibre and the PP matrix.[147]

When a polymer matrix is reinforced with fibres, the mechanical properties of the resulting composite are found to be enhanced. The strong hydrophilic nature of calcium alginate fibres can be overcome by reinforcing them in a polypropylene matrix, thereby developing calcium alginate fibre-reinforced polypropylene composites. Khan *et al.* reported that the mechanical properties of the composites possess greater improvement than the matrix polypropylene. From the degradation tests, it is found that the composites lose 25% of their mechanical properties, thus confirming their biodegradability.[148]

The flame-retardancy characteristic of alginate is explored and studied. When coated on polyester fabric, a flame-retardant system consisting of phosphorus, nitrogen, silicon, and calcium alginate exhibits flame retardancy and anti-dripping properties. The coated fabric surface produced a thick intumescent char layer upon burning. Wang *et al.* found that the flame-retardant system displayed a good smoke suppression efficacy, which is also confirmed by thermogravimetric analysis and cone calorimetry testing. The limiting oxygen index value improved from 19.2 ± 0.2% to 32.5 ± 0.3% during the combustion of the coated polyester fabric.[149]

A polymer matrix composite incorporated with naturally sourced flame retardant materials is tested for its flame retardancy performance. Pallmann *et al.* developed an intumescent flame retardant (IFR) material from polypropylene by integrating it with naturally sourced flame retardants such as phosphorylated sodium alginate, dipentaerythritol, and ammonium polyphosphate. These flame retardants are incorporated into polypropylene by the method of melt blending. The mechanisms of the gas phase and condensed phase synergistic flame-retardant ability during combustion and degradation of the flame-retardant polypropylene make this system an effective IFR. This IFR system improves thermal stability by significantly slowing thermal degradation. This IFR system will find application in the automotive industry and the structure of electronic devices.[150]

Biocompatible scaffolds were designed using alginate and synthetic polymers, developed through 3D printing and tested for their biocompatibility. Kim *et al.* developed PCL/alginate fibrous scaffolds through a combination of electrospinning and rapid prototyping method developments. The improved hydrophilic and water absorption properties were attributed to the alginate fibres, while the enhanced mechanical properties in the developed scaffolds were attributed to the polycaprolactone. Even a small alginate content (5%) contributed to the outstanding performance of these scaffolds in terms of cell viability and proliferation. It has been found that the developed PCL/alginate fibrous composite scaffold could be appropriate for the rejuvenation of various hard tissues.[151]

The antimicrobial property was incorporated to polymer fabrics by the addition of alginate or other materials, and the mechanism/performance of antimicrobial property was explored. Marković *et al.* prepared polypropylene fabrics to be antimicrobial by incorporating alginate biopolymer and nanoparticles of copper oxides. Alginate is bound to the surface of polypropylene fabric by corona discharge, after which the carboxyl groups of alginates are used to bind with Cu^{2+} ions by immersing in copper(II) sulphate solution. The developed composite fabric developed outstanding antimicrobial resistance to Gram-negative bacteria *E. coli*, Gram-positive bacteria *S. aureus* and yeast *C. albicans*. The composite fabric also proved not to be cytotoxic to human keratinocyte cells.[152]

The change in morphology of the composite fibre is found to be dependent on the composition of alginate in the spinning solution. Lee and Lyoo prepared an organic–metallic nanocomposite consisting of PVA, SA and silver nanoparticles by directly mixing and electrospinning the nanocomposite into fibres. When PVA with the degree of polymerization of 1700 is kept fixed, and by increasing the content of SA in a spinning solution, it is found that the obtained morphology transformed from fine uniform fibre to beaded fibre. It was shown that the intermolecular interaction by the hydrogen bonding of PVA with SA increased the spinnability, forming a uniform and continuous nanocomposite fibre. Micrographs confirmed the presence of silver nanoparticles in spherical form with a diameter ∼50 ± 20 nm and were present with uniform dispersion in the PVA/SA matrix.[153]

6.3 Blends of alginate

Blends of alginate are obtained by physically mixing two or more different polymers together; they may be miscible or immiscible with each other. No chemical bonds are formed between the individual constituents of the blend.

The wound healing property of alginate is explored by blending it with gelatin. Alginate fibres, when used in wound dressings, exhibit two properties: an *in situ* moist healing environment and the consequent high absorbency of the wound dressings. Gelatin can also be blended with alginate to make the wound dressing economical. Fan *et al.* prepared gelatin blend fibres in combination with alginate and tested for their performance compared with pure alginate fibres. The blended fibres were named following their gelatin content of 10, 30, 50 and 70 wt% as AG10, AG30, AG50 and AG70, respectively. Pure alginate fibres and gelatin fibres were named AL and G, respectively. The crystallinity of the blended fibres was in the order of G > AG70 > AG50 > AG30 > AG10 > AL, implying that the crystallinity decreased with an increase in alginate content in the blend fibres. This also signifies good miscibility between alginate and gelatin. The thermal stability was also of the order G > AG70 > AG50 > AG30 > AG10 > AL, suggesting that the intermolecular interaction improved the thermal stability of the blended fibres. When the blend's gelatin content is 30 wt%, the blended fibre exhibited a dry tensile strength of 12.31 cN/tex and an elongation of 21.3%. The water retention property increased as the amount of gelatin was increased in the alginate/gelatin blended fibre. This increase in water retention property is due to gelatin's hydrophilic nature compared with calcium alginate.[154]

Alginate nanofibres are found to be spinnable by blending with selective polymer materials. Safi *et al.* demonstrated the spinnability of sodium alginate, sodium alginate/polyvinyl alcohol, and sodium alginate/polyethylene oxide. Sodium alginate is easily soluble in water, so its aqueous solution is not spinnable into ultrafine nanofibers. To make the sodium alginate electro-spinnable, polymer additives like polyvinyl alcohol (PVA) and polyethylene oxide (PEO) solutions are mixed with sodium alginate aqueous solution. SEM analysis showed the electro-spun nanofibers of a sodium alginate/PVA system of volume ratio 70 : 30 and a sodium alginate/PEO system of volume ratio 50 : 50 having diameters of 118.3 nm and 99.1 nm, respectively. The rheological studies confirm the dependence of spinnability and fibre morphology on solution viscosity or the sodium alginate to polymer additive blend ratio. Hydrogen bond interactions between the hydroxyl groups of PVA (or ether oxygen of PEO) and the hydroxyl groups of sodium alginate were confirmed from the FTIR analysis.[155]

Films of alginate which are water insoluble in nature are designed and investigated for their performance in food packaging. Gohil investigated the nature of films made of pectin and sodium alginate blends for their water vapor permeation rate and mechanical properties. A water insolubility property is incorporated into films by subjecting the cast films to $CaCl_2$ treatment, by which physical crosslinking between the molecules of both polymers occurs. Comparing the change in mechanical properties in cast films before and after $CaCl_2$ treatment, it is found that the molecular mobility reduced and the molecular network structure changed, causing a drastic change. It is also observed that an increase in pectin content in the blends showed a rise in film flexibility. Attempts were made to improve water barrier properties by coating a thin layer of an edible beeswax-based formulation. Such bilayer films exhibited a better water vapor permeation rate than non-edible Cellophane films.[156]

A blend membrane used for the selective separation of solution mixtures is designed and tested. Yeom and Lee developed a blend membrane based on sodium alginate (SA), a rigid polymer, and polyvinyl alcohol (PVA), a flexible polymer, for the pervaporation separation of ethanol–water mixtures. During pervaporation, the flexible PVA component helps maintain the consistency of membrane performance, while the rigid SA component exhibited an increased separation factor by the relaxation of polymeric chains.[157]

Numerous patents on alginate blends have been reported especially in the fields of wound healing, drug encapsulation, extrusion and 3D printing. A polymer blend consisting of a combination of lichenan, alginate and solvents of polymers has been developed for the cosmetics, food packaging, or wound dressings in the patent WO 2006/125857 A1.[158] A chitosan–alginate scaffold system has been designed and fabricated for use in anticancer therapeutic drug development in the patent US 9,157,908 B2.[159] A biocompatible polymer blend consisting of alginate had been developed for use as wound dressings and drug encapsulation; the manufacturing methods of such polymers in order to control the mechanical properties have also been disclosed in the patent US 2010/0254900 A1.[160] A highly flowable biodegradable polymer combination has been formulated that can be processed by extrusion and injection moulding and has been designed in the patent 5,523,293.[161] An alginate-based material had been dispensed into a three-dimensional object by layer manufacturing in the patent US 2005/0087902 A1.[162]

Flame-retardant alginate blend fibres are developed for their use as filling materials in toys. Commonly used filling materials are polyester fibres, yet they show melt-dripping and flammable characteristics. To produce flame-retardant fibres, Li *et al.* combined flame-retardant alginate fibres with polyester fibres. When tested in the vertical flame test, the blend containing 20 wt% alginate fibres exhibited fire extinguishment without any melt-dripping. In the cone calorimetry test, the mixture with 50 wt% alginate displayed a notable decrease in smoke and heat release compared with the blend containing 20 wt% alginate fibres. When these blended fibres are exposed to heating, it is found that the alginate fibres decompose prematurely and then delay the weight loss of the polyester fibres. These blended fibres are also found to exhibit good flame-retardant properties in the vapor and condensed phases. These blend fibres show potential applications in filling materials in furniture, toys, and clothing.[163] The various forms and applications of alginate-based systems are compiled in Table 5.

Table 5 Alginate-based bioplastics

Bioplastic combination	Application	Properties investigated	Ref.
Alginate extracted from *Sargassum siliquosum* J. Agardh (cross-linked with Ca^{2+} during the extraction process)	Thin film – packaging material	Mechanical properties, water vapour permeability, water solubility	141
Alginate cross-linked with EDTA + $CaCl_2$, $CaHPO_4$, and $CaCO_3$	Thin film – packaging material	Crosslinking reactivity, transparency, morphology, mechanical, oxygen transmission, water vapor transmission properties	142
Alginate plasticized with tributyl citrate	Thin film – food packaging application	Water vapour permeability, mechanical properties, opacity	143
Sodium alginate cross-linked with glutaraldehyde	Membrane – used for pervaporation	Pervaporation process, swelling properties	144
Alginate and polycaprolactone	Fibres – as multifunctional wound dressings	Thermal properties, wound healing, and blood clotting studies	145
Castor-oil based waterborne polyurethane with sodium alginate	Waterborne films – coatings, wound dressing, drug delivery	Thermal, mechanical, water resistance properties	146
Calcium alginate fibres reinforced in polypropylene matrix	Natural fibre-reinforced composites	Mechanical, interfacial and degradation (in soil) properties	147
Calcium alginate fibres and polypropylene	Fibre-reinforced composite – automobiles, buildings	Mechanical properties, single-fibre fragmentation test	148
Alginate coated on polyester fabric which is then soaked in 10% $CaCl_2$ solution for 30 minutes	Flame retardant coating on polyester fabric	Morphology, element distribution, flammability, thermal, combustion properties	149
Polypropylene, phosphorylated sodium alginate, dipentaerythritol and ammonium polyphosphate	Flame retardant sheets – automotive industry and electronic devices	Chemical structures, thermal properties, and degradation mechanisms	150
Polycaprolactone, alginate fibres	Fibre-reinforced composite scaffolds – tissue engineering	Morphology, hydrophilic, mechanical, cell viability and proliferation properties	151
Polypropylene fabricate, alginate and nanoparticles of copper oxide	Antimicrobial polypropylene nonwoven fabric – healthcare products	Morphology, wettability, antimicrobial, cytotoxic properties	152
Alginate-gelatine blend cross-linked with Ca^{2+}	Fibres – as wound dressings	Morphology, crystallinity, thermal, mechanical and water retention properties	154
Sodium alginate/PVA blend and sodium alginate/PEO blend	Ultrafine nanofibers – biomedical applications	Spinnability, SEM morphology, FTIR	155
Polyvinyl alcohol, sodium alginate and silver nanoparticles	Nanocomposite fibres – wound dressings, optical information storage	Morphology, chemical composition	153
Pectin, sodium alginate and blends of both	Food packaging films	Mechanical properties, water barrier properties	156
Blend of sodium alginate and polyvinyl alcohol	Membrane – used for pervaporation	Pervaporation process, swelling properties	157
Blend of alginate and polyester	Fibres – as filling materials in furniture, toys, and clothing	Thermal, flammability properties	163
Polyvinyl alcohol, chitosan, and sodium alginate	Composite membranes – for shape memory applications	Physical, mechanical, shape memory properties	164

6.4 Drawbacks of alginate-based bioplastics

The efficiency of the alginate extraction process can vary based on the pre-treatment methods applied. For instance, the use of formaldehyde pre-treatment in the extraction process has been shown to increase the extraction yield, but the overall environmental and health impacts of such pre-treatments need to be considered. Alginate-based films may have limitations in terms of mechanical strength. The tensile strength and elongation properties of alginate films are crucial for their performance in various applications, and efforts are needed to optimize these properties for specific uses. Alginate films tend to absorb moisture, and the plasticization process, involving the use of plasticizers like glycerol, can impact the water permeability and susceptibility to moisture. Balancing plasticization for flexibility without compromising moisture resistance is a challenge. Alginate-based composites, such as those blended with polyurethanes or other polymers, may face challenges related to shelf life, especially if the degradation rates of individual components differ significantly. This can impact the overall stability and performance of the composite over time. The crosslinking of alginate, whether through diffusion or internal setting, depends on external factors like polyvalent ions. Controlling these factors during processing is crucial for achieving the desired properties, and variations can affect the final product's characteristics. While alginate has been explored for flame retardancy, achieving optimal performance without compromising other properties can be challenging. The balance between flame retardancy and mechanical strength needs careful consideration.

7. Carrageenan-based bioplastics

Combinations of carrageenan with other natural and synthetic polymers are obtained as carrageenan-based bioplastics. These bioplastics are found to have a wide range of applications ranging from food and pharmaceuticals, to therapeutic drugs. Carrageenan is usually derived from a class of red seaweed (Rhodophycae). It is a safe and natural polysaccharide approved to be used as a food additive. Applications of carrageenan in the food and pharmaceutical industries are well reported.[116] Applications include viscosity modifiers, stabilizing agents, and emulsifiers. Carrageenans are of three types (λ, ί and κ) depending on the 3,6-anhydro-α-ᴅ-galactopyranosyl and the sulphate ester content.[165] The three types of carrageenan have different gelling, solubility, and mechanical properties. They also differ in the ions and the ion-holding positions. K-Carrageenan has more tendency to have monovalent ions like (K+), but iota-carrageenan tends to have divalent ions (*e.g.*, Ca^{2+}).[166–168] It is a biologically inert substance with good biocompatibility and is compostable.[169,170] The use of carrageenan is well-explored in the pharmaceutical industry as a binder matrix in preparing tablets. It is used as a binder in the extrusion of active ingredients. The gelling efficiency of carrageenan helps to manipulate the viscosity and rheology of therapeutic drugs and hence makes it an ideal candidate for controlled drug-release systems.[171]

Film formability and fibre formability have been explored with carrageenan-based formulations. Many researchers have prepared carrageenan-based films and have conducted detailed characterisations and property evaluations.[166,172–175] The K-carrageenan has better film-forming properties than the λ and ί forms, with comparatively better moisture barrier and mechanical properties. K-Carrageenan films have shown moisture permeability of 1.87×10^{-10} ng m m^{-2} s^{-1} Pa^{-1} and tensile strength of 22–32 MPa.[170,176] Efforts have also been made to make pure carrageenan fibres.[177]

Some carrageenan films needed modifications to achieve mechanical and water-vapor barrier properties for commercial applications.[169] Later studies have focussed on chemical modifications and blending with other materials to enhance carrageenan's desirable properties. The major routes of property enhancements are achieved by (a) plasticization, (b) composite making and (c) blending with other materials.

7.1 Plasticization

Carrageenan films when mixed with plasticizers such as glycerol, sorbitol and polyethylene glycol have proved to have improved mechanical and water resistance properties. Unmodified carrageenan film has been shown to exhibit good tensile strength with a tensile strength value of close to 70 MPa, but the films are very brittle. Low molecular weight additives are added to improve the intermolecular slippage and motion within the matrix. This will improve the ductility and elongation of the products. The plasticizer's impact on improving the mechanical properties depends on its compatibility with the matrix, the dosage, and the chemical structure. The type and optimum dosage of the additives are critical to improving the desired properties of the carrageenan film.[178,179] Property variations with plasticizers such as glycerol, sorbitol, and polyethylene glycol-300 in the range up to sixty percent were studied. The thickness and moisture content of the films increased significantly with the plasticizer concentration. Films incorporating sorbitol showed the least moisture absorption but had better tensile strength. In an interesting study, the red seaweed *Kappaphycus alvarezii* was plasticized with polyethylene glycol and sheets were prepared.[179]

Carrageenan plasticized with glycerol was evaluated for its performance in comparison with alginate plasticized with glycerol. Paula *et al.* investigated the mechanical and physical properties of carrageenan/glycerol blends as edible film. Kappa-carrageenan, iota-carrageenan, and alginate were examined as probable candidates. It was demonstrated that κ-carrageenan showed better mechanical properties and water permeability than ι-carrageenan and alginate-based films. Optical clarity was good with alginate-based films compared with both carrageenan types.[172,173]

7.2 Composites of carrageenan

Whole seaweed when reinforced with nanoparticles was investigated for its antibacterial property in comparison with commercial carrageenan reinforced with such nanoparticles.

Sudhakar *et al.* have proposed a process where the whole seaweed is used to make nanocomposites with zinc oxide, copper oxide, and silicon dioxide nanoparticles. These composites were then compared with the respective nanocomposites made from commercial carrageenan. It was observed that the antibacterial activity was good for all the nanocomposites under investigation. It could be inferred that the mixtures based on whole seaweed performed better than those made from commercial carrageenan alone.[180]

Modification of the water absorption property of carrageenan films was possible by reinforcing certain materials in the right quantity. The water absorption characteristics of carrageenan are a problem when used for packaging applications. Modifying carrageenan with water-repellent groups and additives can help improve the hydrophobicity.[172,174] Nano-clay-incorporated semi-refined carrageenan composites were prepared and then laminated with a polycaprolactone sheet. This combination was shown to give desirable moisture resistance and mechanical properties.[181]

The mechanism of water-repellent properties in modified carrageenan composites was studied. Dogaru *et al.* studied nanocomposite formulations with various concentrations of κ-carrageenan and bentonite nano-clay. The morphological and structural features, interactions, and sorption properties of the nano-composites were evaluated. It is believed that physical bonding was enabled between the carrageenan and nano-clay by hydrogen bonding. This impairs the chances of moisture adsorption into the composite.[169]

Incorporating microbial resistance in carrageenan films for its use in food packaging has been attempted and reported. Composites based on carrageenan have been investigated as potential candidates as wrappers in the food industry.[165,182] They are of great interest if microbial protection can be further improved by appropriate blending and composite preparation. This can be achieved by blending antimicrobial or oxidation retarders into the carrageenan films. This will deter bacterial growth, discolouration caused by enzymes, nutrition loss, and oxidation on the carrageenan films. These measures will in turn help to improve the shelf life of the food that is wrapped with these films. In one experiment, grapefruit seed extracts are considered an antibacterial additive. The extract is added to carrageenan solutions at different concentrations and film is cast. Mechanical, antibacterial, and physical parameters characterize the films. It has been shown that these composite films do exhibit good antimicrobial activity against the common microorganisms that affect packaged food.[165]

Carrageenan composites with antimicrobial and biocompatibility are designed to be used as wound dressing materials. K-Carrageenan blended with potassium sorbate has been shown to have good antimicrobial activity. Hence it can improve the longevity of the products packed in it and makes them safer for consumption.[183] Incorporating halloysite–silver nanoparticles into the carrageenan matrix has improved the system's mechanical strength and UV barrier properties. The films have good antimicrobial properties as well. It was observed that sodium dodecyl sulphate helps to improve the incorporation of the silver nanoparticles in the carrageenan films. The better dispersion of nano-particles leads to good mechanical properties, optical clarity, and antibacterial activity of the above film.[184] Innovative bioactive composite scaffolds from k-carrageenan blended with silk fibroin have been developed by Nourmohammadi *et al.* This composite can be used in bone regeneration applications.[185] Carrageenan composites with cellulose have also been studied in detail. These show good bio-compatibility, moisture retention capacity, and mechanical strength to be considered as wound dressing materials.[3,186]

7.3 Blends of carrageenan

Blending biopolymers with other polymer matrices could be used to tailor the desired properties for specific applications. Carrageenan was mixed with cassava starch in an extruder to form a bioplastic with better mechanical properties. Carrageenan in this starch bioplastic positively influences the tensile strength and modulus. The mechanical properties also increased as the carrageenan percentage in the blend increased.[176] Moustafa *et al.* studied K-carrageenan and potato starch blends for making hydrogels. This blend is shown to have good hydrogel properties, especially the ability to absorb water. Hence, this could be a non-toxic, biodegradable, and safe material for manufacturing toys.[187] K-Carrageenan can absorb extracellular fluids and could be applied in wound dressing hydrogels. To improve the degradation of carrageenan, it can be blended with a synthetic polymer such as polyvinyl alcohol, polyvinyl acetate, polyvinyl pyrrolidone, and polyethylene oxide. This will help improve the mechanical properties, water absorption, and shelf life.[4,188] Wound dressing formulations based on carrageenan and carboxy methyl cellulose have been made from hydrogels prepared by blending them with polyethylene oxide. This wound dressing has shown the capability to clot blood and adhere to platelets. This dressing system has shown a similar bleeding time compared with the commercially available dressing made from chitosan. In addition, they have demonstrated reduced inflammations and observed lesser depositions of grain-like structures on the dressing.[4] An interesting work is the preparation of carrageenan fibres by a wet spinning technique. In this method, carrageenan reacts with epoxy chloropropane for improved properties.[177] Boateng *et al.* prepared solvent-cast wound dressings formulations by blending polyethylene oxide and carrageenan. In one experiment, the dressing system had streptomycin incorporated in this film. Another experiment contained diclofenac similarly. The dressing can help to reduce bacterial infection by the antimicrobial action of streptomycin and further improve the efficacy with diclofenac. As an anti-inflammatory, diclofenac will help alleviate the pain and reduce the local swelling around the wound.[189]

Carrageenan/polyvinyl alcohol composite was found to exhibit enhanced elongation when reinforced with bio-polyol. Carrageenan/polyvinyl alcohol-based blends have many applications.[190,191] A flexible carrageenan–polyvinyl alcohol film was uniquely prepared using a bio-polyol called liquefied banana pseudo-stem as a plasticizer and common cations (Ca^{2+} or K^+) as cross-linkers. The elongation of the composite film is significantly increased by up to 440% when adding three percent bio-polyol. This renewable and degradable organic–inorganic hybrid film has the potential for packaging applications.[192]

To make films, blended films can be prepared from K-carrageenan, PVA and red pitaya flesh extract (RPFE). RPFE is found to be rich in betacyanins and is known to be sensitive to pH variations. It is an effective antimicrobial agent and antioxidant. These features can make it a good additive in packaging film for the food industry. The optical properties, barrier properties against light, water retention, and mechanical properties were assessed and reported. The films have shown good sensitivity to pH and ammonia.[193]

Improving the electrical conductivity of carrageenan is attempted by reinforcing it with certain materials to find their use in energy storage applications. Polysaccharides like carrageenan have good compatibility with salts and hence can be candidates in developing electrically conductive materials. Carrageenan is abundant with functional groups like –OH (hydroxyl). This can facilitate carrageenan to form networks with various compounds and form polyelectrolytes.[174,194,195] The conductivity of these films has been reported (10^{-5} to 10^{-3} S cm^{-1}). Iota-carrageenan matrix has been complexed with poly(*ortho*-phenylenediamine-*co*-aniline). These composites can have potential applications as sensors, capacitors, and other energy storage devices.[191] Biopolymer blends based on k-carrageenan and carboxymethyl cellulose derived from kenaf fibres were shown to have a conductivity of 3.25×10^{-4} S cm^{-1}. This composite can form a polyelectrolyte and could also be evaluated for energy storage devices.[196]

The spinnability of carrageenan into fibres has been explored. An interesting work is the preparation of carrageenan fibres by the wet-spinning technique. The carrageenan fibres were reacted with epoxy chloropropane for improved properties. This helped enhance the carrageenan fibers' mechanical properties.[177] A biopolymer composite film containing kappa-carrageenan, PVP (polyvinyl pyrrolidone), and polyethylene glycol (PEG) was formulated. These films were compared with the ones mixed with silver nanoparticles. The silver nanoparticles make the films moisture-resistant and give better tensile strength.[197] The electrical and mechanical properties of a film prepared by the evaporative casting of a carrageenan/carbon nanotube/glycerine system have been evaluated. This film has been tested as a gas sensor and has shown some positive indications of its application.[168] Table 6 gives a concise picture of various carrageenan application sectors, especially bioplastics.

7.4 Drawbacks of carrageenan-based bioplastics

Unmodified carrageenan films, although exhibiting good tensile strength, can be brittle. This brittleness may restrict their use in applications where flexibility and impact resistance are essential. Some carrageenan films may require additional modifications to meet the mechanical and water-vapor barrier properties necessary for commercial applications. This could involve chemical modifications or blending with other materials, which may add complexity to the manufacturing process. The mechanical and water resistance properties of carrageenan films are often improved by the addition of plasticizers such as glycerol, sorbitol, and polyethylene glycol. However, the effectiveness of plasticizers depends on factors such as compatibility with the matrix, dosage, and chemical structure. Finding the optimal conditions for plasticizer incorporation can be challenging. The three main types of carrageenan (λ, ί, and κ) exhibit different properties. While K-carrageenan is reported to have better film-forming properties, moisture barrier, and mechanical properties, the choice of carrageenan type adds complexity to the material selection process, and the desired properties may vary. Different applications may demand specific properties, and achieving a balance between the various desirable characteristics can be challenging. For instance, films suitable for food packaging may require different properties compared with those intended for drug delivery systems.

8. Bioplastics from ulvan

Ulvan is a versatile polysaccharide with immense potential. Its biological activities and physicochemical properties are found to be dependent on the molecular size and degree of branching. Recently, its physicochemical and rheological properties have been tuned to see its use in biomaterials, drug delivery and tissue engineering applications. The widespread usage of plastic in recent decades has caused environmental pollution, as packaging waste alone contributes to one-third of plastic waste. Sustainable alternatives to plastic are being sourced, for which algae are emerging for their potential to be used for bioplastic production. This sustainable approach to using algae in producing bioplastics for packaging applications minimizes waste generation, resource consumption, and combating greenhouse gas emissions.[203]

Ulvan is a polysaccharide extracted from the seaweeds of the *Ulva* genus consisting of sulphated rhamnose and glucuronic and iduronic acids. The extraction yield depends on the conditions followed in each process and the stages of the extraction procedure. A lower pH results in increased ulvan selectivity, higher extraction temperatures permit further ulvan dissolution and increasing the duration of extraction increases the yield. From the data obtained in the literature, the optimized conditions to achieve a high yield are 80–90 °C, 2–4.5 pH, and 1–3 hours duration.[204] To date, ulvan is used in particles, membranes, 3D porous structures, nanofibers, and hydrogels. Ulvan is either used as is or modified by chemical modification, crosslinking, and complexation.[205,206]

8.1 Plasticization with ulvan

The effect of the plasticizer used for film formulations on the properties of the ulvan films is analysed. Edible films of semi-refined carrageenan, ulvan polysaccharides and glycerol can

Table 6 Carrageenan-based bioplastics

Bioplastic combination	Application	Properties investigated	Ref.
Carrageenan/grapefruit seed extract	Active packaging	Antimicrobial	165
Carrageenan/carbon nanotube/glycerine	Gas-sensing films	Mechanical properties, sensory properties	168
K-Carrageenan/bentonite nano-clay	Biopolymer films and coating	Water absorption and mechanical properties	169
K-Carrageenan/nano-clay/*Zataria multiflora*/glycerol	Active food packaging	Antimicrobial	170
Kappa-carrageenan or iota-carrageenan or alginate with glycerol	Edible films	Moisture absorption and mechanical characteristics	173
Carrageenan/cassava starch	Films and moulded articles	Water permeability and mechanical properties	176
Carrageenan/epoxy chloropropane	Fibres	Mechanical properties and structure	177
K-Carrageenan with glycerol/sorbitol and PEG	Packaging films	Mechanical and moisture-absorbing properties	178
Kappaphycus alvarezii biomass based	Films	Oxygen and moisture permeation, mechanical characteristics	179 and 180
Semirefined carrageenan	Packaging film	Moisture barrier, mechanical properties	181
Carrageenan/essential oils	Antimicrobial and antioxidant edible films	Moisture permeability, transparency, antioxidant characteristics	182
K-Carrageenan/potassium sorbate	Antimicrobial food packaging	Controlled release of additives	183
Kappa-carrageenan/silk fibroin	Bone scaffolds	Compressive strength, bone apatite formation	185
Carrageenan/cellulose, carrageenan/carboxy methyl cellulose/polyethylene oxide	Wound dressing materials	Biocompatibility, water retention capacity and mechanical properties	3, 4 and 186
K-Carrageenan/potato starch	Biodegradable water-absorbent children's toys	Hydrogel properties, mechanical properties	187
Carrageenan/polyethylene oxide/streptomycin/diclofenac	Wound dressing films	Mechanical, mucoadhesive and drug-release characteristics	189
i-Carrageenan/poly(*ortho*-phenylenediamine-*co*-aniline)	Energy storage devices	Ionic and electrical conductivity	191
Carrageenan/PVA/bio-plasticizer	Packaging	Hydrophobicity and mechanical properties	192 and 193
k-Carrageenan/carboxymethyl cellulose	Polymer electrolytes	Electrical and mechanical properties	196
K-Carrageenan/polyvinyl pyrrolidone/PEG/silver nanoparticles	Biomedical applications	Fungicide activity, mechanical properties	197
Carrageenan with glycerol	Edible coating	Mechanical properties, moisture permeability	198 and 199
K-Carrageenan composites with pectin and mica flakes	Biodegradable film	Barrier properties to water vapour and gases	200
Carrageenan/rice starch	Biodegradable films	Mechanical and water vapour permeability	201
i-Carrageenan/rice starch/stearic acid/glycerol	Fruit and vegetable packaging	Physical, mechanical and barrier properties	202

be utilized in food packaging. The addition of glycerol improved the physicochemical and mechanical properties of the film required for food packaging.[207] Film formulations made of ulvan polysaccharide are found to be successful irrespective of the extraction procedure. But it is found that specific characteristics such as optical, thermal, structural, physicochemical, barrier, mechanical, and antioxidant characteristics are affected by the extraction conditions and several types and concentrations of plasticizer used. The effects of glycerol, sorbitol, and enzymatic-chemical extract on the characteristics of the films have been analysed.[208,209] Glycerol and polyethylene glycol were chosen, of which the film containing 30% polyethylene glycol exhibited greater tensile strength and lower permeability to water vapor and oxygen.[210] Composite films and laminates of ulvan, polyvinyl alcohol, glycerol, and starch have been produced. Glycerol, when added to contents of 10–20%, contributes to the flexibility of the laminates. The biodegradability of the formulated laminate is carried out, from which it is observed that 80% mineralization in 100 days is achieved.[211]

Ulvan is water-soluble but can be made water-insoluble by crosslinking. Such ulvan crosslinked membranes proved their outstanding water uptake ability (until 1800% of its original dry weight) and improved mechanical performance (1.76 MPa). Ulvan has been evaluated for its use as drug delivery device, where nearly 49% of the drug had been steadily released initially, followed by a sustained slow release for 14 days.[212]

8.2 Composites of ulvan

Ulvan films are synthesized by incorporating silver nanoparticles to make the films antimicrobial for food packaging applications. These bio-nanocomposite films are found to demonstrate a good barrier to water vapour permeability. These films show good antimicrobial properties against Gram-negative and Gram-positive bacteria.[213] The incorporation of ulvan into cellulose films had shown an improvement in film thickness, water solubility, and water vapor permeability, and good barrier properties against UV and visible light but decreased oxygen permeability. The antioxidant properties and thermal stability had improved significantly at higher contents of ulvan.[214]

Wound dressing materials designed from ulvan formulations are designed and reported. Chitosan–ulvan hydrogels containing epidermal growth factor (EGF) and cellulose nanocrystals (CNCs) as reinforcement are designed as wound dressings. The nanocrystal reinforcement reduced the porous microstructure from a pore size of 237 ± 59 μm to 53 ± 16 μm, which in turn increased the mechanical stress curve from 0.57 MPa to 1.2 MPa, as well as the swelling, and thermal behaviour. The addition of EGF is found to encourage the recovery of skin wounds. In addition, the formulated hydrogel possesses non-toxic behaviour and good cell viability.[215]

8.3 Blends of ulvan

Biological scaffolds are designed from a combination of ulvan and chitosan. Scaffolds made of either ulvan or chitosan or a combination of ulvan and chitosan are found to exhibit cytocompatibility. It is found that membranes made of ulvan/chitosan sustained the human cell viability and morphology and also encouraged the attachment and proliferation of 7F2 osteoblasts.[216] Complex films made of chitosan and ulvan by ionic crosslinking are found to demonstrate antioxidant and whitening properties. The ionic crosslinking agent used here is tripolyphosphate, which is found to improve the tensile properties of the chitosan/ulvan complex films. These films are biocompatible with normal human cells and toxic to melanoma cancer cells, demonstrating cell selectivity that could be attributed to generating reactive oxygen species.[217] Scaffolds made of ulvan and chitosan are treated with alkaline phosphatase to deposit calcium phosphate minerals on the surface. The scaffolds with deposited minerals are non-toxic and are found to encourage cell adhesion and differentiation.[218]

Patents on the usage of ulvan as a bioplastic material and paper have been reported. A bioplastic material composed of ulvan blend had been produced by a reactive extrusion process in the patent WO 2016/090511 A1. An algae powder with a reduced content of protein had been prepared from *Ulva* species algae biomass and a bioplastic material had been formulated from such a powder in the patent WO 2017/046356 A1.[219] Paper pulp had been prepared from *Ulva* species seaweed powder by extracting cellulose and using the same with wood cellulose to manufacture paper in the patent WO 2012/114045A1.[220]

The non-cytotoxic nature of ulvan/chitosan blend is evaluated to allow its usage in biomedical applications. Ulvan-based hydrogels have been developed, which displayed thermogelling behaviour. At 30–31 °C, sol–gel transition occurs, thus confirming their usage as *in situ* hydrogels in biomedical applications.[221] Carboxymethylation is done on ulvan/chitosan powder to render it highly acidic, which finds application as a bone cement. This blend possesses enhanced mechanical performance and is found to be non-cytotoxic.[222] The areas of applications of ulvan-based bioplastics are summarized in Table 7.

8.4 Drawbacks of ulvan-based bioplastics

The properties of ulvan, including its biological activities and physicochemical characteristics, are highly dependent on the extraction conditions. Variations in pH, temperature, and extraction duration can influence the yield and specific characteristics of ulvan. The properties of ulvan-based films, such as optical, thermal, structural, physicochemical, barrier, mechanical, and antioxidant characteristics, are influenced by the type and concentration of the plasticizers used. Although ulvan can be crosslinked to improve its mechanical performance, there

Table 7 Ulvan-based bioplastics

Bioplastic combination	Application	Properties investigated	Ref.
Semi-refined carrageenan, ulvan, acetic acid, glycerol	Edible films – food packaging	Viscoelastic, moisture content, opacity, antioxidant, mechanical properties	207
Ulvan, glycerol or sorbitol	Films – food packaging	Optical, thermal, structural and antioxidant properties	208
Ulvan, glycerol or sorbitol	Films – food packaging	Physico-chemical, optical, barrier and mechanical properties	209
Ulva, glycerol, polyethylene glycol	Film – food packaging	Mechanical, water vapor permeability, oxygen permeability, transparency, physicochemical, morphology	210
Ulva, polyvinyl alcohol, glycerol, starch	Films – agriculture and food packaging	Mechanical, thermal, morphology, mineralization studies	211
Ulvan, butanediol diglycidyl ether, sodium hydroxide	Wound dressing and drug delivery applications	Morphology, mechanical, water uptake, drug release properties	212
Ulvan, silver nanoparticles	Bio-nanocomposite film – food packaging	Morphology, physicochemical, water vapour permeability, antimicrobial properties	213
Ulva, cellulose, polyvinyl alcohol, glycerol	Composite film – food packaging	Physicochemical, water vapor permeability, oxygen permeability, antioxidant properties	214
Chitosan, ulvan, cellulose nanocrystals, epidermal growth factor	Hydrogel – wound dressing	Crystal structure, morphology, porosity, mechanical, thermal, *in vitro* cytocompatibility	215
Ulvan, chitosan, ulvan/chitosan	Membranes – scaffold materials	Morphology, cellular compatibility	216
Chitosan/ulvan, tripolyphosphate, glycerol, chlorophyll	Film – biomedical applications	Tensile mechanical, physicochemical, crystalline, swelling, biocompatibility, antioxidant properties	217
Ulvan, chitosan, alkaline phosphatase	Polyelectrolyte complex – scaffolds	Morphology, thermal, crystal structure, rheological, biological properties	218
Ulvan, poly(*N*-isopropylacrylamide)	Hydrogels – biomedical applications	Thermal, rheological properties	221
Ulvan/chitosan, monochloroacetic acid	Powder – bone cement	Structural, mechanical, bioactivity, *in vitro* cytotoxicity	222

may still be limitations in achieving mechanical strength comparable to certain synthetic materials. The mechanical properties of ulvan-based materials may need to be carefully balanced for different applications. Ulvan is naturally water-soluble, which may limit its use in certain applications where water resistance is crucial. However, efforts have been made to make ulvan water-insoluble through crosslinking, presenting a potential solution. The extraction yield of ulvan can be sensitive to various factors, and achieving a high yield may require careful control of the extraction conditions. This sensitivity can impact the scalability and cost-effectiveness of ulvan extraction processes.

9. Bioplastics from fucoidans

Fucoidans are found to be antiviral and anticoagulant in nature which makes them a good candidate for biomedical applications. Fucoidans are generally extracted from brown algae and some echinoderms. They are natural polysaccharides consisting of sulphated α-L-fucose components and varying amounts of other monosaccharides, uronic acids, and proteins.[223,224] The composition of fucoidans can vary with the species of macroalgae they are extracted from.[223] Fucoidans exhibit antiviral, anticoagulant, and antitumor properties, and others of clinical interest.[223–225] Fucoidans have good water solubility, and compatibility with human tissues, and are a safe product.[226,227] They are not cytotoxic components, especially with other commercial antiviral products. This makes them highly acceptable in many therapeutic uses.[223,226] However, fucoidan is not known to form gels or films by itself. Films and other therapeutic applications are developed by blending with other polymers and binders.[138]

9.1 Blends of fucoidans

Blending materials is a plausible solution to bring in the positive elements of the mixture. A remarkably successful film was prepared from the blending of fucoidan, chitosan polyvinyl alcohol and ampicillin, which shows excellent cell regeneration properties. The increased concentration of biopolymers in this system helps to facilitate the proliferation of cells more efficiently. The polyvinyl alcohol makes the film more stable and controls the water absorption and solubility. The chitosan and fucoidan in the blend facilitate the porous structure of the system. This microstructure is critical to help the cells to adhere to the surface and grow.[226]

Patents on fucoidan-based bioplastic and an edible fucoidan-based film have been reported. Bloom Holdings have patented several formulations and processes to effectively use fucoidan in polyurethane, ethylene vinyl acetate and other plastic products. The anti-microbial, anti-fungal, anti-viral and fire-retardant activities of fucoidan can be incorporated into thermoplastics and foams.[228,229] Gomaa *et al.* prepared an edible composition with chitosan, alginate and fucoidan. This film was demonstrated to have better oxygen and moisture permeation resistance. This film also showed good antioxidant properties. Adding fucoidan and/or calcium ions improved the water resistance in the blend with alginate and chitosan. This also helped to make thicker films feasible. The films exhibited better permeation resistance to moisture and oxygen permeability.[138,230]

Fucoidan and chitosan when combined together exhibited good characteristics suitable for drug release applications. Nakamura *et al.* prepared a hydrogel by blending chitosan with fucoidan. This blend was investigated for fibroblast growth factor (FGF-2) drug release characteristics. The bioplastic matrix was used as a carrier for FGF-2, which can bind with heparin. The hydrogel was made into an injectable form with FGF-2 particles and used for the controlled release of FGF-2. It was observed that this hydrogel system is stable and extended the half-life time of the fibroblast growth factor.[231]

9.2 Drawbacks of fucoidan-based bioplastics

Fucoidans are not known to form gels or films. This limitation requires additional processing steps, such as blending with other polymers and binders, to create functional films or matrices for specific applications. This additional step may complicate the manufacturing process. While fucoidans are generally considered safe and compatible with human tissues, the biocompatibility of the blended materials needs to be thoroughly evaluated. The introduction of additional polymers, binders, or drugs in the blend may impact the overall biocompatibility of the composite material. The use of fucoidans in biomedical applications may be subject to regulatory approval, especially when incorporated into blended materials intended for therapeutic use. Meeting the regulatory standards for safety and efficacy is a critical consideration for the successful translation of fucoidan-based products. The composition of fucoidans can vary depending on the species of macroalgae from which they are extracted. This variability may introduce challenges in standardizing the properties of fucoidan-based blends, making it important to carefully select and characterize the source of the fucoidans. While the mentioned film blend with fucoidan, chitosan, polyvinyl alcohol, and ampicillin showed excellent cell regeneration properties, the long-term stability and performance of such films under different conditions need to be thoroughly assessed. Factors such as degradation, mechanical strength, and interaction with the environment should be considered.

10. Laminarin-based bioplastics

Laminarin exhibits low molecular weight, low viscosity, and ready solubility in water which makes it a preferred constituent in many bioplastic formulations. Laminarin is generally extracted from brown algae and comprises glucose units with low molecular weight.[232,233] $\beta(1,3)$ glycosidic bonds link the glucose units, while some β(1,6) side-chain branches are also in the structure. This low molecular weight composition leads to laminarin solutions of very low viscosity. Laminarin has good solubility in water and some organic solvents. This also

Table 8 Bioplastics based on fucoidan and laminarin

Bioplastic combination	Application	Properties investigated	Ref.
Fucoidan/chitosan/polyvinyl alcohol/ampicillin	Cell regeneration	Swelling/antimicrobial/water resistance	163
Alginate/fucoidan/chitosan	Edible films	Barrier properties/water absorption	165 and 168
Polyurethane/EVA/fucoidan	Foams	Anti-microbial/antifungal	166 and 167
Fucoidan/chitosan hydrogel	Controlled drug release	Fibroblast growth factor (FGF)-2 immobilization	169
Fish gelatine/laminarin	Packaging films	Antimicrobial activity	176

explains why they are readily biodegradable in various environments. These properties make them attractive additives in many bioplastic investigations.[232–235] Laminarin is nontoxic and has anti-oxidant, antitumor and many therapeutic properties. Reports of anti-inflammatory and anticoagulant activities are available.[6,55,236,237] Blends and composites based on laminarin have been studied to understand their applications in packaging and medical products.[237,238] Fish gelatine/laminarin blend films have been investigated for food packaging applications. K-Carrageenan/laminarin film mixed with nanocurcumin has been prepared and studied for food packaging applications. This system has shown extended shelf life for fish fillets when used as active packaging.[238] A summary of applications is given in Table 8.

10.1 Drawbacks of laminarin-based bioplastics

Films with low viscosity may have challenges in maintaining physical integrity, especially under stress or load. The low molecular weight and viscosity of laminarin may result in films or products with limited mechanical strength and poor tensile properties. This limitation can impact the range of applications, especially in scenarios where robust and durable materials are required, such as in certain packaging applications. While the solubility of laminarin in water and some organic solvents is beneficial for processing, it can also pose challenges in certain applications. For instance, the susceptibility to dissolution in water may limit the use of laminarin-based materials in environments with high humidity or when exposure to water is undesirable. While laminarin has been studied for various applications, each application may present unique challenges. For instance, the use of laminarin in food packaging, as mentioned in the example of fish gelatine/laminarin blend films, may require addressing specific issues such as moisture resistance, mechanical strength, and compatibility with food products.

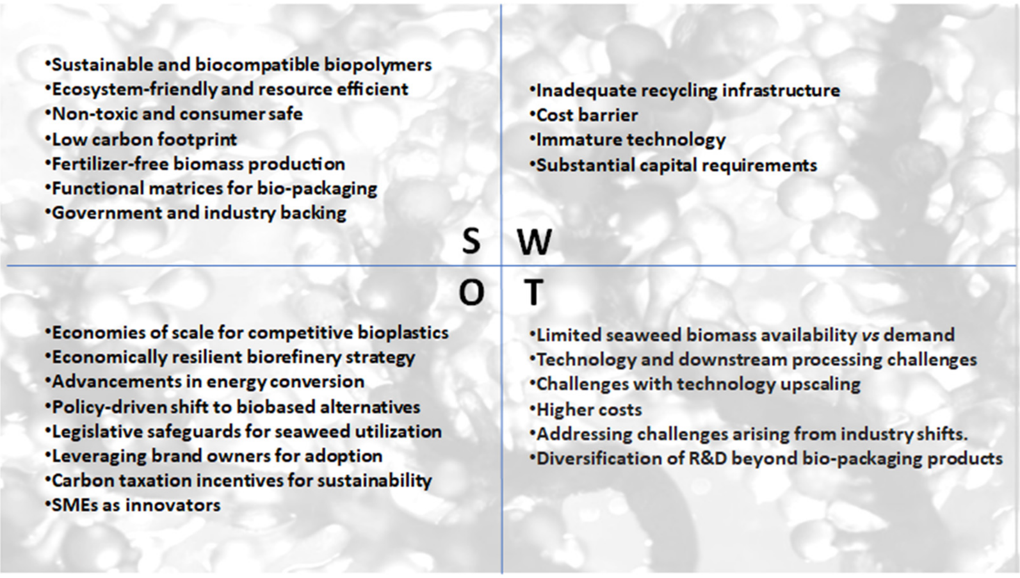
11. Techno-economic aspects and life cycle assessment of seaweed-based bioplastics

Bio-based and biodegradable plastics constitute 58.1% of the overall bioplastic market. The global bioplastics and biopolymers market is anticipated to surge from USD 10.7 billion in 2021 to USD 29.7 billion by 2026, exhibiting a compound annual growth rate (CAGR) of 22.7%. Presently, the cost varies between USD 2 per kg and USD 6 per kg, compared with the USD 1 per kg to USD 2 per kg range of its petrochemical counterparts. Concerning land use for the cultivation of feedstock for bioplastic production, it is minimal, accounting for only 0.015% of the total arable land worldwide (1.4 billion ha). Projections indicate a rise to 1.1 million ha (0.02% of total area) by 2025. Addressing the end-of-life (EOL) phase is crucial in life cycle assessment (LCA).

Mechanical recycling emerges as the most environmentally suitable disposal method for bioplastics, boasting the least carbon footprint. In comparison, the anaerobic digestion, landfilling, composting, and incineration of 1 kg PLA generate 2.2 kg, 1.6 kg, 1.5 kg, and 1.7 kg of CO_2, respectively, while mechanical recycling produces only 0.62 kg CO_2. Mechanical recycling is cost-effective, emits no noxious gases (unlike incineration), and avoids issues like the leachate seepage and uncontrolled methane release associated with landfilling. For effective anaerobic digestion, bioplastics should ideally degrade within 15–30 days; PHB meets this criterion, whereas PVA, PLA, and PCL do not. Algae, often considered waste, could be a valuable resource when converted into new-generation bioplastics. Developing predictive models like BioWin and the Biodegradability Evaluation and Simulation System (BESS) can guide consumers toward the best bioplastic based on application and available EOL options.[239]

A SWOT analysis of seaweed-based bioplastics is shown in Fig. 2. Seaweed-based bioplastics offer a promising array of advantages specific to their unique properties and applications. With seaweed's abundance and renewability, these bioplastics present a sustainable alternative to traditional plastics. Their biodegradability and low environmental impact address pressing concerns regarding plastic pollution. Seaweed's inherent functional properties make it suitable for various applications, ranging from food packaging to biomedical materials. Additionally, seaweed-based bioplastics have the potential for value-added products, as they can be enriched with bioactive compounds. Government support and funding further propel research and development in this field, aligning with global sustainability initiatives.

However, several challenges must be navigated for the widespread adoption of seaweed-based bioplastics. These include the limited infrastructure for cultivation and processing, technological hurdles in scaling production, and higher costs associated with manufacturing compared with conventional plastics. Overcoming perceptions and educating consumers



S

- Sustainable and biocompatible biopolymers
- Ecosystem-friendly and resource efficient
- Non-toxic and consumer safe
- Low carbon footprint
- Fertilizer-free biomass production
- Functional matrices for bio-packaging
- Government and industry backing

W

- Inadequate recycling infrastructure
- Cost barrier
- Immature technology
- Substantial capital requirements

O

- Economies of scale for competitive bioplastics
- Economically resilient biorefinery strategy
- Advancements in energy conversion
- Policy-driven shift to biobased alternatives
- Legislative safeguards for seaweed utilization
- Leveraging brand owners for adoption
- Carbon taxation incentives for sustainability
- SMEs as innovators

T

- Limited seaweed biomass availability *vs* demand
- Technology and downstream processing challenges
- Challenges with technology upscaling
- Higher costs
- Addressing challenges arising from industry shifts.
- Diversification of R&D beyond bio-packaging products

Fig. 2 SWOT analysis of seaweed bioplastics.

about the benefits of seaweed-based bioplastics is essential for market acceptance. Yet, opportunities abound for further research and innovation, collaboration across sectors, market growth, and diversification into new applications. Mitigating environmental risks, addressing competition from conventional plastics, navigating regulatory landscapes, ensuring supply chain resilience, and adapting to technological and market uncertainties are crucial considerations for the industry's sustainable advancement.

The primary tool for evaluating the environmental impact of both bioplastics and conventional plastics is life cycle assessment (LCA) or cradle-to-grave analysis. Protocols have been established for conducting LCA studies on specific bioplastics, such as PLA, currently in the market. These studies often compare the LCA of bioplastics with that of fossil-fuel plastics like polyethylene and PET. A recent study using the LCA cradle-to-grave analysis demonstrated a significant reduction in greenhouse gases when 20% of PET bottles were substituted with PLA bottles during bottle manufacturing. Another study using the Global Warming Potential (GWP) guide showed that substituting petroleum-based plastics with bioplastics could reduce greenhouse gas emissions. LCA also serves as a valuable means of identifying the most effective methods for managing and disposing of bioplastic waste. Incineration or landfilling of bioplastic products has been revealed, through LCA, as an inadequate alternative. Following the LUC emissions principle has confirmed the reliability of bioplastics as an excellent substitute for petroleum-based plastics in waste management. Compared with conventional petroleum-derived plastics, the use of PLA and thermoplastic starch significantly reduces carbon dioxide emissions, with the former achieving a reduction of 50–70%. Similarly, biourethanes and poly(trimethyleneterephthalate) (PTT) exhibit 36% and 44% lower greenhouse gas emissions than their petroleum-derived counterparts. To enhance the intelligent management of bioplastic waste, it is proposed that the reduction of greenhouse gas emissions should aim for zero LUC emissions. Future studies should concentrate on conducting individual LCAs for the expanding range of bioplastics.[240]

Carbon balance estimates for the recirculation of co-products from the alginate extraction step into the bioplastic film have been reported. A scenario based modelling provide insight into the carbon flow within various scenarios. In the no-incineration composting scenario (BASE), where alginate is the sole seaweed component in the bioplastic and accounts for 0.44 kg C in 1 kg of bioplastic, 44% of the carbon is biogenic. When cellulose and glycerol are externally added, 69% of the carbon in the seaweed contributes to seaweed residues. The cellulose incineration composting scenario (CELL) demonstrates the recirculation of alginate and cellulose from the seaweed to the bioplastic film, avoiding 12.5% of carbon in cellulose nanofibers. The cellulose and mannitol incineration composting scenario (MANN) reveals that the mannitol in seaweed is lower than the glycerol required for bioplastics. Incorporation of mannitol to the bioplastic film avoids 5% of the carbon from glycerol. PLA filler pellet incineration composting scenarios PLA5 and PLA30 show how seaweed residues in the base scenario are later used to substitute 5% or 30% of PLA, integrating more original seaweed biomass into the products. Overall, the carbon balance results indicate that recirculating cellulose and mannitol by substituting PLA in scenarios CELL, MANN, PLA5, and PLA30 converts more of the originally absorbed seaweed carbon into products, reducing the need for external carbon inputs. The BASE scenario requires the most external carbon inputs. The contribution analysis of the Global Warming (GW) impact across all life cycle stages of 1 kg of bioplastic film reveals that scenarios with the highest impact are BASE, CELL, and MANN with incineration end-of-life (EoL), having impacts of 3.72 kg CO_2-eq., 3.79 kg CO_2-eq., and 3.77 kg CO_2-eq., respectively. The scenarios with the lowest impacts are PLA substitution scenarios with composting EoL, with PLA30 substitution having the lowest impact at 2.3 kg CO_2-eq. and PLA5 at 2.53 kg CO_2-eq., closely followed by BASE composting at 2.56 kg CO_2-eq. Film fabrication contributes the most to the impact in all cases, primarily due to the production of glycerol with an impact of 2.11 kg CO_2-eq. In all scenarios, the GW impacts of the offshore farm are significantly low, attributed to the carbon uptake in seaweed cultivation.[241]

Micro- or macro-algae, particularly seaweed, are renewable resources that do not compete with land-based food resources. Seaweed production costs, especially in Asian countries, are expected to be lower due to the availability of low-cost manpower and shorter harvest times (30–45 days) for certain marine macroalgae like *Kappaphycus* sp. and *Gracilaria* sp. Bio-based plastics derived from algae feedstock include hybrid plastics, cellulose-based plastics, polylactic acid, and bio-polyethylene. Economically, directly utilizing seaweeds for bioplastic production provides a cost advantage, whereas processing costs are higher for PLA, PHA, and PHB production. Small- and medium-scale industries involved in agar, alginate, and carrageenan production from seaweeds have significant opportunities for small startups. The econometrics of bioplastic production from algal biomass, along with its production costs, have been evaluated at the lab scale, considering factors such as seaweed quantity, plasticizers, water, electricity, and heat. Notably, the manpower cost for producing specific-sized bioplastic films was not included in the assessment. The cost of *Kappaphycus alvarezii* is higher compared with other Indian native species, selling at around Rs. 100–130 per kg dry weight, while *G. edulis* and *G. dura* are sold at around Rs. 35–40 per kg dry weight.[179]

12. Challenges and future prospect

Elevated production costs, amounting to twice those of traditional synthetic plastics, pose a significant challenge. Incomplete degradation under various conditions necessitates a thorough investigation to identify optimal solutions for addressing negative ecological impacts, with a particular emphasis on mitigating greenhouse gas emissions, including methane. Enhancing the pathways of algae-based biopolymers, currently marked by high costs and low efficiency, is crucial for ensuring a sustainable future. Inadequate information on bioplastic labels from producers further complicates the understanding and acceptance of these materials. Poor water-resistance properties may hinder the practical applications of bioplastics, requiring further attention and improvement in this aspect.[242]

There is a need for further exploration into strategies that minimize the use of additives, as their current usage renders the product unsuitable for applications in the medical and food packaging sectors. Additionally, there is a call for innovative, cost-effective, and more efficient conversion technologies. The life cycle assessment (LCA) of bioplastics remains an under-researched area that demands a deeper understanding, particularly when adopting a gate-to-grave approach. The development of bioplastics designed to degrade effectively under mild conditions can significantly broaden their applicability. Economic constraints stand out as a pivotal factor influencing the upscaling of the successful laboratory-scale technologies mentioned earlier.[239]

There has been significant investigation into the various types, benefits, and potential of bioplastics derived from renewable sources such as edible crops and waste. However, there remains ample room for further investigation, particularly in the context of algae-based bioplastics production. Continuous research and progress in this field are essential for advancing the realm of algal-based bioplastics. Each step in the process requires thorough exploration to guarantee the optimal output of algal-based bioplastic at the lowest possible cost.[243]

While bioplastic extracted from algae is in its early stages of development, achieving commercialization remains a goal for industry experts. The genetic engineering of algae to enhance biopolymer accumulation and production is anticipated to play a pivotal role. Presently, some companies produce plastics labeled as biodegradable, utilizing materials like PHA, PLA, low-density polyethylene (LDPE), high-density polyethylene (HDPE), and bio-based polymer blends that are both degradable and recyclable. Seaweeds, in combination with safe and commercially viable plasticizers, offer a promising avenue for producing 100% biodegradable single-use plastics.[244]

13. Conclusions

Algal systems are emerging as a sustainable resource for biomass that is widely investigated for various industrial applications. A major field of research and development is in the manufacturing of bioplastics. This will help reduce our reliance on fossil fuels and create compostable and biodegradable systems. The polymer industry is expected to take a large volume of algal biomass along this route, helping carbon sequestration and creating good economic opportunities for coastal communities. Seaweed components like polysaccharides, lipids, proteins, and cellulose have been used to develop plastics; polysaccharides are of prime importance as the percentage extracted can be economically viable. The major seaweed-derived polysaccharides are alginate, carrageenan, ulvan, fucoidan and laminarin. These are reported to be suitable for bioplastic development due to their compatibility with various matrices and film-forming abilities. This review collates the extraction characterisation and applications of these polysaccharides, especially bioplastics. A wide range of applications are demonstrated for these polysaccharides in biomedical products, food packaging, functional foods, nutraceuticals and the pharmaceutical industry. These systems are combined with other polymers and additives for the desired properties. We can certainly see that seaweed derivatives, especially polysaccharides, will grow in economic importance in the coming days.

Author contributions

All authors contributed equally.

Conflicts of interest

There are no conflicts to declare.

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