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Environmentally benign alginate extraction and fibres spinning from different European Brown algae species☆

Mariana P. Silva [a], Ishrat Jahan Badruddin [b], Thierry Tonon [a], Sameer Rahatekar [b], Leonardo D. Gomez [a,*]

[a] Centre for Novel Agricultural Product, Department of Biology, University of York, Wentworth Way, York YO10 5DD, United Kingdom
[b] Enhanced Composites and Structures Centre, School of Aerospace, Transport and Manufacturing, Cranfield University, Bedfordshire MK43 0AL, United Kingdom

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ABSTRACT

Applications of natural fibres are expanding, and sustainable alternatives are needed to support this growing demand. We investigated the production of fibres using alginates from *Saccharina latissima* (SAC), *Laminaria digitata* (LAM), *Sacchoriza polyschides* (SACC), and *Himanthalia* spp. (HIM). After extraction (3 % *w/v* biomass) using a sustainable protocol based on citric acid, crude alginate represented 61–65 % of the biomass dry weight for SAC and LAM, and 34–41 % for SACC and HIM when experiments were performed at small scale (1.5 g of starting material). Interestingly, scaling-up extraction (60 g of starting material) decreased yields to 26–30 %. SAC and LAM alginates had the highest M/G (mannuronic acid/guluronic acid) ratios and molecular weights when compared to those from SACC and HIM (M/G:1.98 and 2.23, MW: 302 and 362 kDa, vs 1.83 and 1.86, 268 and 168 kDa). When the four types of alginates were tested for spinning fibres cross-linked with $CaCl_2$, only SAC and LAM alginates produced fibres. These fibres showed no clumps or cracks under stretching action and presented a similar Young's modulus (2.4 and 2.0 GPa). We have demonstrated that alginate extracted from *S. latissima* and *L. digitata* can be successfully spun into functional fibres cross-linked with $CaCl_2$.

1. Introduction

The global market for natural fibres is projected to increase substantially in the next five years and this growth is driven by concerns in the public regarding the biodegradability of synthetic fibres, notably in North America and Europe. Although the main demand for natural fibres is for the manufacturing of textiles, their applications are currently expanding to other industries, including automobile and construction. The most abundant natural fibre in the world is cotton, with China, India and the US being the main producers. Despite the predominant role of cotton in the market of natural fibre, its production has been declining over several decades. This was initially due to replacement by synthetic fibres, and more recently to competition for land use with food farming. Hemp and jute have recently regained momentum as alternative sources of natural fibres but growing these crop plants still require arable land and irrigation. In this context, farmed seaweeds, and in particular brown algae (Phaeophyceae), have attracted attention because their cultivation does not require fresh water or arable land, and these organisms have higher growth rates and higher yield when compared to land plants [1]. In line with this, several research projects are currently focusing on the improvement of cultivation techniques for seaweed farming and harvesting, on the implementation of biorefinery processes, and on the development of seaweed-derived products for different industries [2,3].

Polysaccharides and carbohydrates can represent >50 % of seaweed biomass [2]. Alginates and fucose containing sulfated polysaccharides (FCSPs) are the main polysaccharides forming the cell wall of brown algae. Structurally, alginates consist in a linear copolymer block of 1,4-linked β-D-mannuronic acid (ManA) and α-L-guluronic acid (GluA), that can be arranged in homopolymeric (GG and MM) and heteropolymeric (MG) blocks. Guluronic acid and mannuronic acid are stereochemically different due to their difference at C-5. Alginate physical properties depend on several different key factors in which M and G contents play a crucial part. The MM blocks form a relatively straight polymer, linked di-equatorially at C-1 and C-4; whereas the GG blocks are buckled, linked from di-axial groups at both C-1 and C-4 [4–6]. Alginates have well characterized thickening and gel-forming properties and are

☆ *In memory of Professor Simon McQueen-Mason.*

* Corresponding author.
E-mail address: leonardo.gomez@york.ac.uk (L.D. Gomez).

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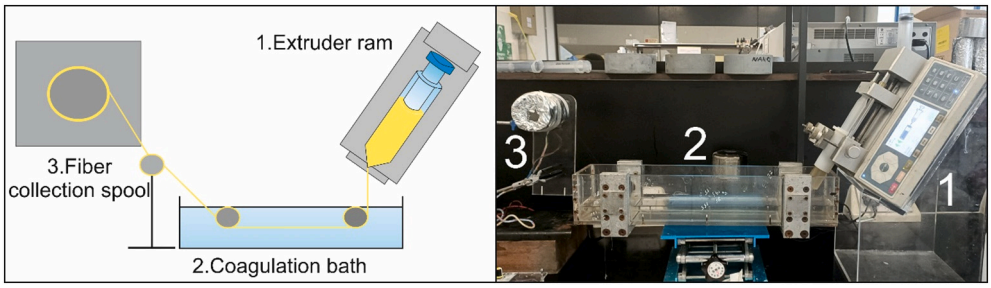

Fig. 1. Lab built wet-spinning equipment for fibre preparation.

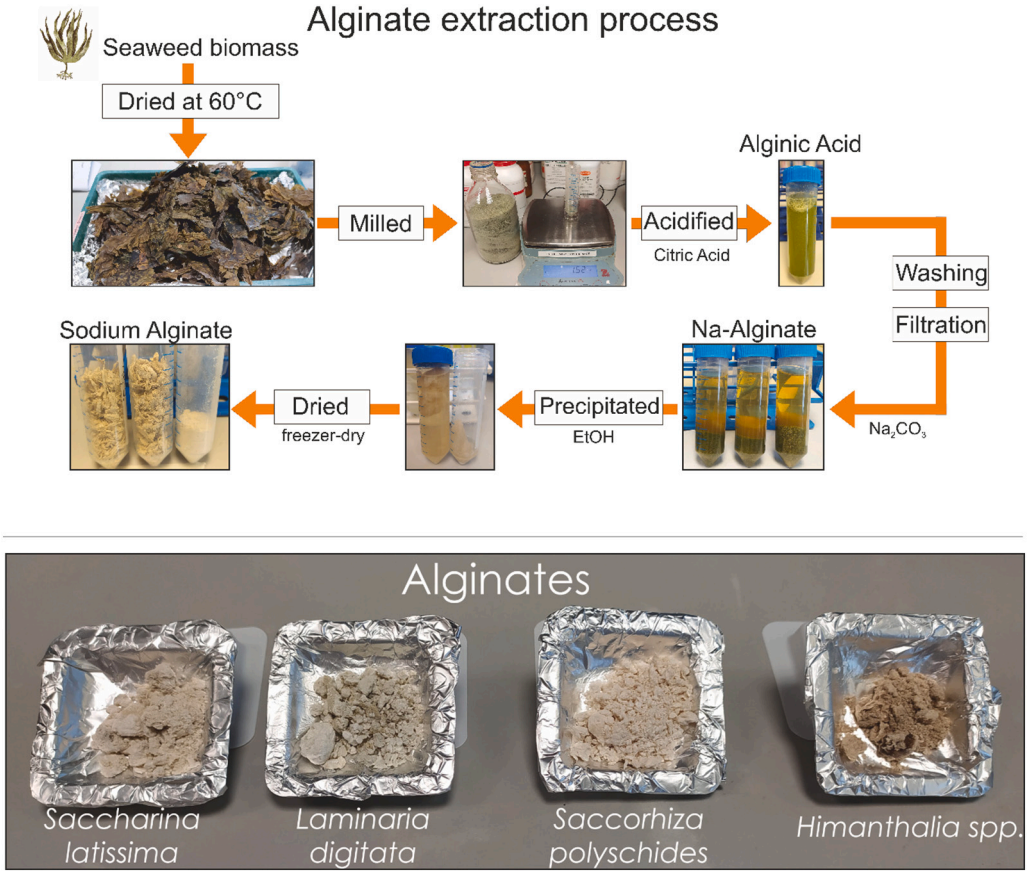

Fig. 2. Alginate extraction from *Saccharina latissima, Laminaria digitata, Sacchoriza polyschides*, and *Himanthalia* spp.

Table 1
Yield, monosaccharide composition and M/G ratios of alginate from *S. latissima* (SAC), *L. digitata* (LAM), *S. polyschides* (SACC), *Himanthalia* spp. (SACC) and *Himanthalia* spp. (HIM) and commercial alginate determined by HPAEC.

Species	Crude alginates yield (%) ± S.E.		Monosaccharide (mol%)											ManA/GulA
	1.5 g	60 g	GulA	ManA	Fuc	Ara	Rha	Gal	Glc	Xyl	Man	GalA	GluA	
SAC	61.14 ± 4.52	29.87 ± 1.47	28.56	56.64	4.55	0.00	0.00	4.11	0.96	1.79	0.00	0.00	3.38	1.98
LAM	64.73 ± 1.28	36.74 ± 7.36	25.60	57.07	6.29	0.00	0.00	3.71	1.31	2.47	0.78	0.00	3.03	2.23
SACC	34.35 ± 0.06	26.44 ± 3.56	31.77	58.00	2.78	0.00	0.00	1.43	1.01	2.15	0.63	0.00	2.44	1.83
HIM	41.41 ± 2.89	32.44 ± 0.92	31.28	58.19	4.31	0.00	0.00	1.33	0.00	3.05	0.44	0.00	1.41	1.86
Sigma-Aldrich	–	–	34.52	63.60	0.73	0.00	0.00	0.10	0.48	0.60	0.03	0.00	0.00	1.84

applied extensively for varied industrial purposes. Fibres derived from alginate are also widely use in wound management due to their well-documented water retention and biocompatibility properties [7]. Moreover, the capacity of alginate fibres to interact with metal, pectin, CM-cellulose and a variety of chemical groups has been exploited for the production of antibacterial fibres and of different types of functional composites [5,7]. Commercial alginate is typically extracted from the brown algae *Laminaria*, *Macrocystis* and *Ascophyllum*. This extraction is a multi-stage process, including the treatment of the algal biomass with formaldehyde to remove pigments, followed by incubation in an acid or

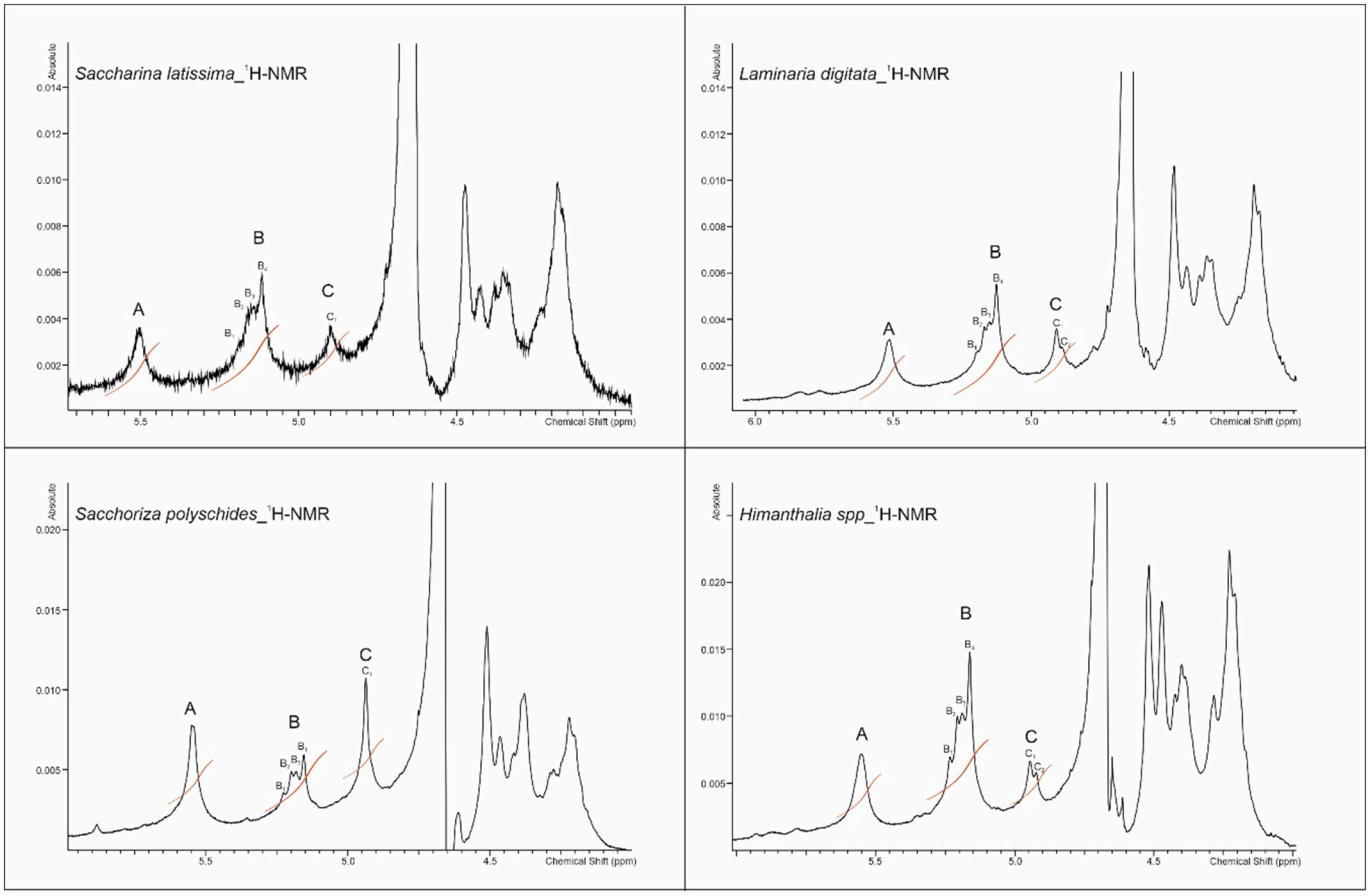

Fig. 3. ^{1}HNMR spectrum (90 °C) of sodium alginate extracted from *Saccharina latissima, Laminaria digitata, Sacchoriza polyschides*, and *Himanthalia* spp. The ^{1}HNMR spectra show specific peaks of the guluronic acid anomeric proton (G-1) peak A, mannuronic acid anomeric proton (M-1) peak B, and guluronic acid H-5 (G-5) and the C-5 of alternating blocks (GM-5) peak C.

Table 2
Composition of extracted alginates determined by NMR. F_G: guluronic acid ratio; F_M: mannuronic acid fraction; ManA/GulA: mannuronic/guluronic acid ratio; F_{MM}: mannuronic homopolymeric blocks, F_{GG}: guluronic homopolymeric blocks; F_{MG}: heteropolymeric blocks mannuronic/guluronic acid; F_{GM}: heteropolymeric blocks guluronic/mannuronic acid; η: relative abundance of homopolymeric blocks MM and GG ($\eta = F_{GM}/[F_M + F_G]$), $\eta < 1$ with abundance of homo-mannuronic blocks.

Sample	F_G	F_M	ManA/GulA	F_{GG}	$F_{GM} = F_{MG}$	F_{MM}	η
SAC	0.35	0.65	1.89	0.25	0.10	0.56	0.10
LAM	0.30	0.70	2.32	0.29	0.01	0.69	0.01
SACC	0.46	0.54	1.18	0.42	0.04	0.50	0.04
HIM	0.34	0.66	1.95	0.28	0.06	0.60	0.06

alkali solution to breakdown the cell wall, and subsequently addition of sodium carbonate to produce soluble sodium alginate [5,6]. Based on this description, effluents and residues of alginate extraction have to be treated and recycled appropriately to limit the environmental impact of this industrial process.

Materials made of or containing alginates encompass a wide range of applications. Fibres made of this polysaccharide are currently used in the skin care, hygienic products and cosmetic sectors [8]. Other types of fibres, produced by wet spinning of single walled carbon nanotubes reinforced with alginate, are considered for the production of super-capacitors, micro electrodes, biomedical sensors, and artificial muscles [9]. Alginate is also utilised as adhesive to obtain biocomposites reinforced with recycled cotton fibres and wood fibres [10], and to produce thermochromic alginate microfibers using microfluidic spinning [11]. Several studies have investigated the spinning of alginate for making fibres whose properties are modulated by altering conditions of production. In complement to this, alginate fibres can be converted into textiles through several established processes [8,12]. For instance, Chen et al. (2021) used wheel spinning and $CaCl_2$ as a cross-linker to manufacture alginate fibres for applications as wound dressing [13]. Such knitted alginate fibres showed good biocompatibility, low level of cytotoxicity, sustained rate of degradation, and good mechanical performance, making them suitable for wound care applications [13]. In line with this, nitrogen has been used for extruding alginate during spinning in $CaCl_2$ solution to produce homogeneous alginate fibres [14].

This study aimed to investigate the development of a process including an environmentally friendly protocol for the extraction of alginate from brown seaweeds that can be farmed in European coastal waters, and the use of the purified polysaccharides for the production of functional fibres. To achieve this goal, alginates from four different brown seaweed species, *Saccharina latissima, Laminaria digitata, Sacchoriza polyschides*, and *Himanthalia* spp., were extracted and analysed. Then, alginate fibres were produced via wet spinning, and their properties assessed. Characterization of alginate fibres obtained from different brown algae allowed to identify the most suitable brown seaweed feedstock for the production of functional spun fibres.

2. Materials and methods

2.1. Sodium alginate extraction and characterization

Saccharina latissima (SAC), *Laminaria digitata* (LAM), *Sacchoriza polyschides* (SACC), and *Himanthalia* spp. (HIM) samples were collected in

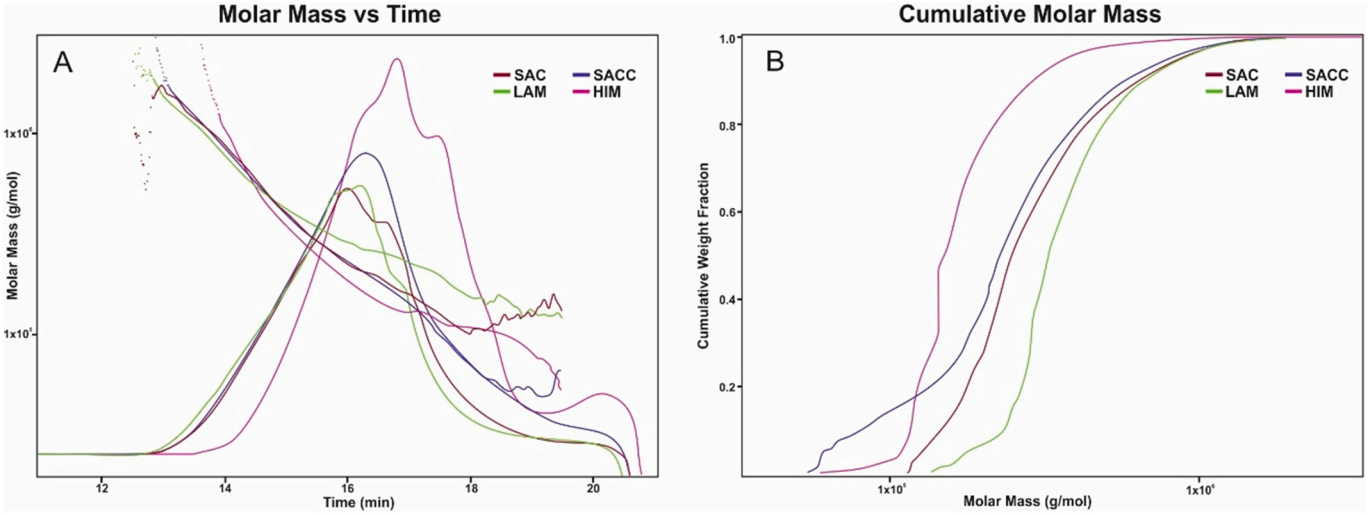

Fig. 4. Alginate SEC-MALLS analysis. A) MW profile and RI chromatogram of sodium alginate from SAC in red, LAM in green, SACC in blue, and HIM in magenta. B) Cumulative weight fraction vs molar mass of sodium alginate from SAC in red, LAM in green, SACC in blue, and HIM in magenta.

Table 3
Alginate molecular weight (MW) averages and polydispersity indices (PI) as determined by SEC- MALLS. PI: polydispersity index is the ratio of the weight-average molecular weight and the number-average molecular weight (Gutierrez et al., 2009).

Sample	MW (kDa)	PI
SAC	302	1.367
LAM	362	1.223
SACC	268	1.659
HIM	168	1.191

Table 4
Viscosity, Coagulation and spinnability of extracted alginates.

Type of alginate	Coagulation	Spinnability
SAC	✔	Good
LAM	✔	Good
SACC	✔	Poor
HIM	✔	Poor

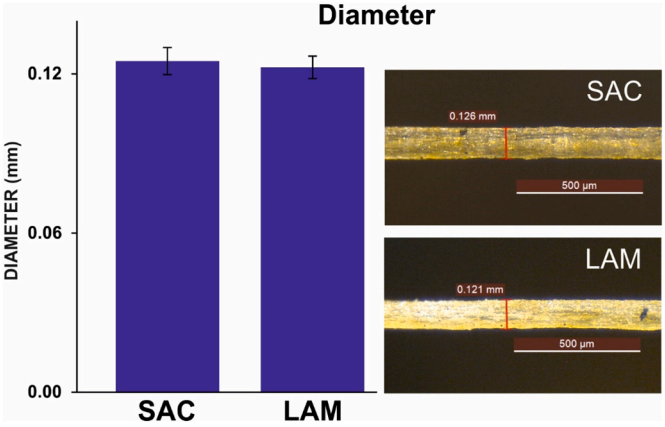

Fig. 6. Mean diameter values of *S. latissima* (SAC) and *L. digitata* (LAM) alginate derived fibres.

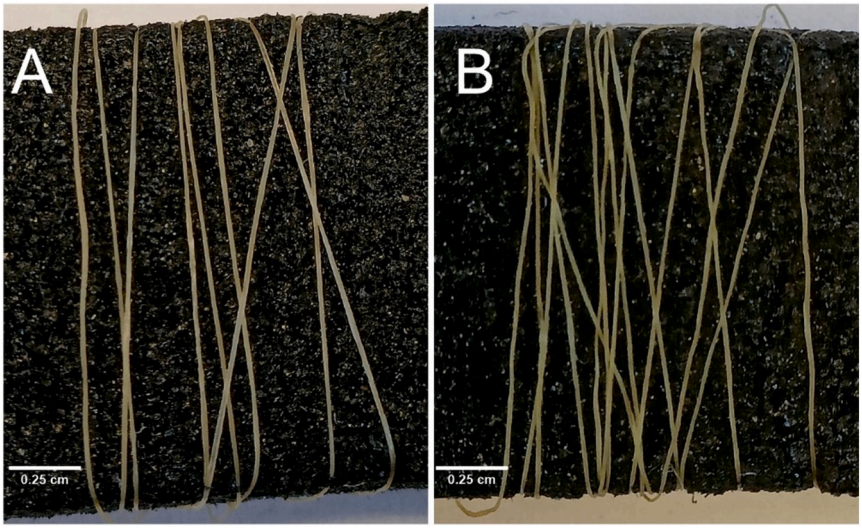

Fig. 5. Dried fibres spun from alginate extracted from *S. latissima* (A) and L. *digitata* (B).

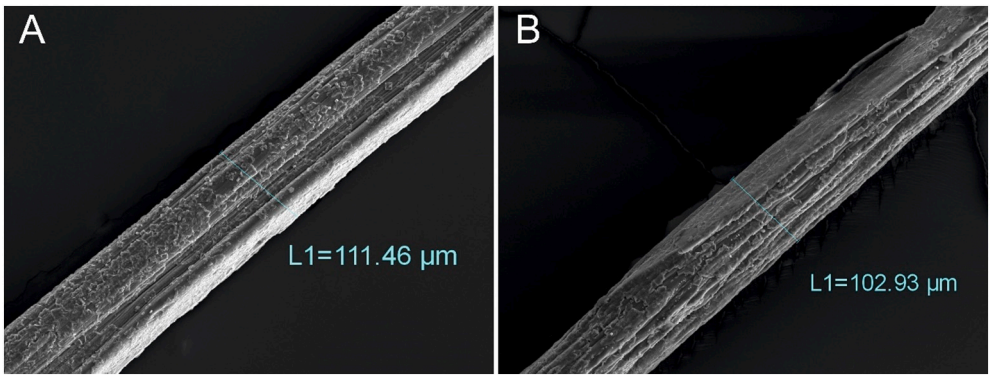

Fig. 7. SEM image of A) *S. latissima* and B) *L. digitata* algintate fibres.

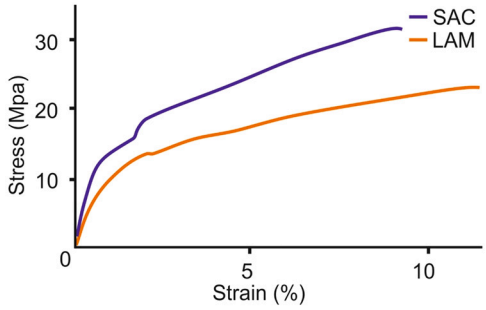

Fig. 8. Stress/Strain curve of SAC and LAM fibres.

Table 5
Mechanical properties of alginate-derived fibres.

Fibre type	Average Youngs Modulus (GPa)	Average Tensile strength (MPa)	Average strain (%)	Average diameter (mm)
LAM	2.0 (±0.3)	26.4 (±5)	12.6 (±3)	0.122 (±0.011)
SAC	2.4 (±0.19)	32.8 (±7.7)	9.4 (±1.6)	0.124 (±0.013)

May 2021 from Porthallow, SAC and SACC, Coverack, LAM, and Lowland Point, HIM, England. The biomass was dried for ~30 h at 40 °C using a dehumidifier and heater, and then milled in a hammer mill through a 1 mm sieve [6]. Commercial sodium alginate was purchased from Sigma-Aldrich (W201502) to use as control in high-performance anion exchange chromatography (HPAEC).

Alginates were extracted as previously described with slight modifications [15]. Milled seaweed biomass (3 % *w/v*) of SAC, LAM, SACC, and HIM were acidified with 4 % citric acid solution under shaking (200 rpm) overnight at 30 °C. The seaweed biomass was filtered (Miracloth 22–25 µM.), washed with distilled water, and collected. It was then re-suspended in 2 % Na_2CO_3 solution (27 mL of Na_2CO_3 per gram of filtered seaweed biomass) and shaking (200 rpm) for 24 h at 30 °C. The soluble fraction was collected by centrifugation 45 min at 3500 rpm [6,16,17]. The alginates were precipitated with absolute ethanol (1:2 *v/v*). The precipitated alginate was collected through filtration and dried using a freezer-dry overnight. The crude alginate yield was calculated using the following equation [18,19]:

$$\text{Alginate yield}\,(\%) = [\text{dry weight of obtained alginate}/\text{dry weight of sample}] \times 100.$$

2.2. Characterization of sodium alginate

2.2.1. Total monosaccharide composition

The monosaccharide composition of alginates was analysed using High-Performance Anion Exchange Chromatography (HPAEC) (Dionex, UK) according to the methodology previously described [20]. A calibration curve obtained for a mixture of 11 monosaccharides -Fucose (Fuc), Arabinose (Ara), Rhamnose (Rha), Galactose (Gal), Glucose (Glc), Xylose (Xyl), Mannose (Man), Galacturonic Acid (GalA), Guluronic Acid (GulA), Glucuronic Acid (GluA) and Mannuronic Acid (ManA)- was used for determination and quantification.

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR spectroscopy analysis was performed on a JEOL JNM-ECS400A spectrometer (JEOL, Peabody, MA, USA) at a frequency of 400 MHz for ^{1}H. All samples were first dissolved in D_2O and freeze-dried to replace exchangeable protons with deuterium. The freeze-dried samples were then dissolved in D_2O at a 20 mg mL^{-1} concentration. Acquisition parameters were: $T = 90$ °C and 128 scans. Samples were not pre-hydrolyzed [21].

2.2.3. Molecular weight analysis

The molecular weight (MW) of alginates was determined by size exclusion chromatography - multi-angle laser light scattering (SEC-MALLS) analysis. The system comprised a Wyatt HELEOS-II multi-angle light scattering detector and a Wyatt rEX refractive index detector linked to a Shimadzu high performance liquid chromatography (HPLC) system (SPD-20A UV detector, LC20-AD isocratic pump system, DGU-20A3 degasser and SIL-20A autosampler) at room temperature (20 ± 2 °C). Solvents were filtered (0.2 µm) before use, and a further 0.1 µm filter was present in the flow path. The running buffer was 25 mM phosphate pH 7.15 (0.2 µm filtered). Samples were dissolved in water at ~2 mg mL^{-1} and used directly. The column (PL-aquagel-OH Mixed-H 8 um 300 × 7.5 mm) was equilibrated with at least two column volumes of buffer before use, and the flow was maintained at the working rate until baselines for UV, light scattering and refractive index detectors were stable. Flow rate was 0.5 mL min^{-1} for 60 min (59 min data collection) and the UV detection was set at 280 nm. Sample injection volume was 100 µL and the injection mass ~ 200 µg (nominal). Shimadzu LabSolutions software was used to control the HPLC and Astra 7 software for the HELEOS-II and rEX detectors. The Astra data collection was 1 min shorter than the LC solutions run to maintain synchronisation. Blank buffer injections were used to check for carry-over between sample runs. Data was analysed using the Astra 7 software. MWs were estimated using the Zimm fit method with degree 1. A value of 0.182 was used for protein refractive index increment (dn/dc).

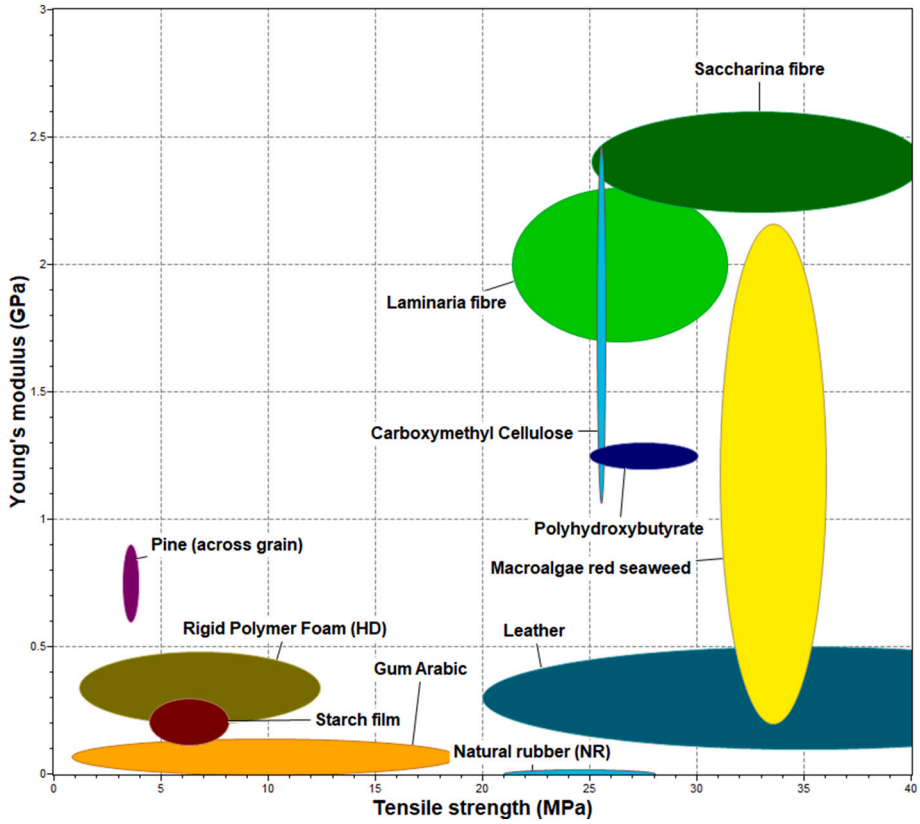

Fig. 9. Comparison of the Young's Modulus and tensile strength of *Laminaria* and *Saccharina* alginate with different polymers.

2.3. Preparation of alginate solution for spinning

For the four species investigated, individual alginate solutions at 8 % *w/v* were prepared by heating at maximum temperature of 40 °C and stirring for 6 h in a fume hood. After alginate dissolution, each solution was transferred into a 20 mL Luer Lock syringe and labeled. The loaded syringes were degassed to remove any bubbles and placed in a vacuum oven for 6 h. For cross-linking, a 4 % (*w/v*) calcium chloride ($CaCl_2$) solution was prepared and transferred to a bath for the wet-spinning process.

2.4. Wet spinning of alginate fibres

For the fibre spinning of the alginate solutions, a lab-built wet spinning equipment consisting of a syringe pump, a $CaCl_2$ bath and a motor regulated winding drum was used as shown in Fig. 1. The properties of the fibres can be modulated using a range of process parameters such as the extrusion die diameter [22], the composition of the solvent used in the fibre coagulation bath [23,24], fibre extrusion speed [25] and fibre winding speed [26]. All these parameters will affect the final fibre diameter, fibre morphology and the resulting physical properties [27]. In the present study we kept the fibres spinning parameters constant for all species to compare properties of fibres spun from different types of alginate sources.

Individual alginate solutions were injected into the $CaCl_2$ bath at fixed extrusion velocity of $V_1 = 20$ mL h^{-1} using a 0.9 mm diameter needle while the winding drum was continuously winding the fibres at winding velocity, $V_2 = 30$ rpm (Fig. 1). The Draw ratio, $DR = V_2/V_1$, is the stretching degree applied to the fluid filament. After spinning, the fibres were air dried for 24 h and stored in airtight bags for further analysis.

2.5. Spinnability

SAC, LAM, SACC and HIM alginate solutions were extruded in a $CaCl_2$ bath, and two main parameters were assessed during the fibre spinning process: coagulation ability, and spinnability. Coagulation is the consolidation of the extruded alginate solution into a fibre as it enters the coagulation bath, and spinnability is the ability to continuously stretch the alginate solution into fibres during the fibre winding process. If incomplete coagulation occurs, or if the fibres are broken due to stretching action, the material would be considered as of poor spinnability.

2.6. Diameter measurements

The spun fibres were observed under 5× magnification to measure their diameter and to study their morphology. Images were acquired for each 1 cm^2 sample at three different locations using a Leica (Nikon Eclipse ME600) microscope and their mean diameter was measured using the LAS Core software which was further used to calculate the standard deviation in each fibre sample.

2.7. Scanning electron microscopy (SEM)

SAC and LAM dried fibres were coated with 10 nm gold in a vacuum evaporator and their structures were examined at 20 kV and 1000× magnification with a VEGA3 TESCAN (UK SEM microscope).

2.8. Mechanical properties

Tensile testing of fibres was performed using a Leica S9D microtest tensile stage controller and the Deben microtest software V6.3.4 at 25 °C in a 5 N load cell under a constant deformation rate of 2 $mm.min^{-1}$. To perform these tests, three different points for eight fibre samples

obtained for each type of alginate were selected using a gauge length of 10.2 mm. The fibres were pasted onto holding tabs to reduce the clamping impact. The fibre breaking point yielded the ultimate tensile strength and strain. Stress-strain curves were obtained using the fibre cross-sectional area measured by microscopy. Young's modulus was calculated from the linear slope portion of the stress-strain curve before yield point. The comparison of the alginate fibres with other polymers was done using the Cambridge engineering Selector Software (CES EduPack software, Granta Design Limited, Cambridge, UK, 2009).

3. Results and discussion

3.1. Sodium alginate extraction and characterization

3.1.1. Determination of monosaccharide composition in extracted alginate by HPAEC

Alginates and fucose containing sulfated polysaccharides (FCSPs) represent the most abundant components in the brown algae cell walls. Both types of polysaccharides play an important role in cell wall rigidity and in the adaptation to the environment [28]. The physical properties of alginates depend on several key factors, including the ManA and GulA content and their position in the polysaccharide chains. M-M blocks binds di-equatorially at C-1 and C-4, while the G-G blocks are linked to di-axial groups of C-1 and C-4 [6]. Depending on the species of algae and the extraction method used, alginates may vary in molecular weight and in the frequency of GG, MM and GM blocks, both parameters having a significant effect on the properties of alginate fibres [8]. In our study, sodium alginates were extracted considering an environmentally friendly protocol as it used citric acid instead of formaldehyde, followed by sodium carbonate treatment and precipitation of alginates by ethanol (Fig. 2). At small scale (1.5 g of dried biomass as starting material) extraction was very efficient, producing between 61 and 65 % (*w*/w) of crude alginate for SAC and LAM, and 34–41 % for SACC and HIM (Fig. 2 and Table 1). After the small-scale extraction, the process was scaled up to start with 60 g of dried seaweed biomass. This reduced the yield of crude alginates to 30 % for SAC, 37 % for LAM, 32 % for HIM and 26 % for SACC, with significant quantities of alginate left in the residual biomass. In spite of this, the yield was similar or higher than those reported using other protocols [29]. The ManA and GulA content and the presence of other monosaccharides is important to understand the purity of alginates for different applications [30]. HPAEC (Dionex) was used for the determination of monosaccharides and uronic acids content in the alginate fractions, and the results are shown in Table 1 and Supplementary Fig. 1. ManA and GulA, as well as other constituents such as Glc, Gal, Xyl, Man, GalA and Fuc were present in alginates from SAC, LAM, SACC, HIM and in the commercial alginate. GulA and ManA were the most abundant monosaccharides, accounting for 25–65 % of all monosaccharides (Table 1). The ManA/GulA ratios were 1.98 for SAC, 2.23 for LAM, 1.83 for SACC and 1.86 for HIM, and similar to the value obtained for the commercial alginate (1.84, Table 1). The relative abundance of the other monosaccharides depended on the species considered. Typically, apart ManA and GulA, the most abundant was Fuc and Gal in SAC and LAM, GluA in SACC, and Xyl in HIM (Table 1). Fuc, Glc and arabinogalactan residues have been reported to remain in alginate after extraction [31]. Glc and Fuc can be attributed to the presence of cellulose and FCSPs respectively [30,32].

3.1.2. Analysis of alginate blocks by NMR spectroscopy

Structural characterization of the alginate blocks was performed by $^{1-}$HNMR spectroscopy [21]. The ManA and GulA molar fractions, F_M and F_G values, and F_{GG} (guluronic homopolymeric blocks), F_{MM} (mannuronic homopolymeric blocks), F_{MG} (heteropolymeric blocks mannuronic/guluronic acid) and F_{GM} (heteropolymeric blocks guluronic/mannuronic acid) frequencies to determine the ManA/GulA ratio of alginate were established according to Soukina et al. [33]. Fig. 3 shows a representative $^{1-}$HNMR spectrum used to determine the ManA/GulA composition of sodium alginate by integration of signal areas of GulA peak 5.4–5.6 ppm ($H_{G\text{-}1}$, A), M peak 5.1–5.25 ppm ($H_{M\text{-}1} + H_{GM\text{-}5}$, B), and GulA peak area ($H_{G\text{-}5}$, $H_{MG—5}$C) 4.8–5.0 ppm. The values in Table 2 indicate that M (FM) was the main component of alginates in all four species. To determine the abundance of homopolymeric or heteropolymeric blocks, the parameter η (η = FGM/[FM + FG]) was calculated [34]. Values of the η parameter lower than 1 indicate that the homopolymeric block is abundant. SAC, LAM, SACC and HIM alginates were characterized by ManA/GulA ratios of 1.18–2.32 and η < 1 with abundance of F_{MM} blocks (Table 2). High ManA/GulA ratios are associated with alginate that produces elastic gels, whereas low ManA/GulA ratios provide brittle gels [33,35,36]. The alginates isolated in this study showed a high content in homomannuronic blocks (F_{MM}) and consequently have the potential to form elastic gels.

3.1.3. Molecular weight analysis by SEC-MALLS

Sodium alginates from SAC, LAM, SACC and HIM were characterized by SEC-MALLS to determine the molecular weight and polydispersity index (PI) (Fig. 4). Although the profiles obtained for the four alginates are similar, the main difference was that HIM alginate shows lower average MW compared to the other extracts. The SAC and SACC alginates were very similar, only diverging in MW for material eluting after 17 min and below 200 kDa. LAM alginate was similar to the SAC and SACC alginates in the high MW components but showed higher MWs for the material eluted later (Fig. 4A). Fig. 4B shows cumulative weight fraction as a function of MW. SAC and SACC alginates were similar except that the SACC had more material at low MW which leads to a larger polydispersity; LAM alginate had more material in the range above 200 kDa, and HIM alginate was mostly below 200 kDa (Table 3). All alginates can be considered as homogeneous because their PI is less than two [37], in agreement with NMR and HPAEC results. The MW of alginates from SACC and HIM was lower than SAC and LAM (Table 3). The content of GulA and ManA, the ManA/GulA ratio and molecular weight suggested that the alginates from SAC and LAM have high quality and potential to produce fibre for the textile industry when compared to alginate extracted from SACC and HIM.

3.2. Spinnability

Table 4 shows the viscosity, the coagulation and spinnability of alginates from SAC, LAM, SACC and HIM. All four alginates showed different degrees of coagulation in the $CaCl_2$ bath, and only alginates from SAC and LAM could actually be stretched and spun into continuous fibres due to the stretching action. Alginates from SAC and LAM showed coagulation ability and good spinnability (defined as ability of the alginate solution to be stretched and spun into continuous fibres), whereas SACC alginates exhibited coagulation ability but poor spinnability. HIM alginates showed coagulation ability and low spinnability. These results correlate with the content of GulA and ManA, the ManA/GulA ratio, and MW obtained for the four species (Table 3). It is well known that the viscosity increases with the molecular weight [38]. The spun SAC and LAM fibres were air-dried and used for further characterization (Fig. 5).

3.3. Microscopy analysis of fibre morphology

The diameter of fibres was determined by optical microscopy and the results are presented in Fig. 6 for SAC (A) and LAM (B). The fibres appear to show no significant variation in their diameter across the fibre at various cross-sections of different lengths and were continuous without any fibre breakage. No sign of larger clumps of alginate or cracks in the fibres were observed. We tested eight different fibre samples and diameter for each of those was measured at three different points. Variations in the mean diameter of LAM samples ranged between 100 and 136 μm, and 100–140 μm for the SAC samples (Fig. 6). The details of the fibre mean diameter for each sample are described in supplementary

Table 1 and Table 2.

3.4. SEM analysis of alginate fibres

SEM images of LAM and SAC alginate derived fibres are shown in Fig. 7. Both fibres were similar and presented particles on their surface as a result of $CaCl_2$ aggregation. The formation of grooved structures on both fibres samples was attributed to the diffusion of Ca^{2+} from the interior of the alginate structure and conjugation with GulA units to form an ionic bond-crosslinked "egg shell" structure [11]. Initially, the fibre surface solidified as a cortex, and subsequently Ca^{2+} passes through the cortex and reacts with the spinning solution. As a result, the surface of the fibre will show "grooves" and tend to be denser.

3.5. Mechanical properties

The stress/strain curves obtained from the tensile test are presented in Fig. 8. Fibres produced from LAM alginates showed a linear response, followed by plastic deformation and net failure at 11.41 % elongation. Similarly, SAC fibres initially showed rigid response and then plastic deformation leading to failure at 9.47 % elongation. A similar behavior has been previously observed for other biopolymer fibres [39–42]. The stretching action caused by the wet-spinning process produces fibres with high molecular alignment [24]. As a result of this improved molecular alignment, the mechanical properties of SAC and LAM alginate fibres such as the Young's modulus and tensile strength (Table 5) were better than other biopolymers such as gum arabic, starch film, polyhydroxybutyrate, and carboxymethyl cellulose (which are not in fibrous form) (Fig. 9). Thermoplastic starch films produced by casting have lower Young's modulus and tensile strength, as well as lower molecular alignment than alginate. This is due to starch's low molecular weight and amorphous rather than fibrous structure. Similarly, films of carboxymethyl cellulose/starch reinforced with cellulose nanocrystals, fish gelatin films conjugated with carboxymethyl cellulose, and gum arabic films [43] have low mechanical properties. Polyhydroxybutyrate and vegetable fibre composites have also shown lower mechanical strength due to lower molecular weight [44].

4. Conclusion

Our results showed that alginates extracted from different species of brown algae with potential for farming in Europe present different physical and mechanical properties that affect the qualities of the derived fibres. Future work will test different cross-linking agents such as ferulic acid or citric acid to enhance tensile strength of alginate fibres. Modification of their mechanical properties would allow a better control of their biodegradability and of their structural integrity to expand their uses in the manufacturing of textile and other industries.

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CRediT authorship contribution statement

Mariana P. Silva: Conceptualization, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Ishrat Jahan Badruddin:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Thierry Tonon:** Conceptualization, Writing – review & editing. **Sameer Rahatekar:** Conceptualization, Writing – review & editing, Supervision, Resources. **Leonardo D. Gomez:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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