

Comparative study of effects of various seaweed parietal polysaccharides on rheological, mechanical and water-durability properties of earth-based materials

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To cite this version:

Yasmine Autem, Nathalie Bourgougnon, Simon Guihéneuf, Arnaud Perrot. Comparative study of effects of various seaweed parietal polysaccharides on rheological, mechanical and water-durability properties of earth-based materials. Materials and structures, $2023, 56$ (6), pp.108. $10.1617/s11527-$ 023-02195-9 . hal-04319995

HAL Id: hal-04319995 <https://hal.science/hal-04319995v1>

Submitted on 20 Dec 2024

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- **Comparative study of effects of various**
- **seaweed parietal polysaccharides on**
- **rheological, mechanical and water-durability**
- **properties of earth-based materials**
- **1,2Y. Autem, ¹N. Bourgougnon, ²S. Guihéneuf*, ²A. Perrot**
- ***** *Corresponding author*
- Yasmine Autem
- *¹ LBCM, Laboratoire de Biotechnologie et Chimie Marines, EA3884, UBS, IUEM, F-56000 Vannes, France*
- *2 IRDL, UMR CNRS 6027, Université de Bretagne Sud – BP 92116, 56321 Lorient Cedex, France*
- E-mail: autem.e2105126@etud.univ-ubs.fr
- Orcid iD:
-
- Nathalie Bourgougnon
- *¹ LBCM, Laboratoire de Biotechnologie et Chimie Marines, EA3884, UBS, IUEM,*
- *F-56000 Vannes, France*
- E-mail: nathalie.bourgougnon@univ-ubs.fr
- Orcid iD: 0000-0001-7755-3357
-
- Simon Guihéneuf (corresponding author)
- *2 IRDL, UMR CNRS 6027, Université de Bretagne Sud – BP 92116, 56321 Lorient*
- *Cedex, France*
- E-mail: simon.guiheneuf@univ-ubs.fr
- Orcid iD: 0000-0001-6591-1858
-
- Arnaud Perrot
- *2 IRDL, UMR CNRS 6027, Université de Bretagne Sud – BP 92116, 56321 Lorient Cedex, France*
- E-mail: arnaud.perrot@univ-ubs.fr
- Orcid iD: 0000-0002-7105-4212
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Declarations

Funding

- The authors would like to thank IUEM (Institut Universitaire Européen de la Mer)
- who funded this study.

Conflicts of interest

The authors declare no conflict of interest.

Availability of data and material

- The data that support the findings of this study are available from the corresponding
- author, S. G., and the first author Y.A. upon reasonable request.

Authors contributions

- Conceptualization, N.B., A.P.; S.G.; Validation, Y.A., N.B., S.G., A.P.;
- Investigation, Y.A., S.G., A.P.; Writing-original draft, Y.A.; Writing-review and
- editing, N.B., S.G., A.P.; Funding, N.B, A.P.

Abstract

 In Brittany, invasive algae represent a real problem, unbalancing local ecosystems and threatening the economy and tourism, with massive strandings, especially in summer. The valorization of invasive algae in green processes and materials such as ecological building materials could represent a real opportunity to try to control the spread of these species. Raw earth is a locally sourced building material, non- toxic and sustainable. In this work, we propose then to compare the effect of four invasive Brittany seaweeds, exotic or indigenous, on the fresh state and hardened properties of raw earth material. In particular, we investigated the performance of *Polyopes lancifolius, Solieria chordalis, Ulva sp*. and *Sargassum muticum* on the compressive strength, water resistance and extrudability of the raw earth material. Several forms of seaweed extracts were tested, raw seaweeds dried and ground, freeze-dried hot water extracts and extracted polysaccharides. Our results showed that the incorporation of *S. chordalis* and *S. muticum*, in the freeze-dried form or

- polysaccharides, allows a 3-fold increase in the compressive strength and a better resistance to water.
- *Keywords: Invasive seaweeds, Polysaccharides, Raw earth construction,*

Compressive strength, Water durability, Extrusion

1. Introduction

 Global warming, environmental degradation and pollution are among the major concerns for the decades to come. The construction sector, with its extensive need of natural materials like sand or gravel for concrete production [1, 2], is responsible for resources overconsumption and generation of large quantities of greenhouse gases and wastes [3]. The production of cement-based materials, with high energy consumption and carbon footprint is one of the main causes of pollution [4]. The development of less polluting construction techniques and materials, using local and sustainable resources, is now required to meet the growing need for housing and equipment of our societies (United Nations, Department of Economic and Social Affairs, World population prospects Highlights, 2019). In this context, earthen construction could be one of the solutions. Earthen construction is a traditional technique that has been used for thousands of years across the world, but was within a certain limit neglected in the last century due to the industrial development of steel and concrete building that ensures better mechanical performance, production rate and reproducibility [5]. Yet this material presents some advantages: it has a low environmental impact, it is recyclable and available locally [6] and presents good hygrothermal [7] and sound insulation properties. However, its water sensitivity is often quoted as its main weakness related to durability because humidity can alter the material and strongly reduce its mechanical properties [8]. However, the ability of this material to adsorb and release moisture from the atmosphere of a building and regulate its indoor temperature and humidity is a strong asset. Nowadays, the development of earthen construction is still limited due to limited industrial implementation and drying times and by the difficulty to achieve a mix-design that allows for both fast processing and sufficient strength at dry state [9].

 An often-quotes method to improve the mechanical and water durability properties of raw earth is its stabilization with cement or lime [10, 11]. But these stabilisers are non-renewable, present large carbon footprint and require high energy consumption. New alternatives to these stabilisers inspired from vernacular earthen construction techniques must be developed, that offer more environmentally friendly solutions. Several organic additives have been used historically in the production of earthen buildings, depending on what was locally available, such as fibres, seaweed, barks, fruits, oil [12]. With the purpose to optimize mechanical properties, to reduce the water sensitivity and to improve existing or develop new and more efficient processing methods such as 3D printing, extrusion or poured earth, several bio-based additives such as xanthan gum, linseed oil, ovalbumin, casein, alginates or tannins have been already studied [9] [13].

 Over the past few decades, various macroalgae have been introduced in Brittany. Among these species, *Polyopes lancifolius* and *Sargassum muticum*, both native from Asia, were probably introduced in Brittany via the imports of Pacific oysters (*Crassostrea gigas*). *P. lancifolius* red algae (*Halymeniales*) has been first observed in the gulf of Morbihan during the summer of 2008 [14] and *S. muticum* brown algae (*Fucales*) has been first observed in France in 1980 at Brest and Port Blanc [15]. *Ulva sp.* and *Solieria chordalis* native macroalgae have developed significantly in recent years as a result of global warming and eutrophication of the marine waters mainly due to land runoff, with significant strandings on Brittany beaches. *Ulva sp.* green seaweeds (*Ulvales*) mass blooms have been frequently reported during spring and summer in semi-enclosed lagoons since 1970 but also along beaches largely open to the sea and subject to a strong tidal movement [16]. 100 000 tons of green stranded seaweeds are collected each year in Brittany. *S. chordalis* red seaweed (*Gigartinales*) appears every year from June to November in south Brittany, on the peninsula of Rhuys [17]. In Morbihan, up to 15 000 tons

per year of red stranded seaweeds, essentially *S. chordalis* are collected.

 Worldwide, seaweeds have been increasingly exploited for their ability to produce compounds of interest. The use of invasive species to obtain natural compounds presents therefore a two-folded opportunity: a high availability of the biological material and through specimen collection, mitigation of negative effects caused by invasive species, contributing for ecosystem integrity and sustainability. Among all these compounds of interest, cell wall polysaccharides are used in a wide range of applications, particularly in the food industry [18] and pharmaceutical fields [19, 20], for their capacity to hold water, form gels and stabilize emulsions. They have a biological function similar to that of hemicellulose in terrestrial plants, but with higher flexibility that can withstand strong ocean waves and currents. Polysaccharides also prevent seaweed desiccation and allow ion-exchange function [21]. Above all, they are non-toxic and biodegradable. Cell wall polysaccharides have also been used in recent years for the production of eco-materials, such as bioplastics [22], aerogels for insulation boards [23] or bioasphalts [24].

 Red algae cell walls are known to be composed of galactans generally built on repeated alternating 1,3 linked alpha-D-galactopyranose and 1,4 linked beta-D- galactopyranose units, and differ in their level and pattern of sulfation, in substitution by methoxyl and/or pyruvate groups and by other sugar residues (anhydrogalactose, glucose, xylose). There are also differences in 3,6- anhydrogalactose content and the configuration of 1,3-linked ol-galactopyranose residues (L for agars and D for carrageenans) [25]. The genus *Solieria* is 140 acknowledged to contain mainly *u*-carrageenan disaccharide repeating units (beta- D-galactose-4-sulfate linked to 3,6-anhydro-alpha-D-galactose-2-sulfate) [26] [17]. *P. lancifolius* matricial cell wall contains mainly κ -carrageenan (beta-D-galactose- 4-sulfate linked to 3,6-anhydro-alpha-D-galactose) with potential presence of agar [32]. Brown seaweed *S. muticum* is the main source of alginate linear co-polymer 145 made of β-D-mannuronic acid (M) and α -l-guluronic acid (G) [28]. In the seaweed, alginate is present as a mixed sodium and/or potassium, calcium and magnesium salt. Ulvan is a cell wall polysaccharide of green seaweed and is mainly composed of sulfated rhamnose, uronic acids (glucuronic acid and iduronic acid) and xylose [29]. All these polysaccharides have the capacity to hold water and form gel. This effect is reinforced by the presence of metal cations (Na+, K+, Mg2+, Ca2+, Fe2+, Fe3+, Al3+, Cr3+), thanks to the capacity of polysaccharides to form bonds with the cations [30, 31, 32]. But these cations can induce different gelling properties and mechanisms with the different chemical structures of all these polysaccharides and difference in sulfation degree.

 In our study, the research is focused on the field of building materials, in particular the incorporation of polysaccharides in raw earth constructions. The objective is mainly to increase mechanical properties and water resistance of this natural but still sensitive material, with the ultimate goal to replace highly polluting cements and concretes. Several studies have demonstrated a stabilizing effect of alginates extracted from brown seaweeds on raw earth construction [33], attributed to the ionic bonding between the alginate polymer and the soil's divalent calcium cations [34], [32]. Even if previous studies have already shown the positive effects of carrageenan extracted from red seaweeds on water durability and mechanical strength of earth material [3], this type of mechanism is not precisely described for agar and ulvan extracted respectively from red and green seaweeds. This paper describes an experimental study aimed at investigating the potential of ingredients/products from invasive Brittany seaweeds to fine-tune its fresh-state properties and to increase mechanical properties of raw earth-based building materials. We propose to evaluate three ingredients/products: 1) at very low cost whole dried seaweed milled, 2) at low cost hot aqueous/water extract that has been lyophilized, 3) at a higher cost purified polysaccharide. Four different species of Brittany seaweeds are studied. The objective is twofold: on the one hand, the development of a low-polluting eco material for building construction, and on the other hand, the valorisation of invasive algae, an available material with negative impacts today.

2. Materials and methods

2.1. Materials

2.1.1. Seaweeds

 S. chordalis were collected in Saint Gildas de Rhuys (latitude: 47°30'0''N, longitude: 2°49'60''O, France) and samples of *P. lancifolius* in Locmariaquer (latitude: 47°33'14''N, longitude: 2°56'23''O), France) in September 2020. *S. chordalis* and *P. lancifolius* are red seaweeds.

Samples of brown algae *S. muticum* were collected in January 2022 in Saint Gildas

de Rhuys (latitude: 47°30'0''N, longitude: 2°49'60''O, France).

Samples of *Ulva* were collected in February 2019 in Sarzeau (latitude:

47°31'39''N, longitude: 2°46'09''O, France).

The chemical compositions of the seaweeds, based on measurements carried out in

the authors institute [27, 35, 36] are provided in Table 1.

189 **Table 1:** Chemical composition of the seaweeds. Values are means \pm SD (n =3). Values with * are

2.1.2. Tested earthen materials

 In order to improve the earth particle size distribution as done in the work of Perrot et al. [35], two reference soils were reformulated in laboratory, using a clayey material (0-80 µm), fine sand (63-200 µm) and normalised sand (0-4 mm). The

¹⁹⁰ significantly different $(p < 0.05)$ [27, 36]

 clayey material is a quarry waste (Clayey mud) originated from Brittany and 197 displays the following properties: A plastic limit (W_P) of 27.7%, a liquid limit (W_L) of 64.6%, a methylene blue value (MBV) of 2.1 and 67.8% of its particles finer than 20 µm (PSD laser diffraction analysis). Fine sand and normalised sand are supplied by Société Nouvelle du Littoral (Leucate, France). The two reformulated soils present the following compositions: Soil n°1 is

composed of 20% clay, 30% fine sand and 50% normalised sand, Soil n°2 is finer

and composed of 40% clay and 60% find sand.

2.1.3. Other materials

 A commercial alginate was used in this study for build-up tests. It was a white powder alginic salt Cimalgin HS3® provided by Cimaprem (Redon) [33]. Hexametaphosphate (HMP) was used as a dispersant for clay particles to make the mixtures more flowable and reduce water content. Minimizing the water ratio in the mixtures allows to increase material density and thus increase its mechanical properties and its resistance to water [9].

2.2. Methods

2.2.1. Seaweed extracts preparation

 All seaweed samples were cleaned from their epiphytes and rinsed with tap water to remove salts and debris. Samples of *P. lancifolius*, *S. chordalis* and *S. muticum* were then dried in an oven at 40°C for 24h. After rinsing, samples of *Ulva sp*. were pre-mixed and freezed.

 Three experiments have been conducted with different treatments realized on each type of seaweeds from raw material (RM), freeze-dried hot water extract (FDE) and 219 purified polysaccharides (PP) (Fig. 1).

 Fig. 1: (a) raw seaweed (*S. muticum*); (b) dried and ground seaweed (*S. chordalis*); (c) : freeze- dried extract (*P. lancifolius*); (d.1) and (d.2) : wet and dry precipitated polysaccharides (*P. lancifolius*)

Raw material (RM)

 Raw material corresponds to the whole dried seaweed milled. For each species, dried seaweeds were powdered in a mixer.

Freeze-dried hot water extract (FDE)

 Freeze-dried hot water extract corresponds to an hot aqueous/water extract that has been lyophilized. The method of preparation of the aqueous extract is specific to each type of alga wall. Polysaccharides from dried seaweed powder (< 5 mm particle sire) were extracted in hot distilled water under agitation, with an initial dry matter content of 5% for *S.chordalis, S. muticum* and *Ulva sp.* and 3.5% for *P. lancifolius.* For *S. chordalis* the heating temperature was 85°C during 4h [26], for *P. lancifolius* it was 80°C for 4h, for *Ulva sp.* It was 90°C for 2h [38] and for *S. muticum* it was 80° C for 4h with the addition of a reagent (Na₂CO₃ 3%) [39]. The total hot water extract was then freeze-dried and the dry extract was crushed in a mixer.

Purified polysaccharide extracts (PP)

 Cell wall polysaccharide extract corresponds to purified polysaccharide extracted from seaweed. Polysaccharides from air-dried seaweed powder (< 5 mm particle size) were extracted in hot distilled water under agitation, with an initial dry matter content of 5% for *S. chordalis, S. muticum* and *Ulva sp.* and 2% for *P. lancifolius*. Process parameters and duration for each seaweed were similar to those applied for freeze-dried hot water extraction. The separation of the soluble extract from insoluble debris was done by centrifugation. The filtrate was poured into 2 volumes of absolute ethanol, with stirring. The precipitate was recovered, washed with acetone and dried under fume hood. Finally, the dry extract was crushed in a mixer. For each of these purified polysaccharide extracts, extraction yield (%) was calculated by equation 3 according to:

250 Polysaccharide yield =
$$
\frac{extracted \text{ polysaccharide weight (dry)}}{\text{initial seawed weight (dry)}} \times 100
$$
 (3)

 The yields of extraction (in % of algal dry weight) of the different polysaccharides 252 from seaweed dried powders with hot water are as follows: 61.8 ± 2.2 (% w/w) for *P. lancifolius,* 13.3 ± 2.2 (% w/w) for *S. chordalis,* 29.6 ± 3.7 (% w/w) for *Ulva sp.* And 29.3 (% w/w) for *S. muticum*. The extraction yield for *S. chordalis* is consistent with the results obtained by Bondu et al. [26] who reported a yield of 14,6%. Kidgell et al. [29] have compiled on their side median extraction yields of 40% for *Ulva armoricana* and 16,6% for *Ulva lactuca*. Mohamed et al. [28] obtained a yield of 20% for alginate extraction from *S. muticum* at 50°C. It must be noted that real extraction yields may be slightly lower than those found as final purification steps were not performed during the extraction procedure and some compounds like pigments, phenols and/or fucoidans must be still present. It was then estimated, for the specimens' preparation used in the different tests on earth, that the concentration of free polysaccharides in the freeze-dried extracts (FDE) and the concentration of polysaccharides present in the seaweed walls in raw seaweed extracts (RM) were identical to the extraction yields determined above. For instance, to aim for a 0.25% concentration of *P. lancifolius* polysaccharide using RM or FDE, we had to add 0.38% of RM or FDE ($\frac{Aimed\ concentration\ (0.25\% \ or \ 0.5\%)}{polysaccharide\ extraction\ yield})$).

2.2.2. Preparation of earth material specimens and testing procedure

Compressive strength and water durability tests

 For the preliminary study, the experimental methodology to prepare the samples is based on the preparation of different mixes of soil, water and specific seaweed extract (raw material, freeze-dried extract, polysaccharides). Mix proportions were adapted for each product to ensure that each batch contained approximatively a polysaccharide equivalent of 0.25% or 0.5% of dry earthen material content (Table 2). The materials were then homogenized in a mortar mixer and hand compacted in moulds (40 mm x 40 mm x 160 mm). Samples were conserved during one week at 277 ambient temperature then dried in an oven at 45° C until weight stabilization. Tests performed on each sample were dry density measurement, compressive strength at dry state and after a five-minutes immersion in water (water durability). Density and compressive strength were determined on one half of each specimen, after breaking them in a three-point bending device, whereas water durability was tested on the second half of each specimen after immersing them in water during 5 minutes. Density of dry specimens was determined by using a hydrostatic balance and compressive strength on dry and wet specimens was determined using a 50 kN loading frame and controlled at a constant displacement rate of 1 mm/min. Tests were also carried out on reference specimens made with soil and different amounts of water. All of the compressive tests were carried out on samples with an aspect ratio of 1 following an adopted procedure in agreement with different French compressive test procedures (AFNOR [NF EN 196-1], AFNOR [XP P 13-901] and AFNOR [NF EN ISO 17892-7]). For the second part of the study, four specimens containing 0.5% of *S. chordalis* polysaccharides and four specimens with *S. muticum* freeze-dried extract containing a polysaccharide equivalent of 0.5 % were prepared using the same methodology as for the preliminary study. Four reference soil specimens were also prepared with 18% of water. After a prior drying phase, specimens were broken in a three-point bending tester. Two halves of specimen were kept in the oven, one half was kept during 5 days at room temperature and humidity in the laboratory, one half was kept during 7 days in a room at a 298 temperature of 22° C and a relative humidity of 80%. Finally, four halves were kept in an atmosphere saturated in moisture. Compressive strength tests were performed on each sample. For samples kept in saturated atmosphere, tests were performed after 24h, 48h, 72h and 7 days as in a previous study [9] in order to see the impact of the water uptake due to environmental ambiance on the material compressive strength.

T18		100		18
T20		100		20
T22		100		22
T ₂₅		100		25
Pp0.25	P. lancifolius PP	100	0.25	22.4
Pp0.5	P. lancifolius PP	100	0.5	26
Pl0.25	P. lancifolius FDE	100	0.38	20.3
PI0.5	P. lancifolius FDE	100	0.77	22.6
Pa0.25	P. lancifolius RM	100	0.38	16.5
Pa0.5	P. lancifolius RM	100	0.77	18.3
Sp0.25	S. chordalis PP	100	0.25	16.5
Sp0.5	S. chordalis PP	100	0.5	16.5
S10.25	S. chordalis FDE	100	1.25	21.9
SI0.5	S. chordalis FDE	100	2,5	25,3
Sa0.25	S. chordalis RM	100	1.25	18.1
Sa0.5	S. chordalis RM	100	2.5	22
Up0.25	$Ulva$ sp. PP	100	0.25	20.8
Up0.5	Ulva sp. PP	100	0.5	22.1
UI0.25	Ulva sp. FDE	100	0.71	21.9
UI0.5	Ulva sp. FDE	100	1.43	23.5
Ua0.25	Ulva sp. RM	100	0.71	18.6
Ua0.5	Ulva sp. RM	100	1.43	20.6
SAp0.25	S. muticum PP	100	0.25	16.5
SAp0.5	S. muticum PP	100	0.5	18.6
SA10.25	S. muticum FDE	100	0.71	16.5
SA10.5	S. muticum FDE	100	1.43	19.2
SAa0.25	S. muticum RM	100	0.71	18
SAa0.5	S. muticum RM	100	1.43	19.7

304 **Table 2:** Samples composition for compressive strength tests (% / dry soil weight)

305 **Structural build-up test**

 The evolution of the consistency of the earth-based materials with time is of importance when considering new processing routes such as poured earth and 3D printing [37] [40]. In order to follow the structural build-up of earth with time, a fall cone penetrometer, which enables to determine the yield stress, is used. The fall cone penetrometer is usually used to determine the consistency limits of soil but can also be used to follow the shear yield strength of soil with time. The end of penetration is reached when the friction forces acting on the cone surface balance the weight of the penetration cone. When the material consistency is liquid or plastic, it is generally considered that the friction stress is equal to the shear yield stress of material [41]. The shear yield stress depends on both cone geometry and penetration depth according to the equation:

$$
\tau_0 = \frac{wg \sin \alpha/2}{\pi (h \tan \alpha/2)^2} \tag{1}
$$

Extrusion tests

 Extrusion is an efficient industrial process that is able to industrially shape building blocks as done for fired blocks [42, 43]. However, extrudability depends on earth materials fresh properties that could not suit the process requirements [44, 45]. Therefore, it is interesting to study the improvement of extrudability of an earth- based material using algae extracts. Extrusion tests were conducted using a ram extruder and a 50 kN loading frame and carried out at a constant velocity of 5 mm/s. The extruder barrel is a vertical stainless-steel barrel with an inlet diameter of 50 mm and a total length of 200 mm. Two die orifice diameters were tested (16 mm and 24 mm). The material is pushed inside the barrel with a Teflon ram. The total extrusion force (F) required to overcome the friction force on the extruder barrel and the shaping force at die outlet is measured. Curves representing the evolution of the total extrusion force (F) versus the remaining billet length (LB) are plotted. In their study, Perrot et al. [46] highlight an example of the curve obtained for a material with a good formulation to be extruded that remains homogeneous during the process. Three different parts are visible on the curve they obtained. The first part corresponds to the flow initiation. During this moment, when the ram begins to move, the material is compacted in the barrel. The extrusion total force increases very strongly and reaches a maximum which corresponds to the beginning of the extrusion process. In the second part of the curve, the extrusion force linearly decreases with the ram movement. As the billet length reduces, the surface of friction between the material and the extruder barrel wall linearly decreases. It is worth noting that if the earth does not show sufficient water retaining properties, the material inside the barrel will consolidate and the extrusion force increase. Such 342 behaviour is not suited for extrusion. The friction stress (K_w) can then be deduced from the slope of the second part of the curve by the following equation:

344
$$
K_w = \frac{1}{\pi D} \frac{dF}{dL_B}
$$
 (2)

 where F (N) is the total extrusion force, LB (m) the remaining billet length and D is the extruder barrel inlet diameter (m). The third part of the curve corresponds to the end of the extrusion process, when the ram approaches the die orifice. The recorded force can be constant or increases [46]. The experimental methodology to prepare the samples is based on the preparation of different mixes of soil, water, and specific seaweed extracts (freeze-dried extract and polysaccharides). Mix proportions were adapted for each product to ensure that each batch contained approximatively a polysaccharide equivalent of 0.5% of dry material content and that its shear yield stress, which reflects the material consistency, was equal to 10 kPa, 15 kPa or 20 kPa (controlled by a fall cone penetrometer before the beginning of the extrusion test). The materials were then homogenized in a mortar mixer and the extruder barrel was filled by hand. The material billet length was determined at the beginning of each test. Tests were performed twice on each mixture and for each die orifice diameter.

3. Effect of seaweeds extracts on compressive strength

- **3.1. Preliminary study**
- *3.1.1. Tests on dry specimen*

 The obtained results during for the compressive strength test in the preliminary study are shown in Fig. 2. Each value represents the strength measured on a single specimen. The dry density of the specimens ranges between 1500 and 2000 kg/m3, which corresponds to the expected range. Variations could be caused by variations in hand compaction during the specimens' production and by the amount of water required to obtain a workable mixture. Compressive strength results on dry specimens show that the addition of raw seaweed extracts does not increase the mechanical resistance for any species of seaweed, the compressive strength remaining between 0.5 MPa and 1.5 MPa, which is similar to soil reference specimens, which display an average compressive strength around 1 MPa. *For P. lancifolius*, freeze-dried extract and polysaccharides (κ -carrageenan/agar) have no positive effect on mechanical resistance increase. For *Ulva sp*. a moderate improvement of mechanical resistance is observed for the freeze-dried extract and polysaccharides (ulvan), with a compressive strength between 1.5 MPa and 2.5 MPa. Best results are observed with the addition of polysaccharides of *S. muticum* (alginate) and *S. chordalis* (-carrageenan), which improve significantly the compressive strength at similar dry density, from 1 MPa on average for soil reference specimens to almost 4 MPa for *S. chordalis*. This phenomenon is also observed in the same range for *S. muticum* freeze-dried extract whereas *S. chordalis* freeze-dried extract does not allow to increase compressive strength. This could be explained by the very low carrageenan concentration in the *S. chordalis* freeze- dried extract. For *S. muticum* and *S. chordalis*, the compressive strength seems to increase with the polysaccharides' concentration in the mixture. Several studies have demonstrated a stabilizing effect of alginates on raw earth construction [33, 47] attributed to the ionic bringing which takes place between the alginate polymer and divalent calcium cations contained in the soil. A soluble form of alginate is converted to insoluble gel through the addition of divalent metal cations such as Ca^{2+} . This gel forming mechanism is described by the "egg box model". This involved cooperative binding in water where interactions between the G blocks of the negatively charged alginate polymer and the positively charged ions create chain to chain associations. This is due to the formation of junction zones between two or more chains where the cations sit within the buckled parts of the molecule, like eggs in an egg box [48] (Fig. 3). During the gelation process, the number of chain to chain associations increases, eventually leading to the formation of a continuous network [34]. This network could act like a secondary network that would reinforce the structure created by the clay particles arrangement and their interactions with water molecules and could explain the efficiency of *S. muticum* to increase the mechanical strength. Some measurements still must be conducted to prove the presence of divalent metal cations in the studied quarry waste that composes the clayey part of the studied earth to confirm this assumption.

 Fig.2: Compressive strength as a function of the dry density for raw earth dry specimen with and without seaweed extract additives (**-** = Soil; ■ = PP - purified polysaccharides 0.25%; □ = PP-407 purified polysaccharides 0.5%; \bullet = FDE - freeze dried hot water extract 0.25% eq.; \diamond = FDE -408 freeze dried hot water extract 0.5% eq.; \triangle = RM - raw material 0.25% eq.; \triangle = RM - raw material 0.5% eq.)

 -carrageenan and κ -carrageenan also have the ability to create interaction and 411 binding with metal cations. *u*-carrageenan forms a threefold, parallel double helix in the presence of calcium ions [49]. Calcium ions and water molecules, connected to peripheral sulfate groups of -carrageenan are holding the helices tight. Rheological studies on -carrageenan, gels suggest that calcium is more effective compared to monovalent ions like potassium or sodium.

Fig. 3: Formation of an alginate gel: Egg-box model: Ca^{2+} attaches itself into the G bloc 418 structure[48]

419 On the contrary, $K+$, $Cs+$ and $Rb+$ are much more effective in stabilizing κ - carrageenan helices than monovalent cations and divalent cations such as Ca2+ and Mg2+. As calcium ions are often present in large quantity in earthen materials, this could explain the good efficiency of *S. chordalis* extracts on compressive strength increase, by its capacity to create a strong and tight secondary network. In comparison *P. lancifolius* extracts would be less effective with a less dense network. Ulvan exhibits also good capacity to bind with metal ion through covalent, electrostatic or redox reactions but the affinity is less important with Ca2+ than other metal cations such as Cr3+ or Cu2+ [30]. Ulvan demonstrates different affinities toward various ions, such as Al>Cu>Pb>Zn>Cd=Mn>Sr>Mg=Ca [50]. Thus, the efficiency of *Ulva sp.* extracts on compressive strength improvement could be slightly lower than the efficiency of *S. muticum* or *S. chordalis* extracts.

3.1.2. Tests on wet specimens (after a 5 min immersion in water)

 Visual observations on reference soil specimens showed that these specimens partially disintegrated after 5 min of immersion in water, making it impossible to perform compression strength test. However, the core of the brick remained dry, as presented in Fig. 4.

 All the tested polysaccharides and freeze-dried extracts have allowed to keep the shape of the brick after 5 minutes immersion in water, whereas only *Ulva sp.* raw extract has allowed to avoid the brick partial disintegration (Fig. 4).

Sample	Seaweed extract	Compressive	Strength retention	
reference	type	strength (MPa)	ratio	
Pp0, 5	P. lancifolius PP	0.03	0.02	
Sp0.25	S. chordalis PP	1.07	0.39	
Sp0.5	S. chordalis PP	1.00	0.27	
SI0.5	S. chordalis FDE	0.02	0.015	
Up0.5	Ulva sp. PP	0.09	0.04	
U10.25	Ulva sp. FDE	0.08	0.05	
UI0.5	Ulva sp. FDE	0.07	0.03	
Ua0.25	Ulva sp. RM	0.08	0.05	
SAp0.25	S. muticum PP	0.29	0.15	
SAp0.5	S. muticum PP	1.41	0.47	
SA10.25	S. muticum FDE	1.52	0.55	
SAI0.5	S. muticum FDE	2.35	0.78	
SAa0.25	S. muticum RM	0.24	0.19	

439 **Table 3:** Results for compressive strength tests on wet specimen

 The core of the specimen remained dry for *S. chordalis* and *S. muticum* extracts (polysaccharides and freeze-dried extracts) but was totally wet for *P. lancifolius* and *Ulva sp.* Compressive strength tests were done on the bricks which have kept their shape. The results are summarized in table 3. Due to loss of shape and sample disintegration, no compressive strength test could be performed on wet reference soil specimens. Their compressive strength after 5 minutes immersion in water is therefore considered to be zero. Only *S. muticum* freeze-dried extract and polysaccharide and *S. chordalis* polysaccharide allowed to obtain significant results with compressive strength higher than 1 MPa. *S. muticum* and *S. chordalis* polysaccharides acted as water repellents, with a sort of waterproofing effect that prevented water to penetrate in the core of the specimen. This effect is particularly visible on specimens containing *S. muticum* extracts. On the contrary, *P. lancifolius* and *Ulva sp.* extracts have accelerated water diffusion in the center of the specimen compared to soil reference specimen. This could be due to the gel formation kinetic or by the different binding behaviour between polysaccharides and water. The hypothesis can also be made that the formation in a first step of a gel at the specimen surface, with a specific network structure allows to maintain the shape of the specimen and prevents its disintegration. But a much longer immersion in water could lead also to specimen disintegration.

Fig. 4: Visual aspect of specimens after 5 minutes immersion in water

3.2. Study on S. muticum and S. chordalis

 Following the results obtained during the preliminary study, *S. chordalis* polysaccharides (-carrageenan) and *S. muticum* freeze-dried extract (containing alginate) were selected to continue the study *S. muticum* polysaccharides (alginate) gave satisfactory results but the quantity extracted was insufficient to perform more tests. Fig. 5a represents the evolution of specimen water content with time for

 specimens maintained in an atmosphere saturated with humidity. The evolution is quite similar for the reference soil and specimen containing *S. chordalis* polysaccharide, with a rapid increase of water content until 1% the first day then a slower increase the following days to reach less than 2% after 7 days.

Water content increases more rapidly for specimen containing *S. muticum* freeze-

dried extract to reach 4.5% after 7 days.

 Fig. 5: 5a) Evolution of specimen water content with time in saturated atmosphere; 5b) Specimen 475 water content evolution with storage room relative humidity. Storage time was 5 days at 60%, 7

 days at 80% and 7 days at 100%; 5c) Evolution of compressive strength with specimen water content (*S. muticum* freeze-dried extract; *S. chordalis* purified polysaccharide)

 This could be due to the form of the extract which is a freeze-dried extract. It contains material other than polysaccharides and was added in larger quantities in the mixture. It tends to rehydrate with water vapor contact. Therefore, the amount of water absorbed will be greater for the freeze-dried extract than for the pure polysaccharide. A test with pure alginate should be done to determine if the high- water content of specimen with *S. muticum* freeze-dried extract is explained only by the extract form or also by the polysaccharide capacity to absorb water.

 After 7 days in the room at 80% relative humidity, reference soil specimen and specimen containing *S. chordalis* polysaccharide reach a water content of approximately 0.5%. The water content of specimen with *S. muticum* freeze- dried extract is 1.3% (Fig. 5b). Again, the difference of behavior between *S. chordalis* and *S. muticum* specimens could be due to *S. muticum* extract form. The evolution of the compressive strength with specimen water content for reference soil, earth containing *S. chordalis* polysaccharide and *S. muticum* freeze-dried extract are plotted in Fig. 5c. At dry state, specimens with *S. chordalis* polysaccharide and *S. muticum* freeze dried extract present much higher compressive strength than the reference soil (4 MPa against 1.7 MPa), that confirms the previously obtained results.

 Even if compressive strength rapidly decreases with water content for specimens containing seaweed extract, seaweed extract addition allows to maintain a higher compressive strength for a water content lower than 1%. It means that addition of *S. chordalis* and *S. muticum* extracts allows to increase compressive strength in 500 indoor conditions and that *S. chordalis* polysaccharide (1-carrageenan) allows also to increase the mechanical resistance in an atmosphere having a relative humidity of 80%. Additional test should be done on *S. muticum* polysaccharide (alginate) to check if pure alginate allows also to increase the compressive strength in an atmosphere having a relative humidity of 80%.

4. Structural build-up test: influence of seaweed extracts

 The structural build-up speed is an important parameter for the development of raw earth construction. The faster the material becomes firm, holds its shape and can sustain weight on top, the faster it will be possible to stack the layers and build a wall. Construction time can then be reduced. This is valid for vernacular construction techniques such as rammed earth or cob, but also for new processes such as poured earth or 3D printing. This parameter is particularly important for 3D printing where layers of material are stacked quickly. A compromise should be found between the printing speed and the structural build-up of the deposited layer to sustain its own weight and the weight of the layers above [51]. The evolutions of the apparent yield stress with time of earth without seaweed extract and earth containing 0.25% of different seaweed polysaccharides are plotted in Fig. 6a, as well as the stress induced by a wall of 1 m high [52]. The evolution of yield stress for the mix soil-HMP was quite linear, mainly due to drying, whereas the evolution for the mixtures containing polysaccharides were highly non-linear, with a strong increase of yield stress during the first 20 minutes. *S. chordalis*, *P. lancifolius* and *Ulva sp.* polysaccharides were the most efficient to obtain a fast-structural build-up of the earth, with a yield stress at 20 minutes around 100 kPa, which is similar to earth after 160 minutes. The structural build-up was therefore 8 times faster with polysaccharides addition. After only 5 minutes, earth containing these polysaccharides reached sufficient strength to support the weight of a 1 m high wall, whereas it took 70 min for the earth without polysaccharide. *S. muticum* polysaccharide was slightly less efficient and the result was comparable to the one obtained with the commercial alginates.

 Fig. 6: 6a) Evolution of yield stress with time of earth with and without seaweed polysaccharides addition (PP); 6b) Evolution of yield stress according to seaweed extract form and concentration for P. lancifolius (FDE or PP)

 Tests with different forms of *P. lancifolius* extract (polysaccharide and freeze-dried extract) and different concentrations of *P. lancifolius* freeze-dried extract show that the efficiency on the structural build-up seems to be quite independent of the extract concentration in the mixture, and that freeze-dried extract and polysaccharide efficiencies were similar (Fig. 6b).

 Results show that a low concentration of seaweed extract is sufficient to have a good efficiency and increase the build-up rate. The seaweed extracts incorporation procedure was important to obtain significant results. The dry seaweed extracts in powder form were added to the mixture "soil + water" at the last moment. It can be of interest to develop processes where seaweed extracts are added when it is needed like accelerators at the level of printing head for 3D printed concrete [53]. The aim was that the gelation of the polysaccharides occurred directly in the material in the mould and not during the preparation phase. Some tests were carried out by first mixing the seaweed extracts with water, waiting for gelation and then mixing this sirup with the soil. But on one hand this procedure required a larger amount of water to get a workable mixture, and on the other hand the results were not significant. As the gelation process occurred in the water prior to mixing, no mechanism except drying allowed to reduce the structural build-up time once the mixture was in placed in the mould. The formation of a gel in situ, with the creation of bonds between the polysaccharides and water molecules and metal ions already present in the mixture, allows to obtain quickly a harder mixture with high yield stress. Once the gelation process is complete, the yield stress of the mixture increases slowly, mainly due to drying.

5. Extrusion: effects of seaweed extracts

 Extrusion is a manufacturing process in which a plastic material is compressed and forced through a die whose cross-section has the shape of the part to be supplied. The extrudate is continuously formed. Extrusion is used in particular for the production of fired earth bricks. 3D printing is also based on the extrusion process. The development of this technique on raw earth requires precise rheological properties to have a smooth extrudate, without asperities, and to avoid the phenomena of drainage and consolidation of the material [44]. All the tested seaweed extracts allowed to reduce the required force to begin extrusion process compared to the reference soil (Table 4), and this for both die orifice diameters. The seaweed extract that allowed to obtain the minimal force to start the extrusion process is *Ulva sp.* freeze-dried extract, with a required force divided by 2 compared to the soil reference. *S. muticum* freeze-dried extract allowed also to greatly reduce the force required for extrusion. A low force to start extrusion means less stress on the material to be extruded and on the tools. It could be noted that the extrusion force is the combination of the friction force at the interface between the material and the extruder wall and the shaping force that is needed to change the diameter of the extruder in the die area and is proportional to the shear yield stress [45, 46]. It could be assumed that the seaweed extracts act as lubricants and help to reduce the friction force on the extruder surface as the shear yield stress remains constant for each material presented in Table 4. Fig. 7 represents the evolution of the required force to start the extrusion process for reference soil and mixtures with *S. muticum* freeze-dried extract at different consistencies, for different yield stresses.

	Ref.	P. lancifolius	S. chordalis	Ulva sp.	S. muticum
	soil	PP 0.5%	PP 0.5%	FDE 0.5%	FDE 0.5%
Measured τ_0 (kPa)	<i>15.1</i>	14.5	15.1	14.4	16.6
Force (N) D ₂₄	276	169	200	129	154
Force (N) D16	428	350	340	199	256

580 **Table 4:** Required force to start the extrusion process at a yield stress (τ_0) of 15 kPa for die orifice

582

583 **Fig. 7:** Evolution of the required force to start the extrusion versus yield stress for reference soil 584 and mixtures containing *S. muticum* freeze-dried extract

 The required force to start the extrusion process strongly increases with the yield stress for the reference soil, in particular for the 16 mm die orifice, whereas it grows more slowly for mixture with *S. muticum* freeze-dried extract (Fig. 7). The addition of *S. muticum* freeze-dried extract helps to maintain some ease of extrusion for different consistencies, especially when the mixture contains less water. A figure is available in supplementary material and presents the evolution of the total extrusion force versus the remaining billet length for reference soil and mixtures containing seaweed extract on the first 60 mmm extruded. On each curve, the strong increase corresponding to material compaction is visible on the right part.

594 For reference soil, no decrease of the force in the second part of the curve can be 595 observed, the total extrusion force remaining almost constant or slightly increases. This could indicate the presence of drainage and consolidation phenomena in the material, and friction force remain important despite the frictional surface reduction during the extrusion process. These observations lead to the conclusion that it is impossible to have a correct extrusion with the reference soil. This phenomenon can also be observed for mixture containing *Ulva sp.* freeze-dried extract. Even if *Ulva sp.* freeze-dried extract allows to reduce the initial force required to start the extrusion, it does not allow to have a correct extrusion behaviour over time. For mixture containing *S. muticum* freeze-dried extract, a first decrease can also be observed then the required force for extrusion remains almost constant. For mixture containing *P. lancifolius* polysaccharide, for both die orifices, the curves are quite smooth and decrease regularly, even if for die orifice of 24 mm, an increase of the require force is observed at 65 mm.

Table 5: Average friction stress values Kw at a yield stress of 15 kPa

 The profile of the curves suggests that the addition of *P. lancifolius* polysaccharide could improve the ability to extrude the material. For mixture containing *S. chordalis*, the curves decrease very slowly on the first 60 mm extruded. Table 5 summarizes the friction stress values Kw obtained with equation (2) for a yield stress of 15 kPa. It was not possible to determine a friction stress value for the reference soil. Friction stress values vary with the die orifice diameter. Friction stress values are higher for the 16 mm die orifice, except for mixture containing *P. lancifolius* polysaccharide. The mixture containing *S. chordalis* polysaccharide has the lowest friction stress value, whereas mixtures with *Ulva sp.* freeze-dried extract and *S. muticum* freeze-dried extract have higher friction stress values. To conclude, some seaweed extracts seem to have a real impact on the ability to extrude earth material. But some additional tests are necessary to better understand the parameters affected.

6. Conclusion

 The results obtained in this study demonstrate a certain effectiveness of parietal polysaccharides extracted from certain invasive Brittany seaweeds in improving the mechanical and rheological properties of raw earth-based material. The - carrageenan extracted from *S. chordalis* and the alginate extracted from *S. muticum* thus allowed to increase the compressive strength of raw earth specimens in dry conditions and in wet conditions until a relative humidity of 80%. All the tested polysaccharides were able to significantly accelerate the structural build-up rate, thus allowing to reduce processing times during building erection or the development of 3D printing with raw earth. And visual observations on the impact of the alginate extracted from *S. muticum* shows that this extract seems to improve the rheological properties of the raw earth material to obtain a material which is more easily extrudable than raw earth alone. These results represent a base, additional tests must be conducted to have a better understanding of the mode of action of these polysaccharides and to determine the best procedure for adding these compounds to the mix soil and water. Additional tests must also be conducted on other types of soil, with different clay content and calcium content.

 In order to industrialize the process in the future, the polysaccharide extractions were carried out with as few steps as possible. Some results with freeze-dried extracts containing other molecules than polysaccharides showed that high purity is not necessary. However, the polysaccharides precipitation required the use of absolute ethanol, and the freeze-dried extracts used during these tests have three main disadvantages, they require higher water additions to obtain a good consistency, are less concentrated in polysaccharides as they still contained the algal residues and the freeze-drying process is a rather high energy consumer process and operates in batch. Other production processes could be considered to obtain an extract with a high polysaccharide concentration. After the first step of polysaccharide extraction with hot water, a second filtration step to separate the solid residues could be carried out, followed by a atomization drying step. The final goal would be to obtain an algae extract by the cleanest and most-efficient process.

Acknowledgements

 The authors would like to thank LCBTP-Pigeon, for their supply of quarry waste used to formulate a lab-designed earthen material for the experiments.

References

1. Ioannidou D, Meylan G, Sonnemann G, Habert G (2017) Is gravel becoming scarce? Evaluating

 the local criticality of construction aggregates. Resources, Conservation and Recycling, 126, 25–33. <https://doi.org/10.1016/j.resconrec.2017.07.016>

- 2. Peduzzi P (2014) Sand, rarer than one thinks. Environmental Development, 11, 208–218. <https://doi.org/10.1016/j.envdev.2014.04.001>
- 3. Nakamatsu J, Kim S, Ayarza J, Ramírez E, Elgegren M, Aguilar R (2017) Eco-friendly
- modification of earthen construction with carrageenan: Water durability and mechanical assessment.

 Construction and Building Materials, 139, 193–202. <https://doi.org/10.1016/j.conbuildmat.2017.02.062>

- 4. Barcelo L, Kline ., Walenta G, Gartner E (2014) Cement and carbon emissions. Materials and
- Structures/Materiaux et Constructions, 47(6), 1055–1065. [https://doi.org/10.1617/s11527-013-](https://doi.org/10.1617/s11527-013-0114-5) [0114-5](https://doi.org/10.1617/s11527-013-0114-5)
- 5. Saiter JM, Dobircau L, Leblanc N (2012) Are 100 % green composites and green thermoplastics
- the new materials for the future? International Journal of Polymer Science (Vol. 2012). Hindawi
- Limited.<https://doi.org/10.1155/2012/280181>
- 6. Morel JC, Mesbah A, Oggero M, Walker P (2001) Building houses with local materials: means
- to drastically reduce the environmental impact of construction. In Building and Environment (Vol.
- 36). www.elsevier.com/locate/buildenv
- 7. Cagnon H, Aubert JE, Coutand M, Magniont C (2014) Hygrothermal properties of earth bricks.
- Energy and Buildings, 80, 208–217.<https://doi.org/10.1016/j.enbuild.2014.05.024>
- 8. Bruno AW, Gallipoli D, Perlot C, Mendes J (2017) Effect of stabilisation on mechanical
- properties, moisture buffering and water durability of hypercompacted earth. Construction and
- Building Materials, 149, 733–740.<https://doi.org/10.1016/j.conbuildmat.2017.05.182>
- 9. Guihéneuf S, Rangeard D, Perrot A, Cusin T, Collet F, Prétot S (2020) Effect of bio-stabilizers
- on capillary absorption and water vapour transfer into raw earth. Materials and Structures/Matériaux
- et Constructions, 53(6).<https://doi.org/10.1617/s11527-020-01571-z>
- 10. Ouedraogo KAJ, Aubert JE, Tribout C, Escadeillas G (2020) Is stabilization of earth bricks using

 low cement or lime contents relevant? Construction and Building Materials, 236. <https://doi.org/10.1016/j.conbuildmat.2019.117578>

- 11. Venkatarama Reddy BV, Prasanna Kumar P (2011) Cement stabilised rammed earth. Part A:
- Compaction characteristics and physical properties of compacted cement stabilised soils. Materials
- and Structures/Materiaux et Constructions, 44(3), 681–693. [https://doi.org/10.1617/s11527-010-](https://doi.org/10.1617/s11527-010-9658-9)
- [9658-9](https://doi.org/10.1617/s11527-010-9658-9)
- 12. Vissac A, Bourgès A, Gandreau D, Anger R, Fontaine L (2017) Argiles & biopolymères les
- stabilisants naturels pour la construction en terre. CRAterre éditions
- 13. Ouedraogo KAJ, Aubert JE, Tribout C, Millogo Y, Escadeillas G (2021) Ovalbumin as natural
- organic binder for stabilizing unfired earth bricks: Understanding vernacular techniques to inspire
- modern constructions. Journal of Cultural Heritage, 50, 139–149. <https://doi.org/10.1016/j.culher.2021.05.004>
- 14. Mineur F, de Clerck O, le Roux A, Maggs CA, Verlaque M (2010) Polyopes lancifolius
- (Halymeniales, Rhodophyta), a new component of the Japanese marine flora introduced to Europe. Phycologia, 49(1), 86–96.<https://doi.org/10.2216/09-45.1>
- 15. Plouguerné E, le Lann K, Connan S, Jechoux G, Deslandes E, Stiger-Pouvreau V (2006) Spatial
- and seasonal variation in density, reproductive status, length and phenolic content of the invasive
- brown macroalga Sargassum muticum (Yendo) Fensholt along the coast of Western Brittany
- (France). Aquatic Botany, 85(4), 337–344.<https://doi.org/10.1016/j.aquabot.2006.06.011>
- 16. Ménesguen A, Perrot T, Dussauze M (2010) Ulva mass accumulations on Brittany beaches :
- explanation and remedies deduced from models. Mercator Ocean Quarterly Newsletter
- 17. Burlot AS (2016) (Thesis) Etude de la macroalgue rouge Solieria chordalis : aspects écophysiologiques, production d'extraits et perspectives d'appications
- 18. Menon, VV (2011) 36 Seaweed Polysaccharides-Food Applications. Handbook of Marine
- Macroalgae: Biotechnology ans Applied Phycology
- 19. Cunha L, & Grenha A (2016) Sulfated seaweed polysaccharides as multifunctional materials in
- drug delivery applications. In Marine Drugs (Vol. 14, Issue 3). MDPI AG. <https://doi.org/10.3390/md14030042>
- 20. Smit AJ (2004) Medicinal and pharmaceutical uses of seaweed natural products: A review. In
- Journal of Applied Phycology (Vol. 16). Kluwer Academic Publishers.
- 21. Deniaud-Bouët E, Kervarec N, Michel G, Tonon T, Kloareg B, Hervé C (2014) Chemical and
- enzymatic fractionation of cell walls from Fucales: Insights into the structure of the extracellular
- matrix of brown algae. Annals of Botany, 114(6), 1203–1216.<https://doi.org/10.1093/aob/mcu096>
- 22. Dang BT, Bui XT, Tran DPH, Hao Ngo H, Nghiem LD, Hoang TKD, Nguyen PT, Nguyen HH,
- Vo TKQ, Lin C, Yi Andrew Lin K, Varjani S (2022) Current application of algae derivatives for
- bioplastic production: A review. In Bioresource Technology (Vol. 347). Elsevier Ltd.
- <https://doi.org/10.1016/j.biortech.2022.126698>
- 23. Berglund L, Nissilä T, Sivaraman D, Komulainen S, Telkki VV, Oksman K (2021) Seaweed-
- Derived Alginate-Cellulose Nanofiber Aerogel for Insulation Applications. ACS Applied Materials
- and Interfaces, 13(29), 34899–34909[. https://doi.org/10.1021/acsami.1c07954](https://doi.org/10.1021/acsami.1c07954)
- 24. Micaelo R, Al-Mansoori T, Garcia A (2016) Study of the mechanical properties and self-healing
- ability of asphalt mixture containing calcium-alginate capsules. Construction and Building
- Materials, 123, 734–744.<https://doi.org/10.1016/j.conbuildmat.2016.07.095>
- 25. Usov, AI (1992) Sulfated polysaccharides of the red seaweeds. Topics in Catalysis, 6(1), 9–23.
- [https://doi.org/10.1016/S0268-005X\(09\)80055-6](https://doi.org/10.1016/S0268-005X(09)80055-6)

 chordalis (Gigartinales): Structural analysis and immunological activities of the low molecular weight fractions. Carbohydrate Polymers, 81(2), 448–460. 27. Hardouin K, Bouyer R, Pliego-Cortés H, Le Men T, Cérantola S, Marty C, Douzenel P, Bedoux G, Bourgougnon N (2022) Chemical characterization of the invasive red alga Polyopes lancifolius (Harvey) Kawaguchi & Wang (Halymeniales) from the Gulf of Morbihan (France) Phycologia. • DOI[:10.3390/md20020116](https://doi.org/10.3390/md20020116) 28. Mohamed DA, Hassan AA, Helmy MM (2021) Extraction and Characterization of Sodium Alginates Extracted from Sargassum muticum and Turbinaria conoides. In IJISET-International Journal of Innovative Science, Engineering & Technology (Vol. 8, Issue 1). www.ijiset.com 29. Kidgell JT, Magnusson M, de Nys R, Glasson CRK (2019) Ulvan: A systematic review of extraction, composition and function. In Algal Research (Vol. 39). Elsevier B.V. <https://doi.org/10.1016/j.algal.2019.101422> 30. Chi Y, Li H, Fan L, Du C, Zhang J, Guan H, Wang P, Li R (2021) Metal-ion-binding properties of ulvan extracted from Ulva clathrata and structural characterization of its complexes. Carbohydrate Polymers, 272.<https://doi.org/10.1016/j.carbpol.2021.118508> 31. Cao Y, Li S, Fang Y, Nishinari K, Phillips GO, Lerbret A, Assifaoui A (2018) Specific binding of trivalent metal ions to λ-carrageenan. International Journal of Biological Macromolecules, 109, 350–356[. https://doi.org/10.1016/j.ijbiomac.2017.12.095](https://doi.org/10.1016/j.ijbiomac.2017.12.095) 32. Seely GR, Hart RL (1974) The Binding of Alkaline Earth Metal Ions to Alginate. Macromolecules.<https://pubs.acs.org/sharingguidelines> 33. Guihéneuf S, Rangeard D, Perrot A (2019) Addition of bio based reinforcement to improve workability, mechanical properties and water resistance of earth-based materials, in: Academic Journal of Civil Engineering - Vol 37 No 2 (2019): Special Issue - ICBBM 2019, pp. 184–192.<https://doi.org/10.26168/icbbm2019.26>

26. Bondu S, Deslandes E, Fabre MS, Berthou C, Guangli Y (2010) Carrageenan from Solieria

- 34. Dove C (2014) The development of unfired earth bricks using seaweed biopolymers. WIT
- Transactions on the Built Environment, 142, 219–230.<https://doi.org/10.2495/ARC140201>
- 35. Déniel M, Puspita M, Douzenel P, Stiger-Pouvreau V, Bedoux G, Bourgougnon N, Vandanjon
- L (2017) Seasonal Variation of Sargassum Muticum Biochemical Composition Determined by
- Fourier Transform Infra-Red Spectroscopy. JABST 2:75–84. [https://doi.org/10.15436/2476-](https://doi.org/10.15436/2476-1869.17.1555) [1869.17.1555](https://doi.org/10.15436/2476-1869.17.1555)
- 36. Hardouin K, Burlot A-S, Umami A, Tanniou A, Stiger-Pouvreau V, Widowati I, Bedoux G, Bourgougnon N (2014) Biochemical and antiviral activities of enzymatic hydrolysates from
- different invasive French seaweeds. J Appl Phycol 26:1029–1042. [https://doi.org/10.1007/s10811-](https://doi.org/10.1007/s10811-013-0201-6)
- [013-0201-6](https://doi.org/10.1007/s10811-013-0201-6)
- 37. Perrot A, Rangeard D, Menasria F, Guihéneuf S (2018c) Strategies for optimizing the mechanical strengths of raw earth-based mortars. Construction and Building Materials, 167, 496–
- 504[. https://doi.org/10.1016/j.conbuildmat.2018.02.055](https://doi.org/10.1016/j.conbuildmat.2018.02.055)
- <https://doi.org/10.1016/j.carbpol.2010.02.046>
- 38. Paradossi G, Cavalieri F, Pizzoferrato L, Liquori AM (1999) A physico-chemical study on the
- polysaccharide ulvan from hot water extraction of the macroalga Ul6a. In International Journal of
- Biological Macromolecules (Vol. 25)

 39. Mazumder A, Holdt SL, de Francisci D, Alvarado-Morales M, Mishra HN, Angelidaki I (2016) Extraction of alginate from Sargassum muticum: process optimization and study of its functional activities. Journal of Applied Phycology, 28(6), 3625–3634. [https://doi.org/10.1007/s10811-016-](https://doi.org/10.1007/s10811-016-0872-x) [0872-x](https://doi.org/10.1007/s10811-016-0872-x) 40. Ardant D, Brumaud C, Habert G (2020) Influence of additives on poured earth strength development. Mater Struct 53, 127.<https://doi.org/10.1617/s11527-020-01564-y> 41. Perrot A, Rangeard D, Lecompte T (2018a) Field-oriented tests to evaluate the workability of cob and adobe. Materials and Structures/Materiaux et Constructions, 51(2). <https://doi.org/10.1617/s11527-018-1181-4> 42. Khelifi H, Lecompte T, Perrot A, Ausias G (2016) Mechanical enhancement of cement- stabilized soil by flax fibre reinforcement and extrusion processing. Materials and Structures, 49(4), 1143-1156 43. Maskell D, Heath A, Walker P (2013) Laboratory scale testing of extruded earth masonry units. Materials and Design, 45, 359–364.<https://doi.org/10.1016/j.matdes.2012.09.008> 44. Khelifi H, Perrot A, Lecompte T, Rangeard D, Ausias G (2013) Prediction of extrusion load and liquid phase filtration during ram extrusion of high solid volume fraction pastes. Powder Technology, 249, 258-268. 45. Perrot A, Rangeard D, Nerella VN, Mechtcherine V (2018d) Extrusion of cement‐based materials ‐ an overview. RILEM Technical Letters, 3, 91–97. <https://doi.org/10.21809/rilemtechlett.2018.75> 46. Perrot A, Mélinge Y, Rangeard D, Micaelli F, Estellé P, Lanos C (2012) Use of ram extruder as a combined rheo-tribometer to study the behaviour of high yield stress fluids at low strain rate. Rheologica Acta, 51(8), 743–754.<https://doi.org/10.1007/s00397-012-0638-6> 47. Menasria F, Perrot A, Rangeard D (2017) Using alginate biopolymer to enhance the mechanical properties of earth-based materials. EcoGRAFI 2 nd International Conference on Bio-based Building Materials & 1 st Conference on ECOlogical valorisation of GRAnular and FIbrous materials 48. Bourgougnon N, Gervois A (2021) Les algues marines, Ellipses, Illustrated édition. ISBN- 978- 2340056541 49. Janaswamy S, Chandrasekaran R (2002) Effect of calcium ions on the organization of iota- carrageenan helices: an X-ray investigation. In Carbohydrate Research (Vol. 337). 50. Alves A, Sousa RA, Reis RL (2013) A practical perspective on ulvan extracted from green algae. 801 In Journal of Applied Phycology (Vol. 25, Issue 2, pp. 407–424). Kluwer Academic Publishers. <https://doi.org/10.1007/s10811-012-9875-4> 51. Perrot A, Rangeard D, Pierre A (2016) Structural built-up of cement-based materials used for 3D-printing extrusion techniques. Materials and Structures/Materiaux et Constructions, 49(4), 1213–1220[. https://doi.org/10.1617/s11527-015-0571-0](https://doi.org/10.1617/s11527-015-0571-0) 52. Perrot A, Rangeard D, Courteille E (2018b). 3D printing of earth-based materials: Processing aspects. Construction and Building Materials, 172, 670–676. <https://doi.org/10.1016/j.conbuildmat.2018.04.017>

- 53. Wangler T, Pileggi R, Gürel S, Flatt RJ (2022) A chemical process engineering look at digital
- concrete processes: critical step design, inline mixing, and scaleup. Cement and Concrete Research,
- 811 155[. https://doi.org/10.1016/j.cemconres.2022.106782](https://doi.org/10.1016/j.cemconres.2022.106782)
- NF EN 196-1 2016. Methods of testing cement Part 1: Determination of strength. AFNOR; 2016.
- NF EN ISO 17892-7 2018. Geotechnical investigation and testing Laboratory testing of soil Part
- 814 7 : unconfined compression test. AFNOR ; 2018
- XP P13-901 2022. Earth bricks and earth blocks for walls and partitions Definitions –
- Specifications Test methods Delivery acceptance conditions. AFNOR ; 2022.