

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

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- **4** properties of earth-based materials
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- 33

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39 The authors declare no conflict of interest.

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43 Authors contributions

44 Conceptualization, N.B., A.P.; S.G.; Validation, Y.A., N.B., S.G., A.P.;

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47 Abstract

48 In Brittany, invasive algae represent a real problem, unbalancing local ecosystems 49 and threatening the economy and tourism, with massive strandings, especially in 50 summer. The valorization of invasive algae in green processes and materials such 51 as ecological building materials could represent a real opportunity to try to control 52 the spread of these species. Raw earth is a locally sourced building material, non-53 toxic and sustainable. In this work, we propose then to compare the effect of four 54 invasive Brittany seaweeds, exotic or indigenous, on the fresh state and hardened 55 properties of raw earth material. In particular, we investigated the performance of 56 Polyopes lancifolius, Solieria chordalis, Ulva sp. and Sargassum muticum on the 57 compressive strength, water resistance and extrudability of the raw earth material. 58 Several forms of seaweed extracts were tested, raw seaweeds dried and ground, 59 freeze-dried hot water extracts and extracted polysaccharides. Our results showed 60 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 betterresistance to water.
- 63 Keywords: Invasive seaweeds, Polysaccharides, Raw earth construction,

64 *Compressive strength, Water durability, Extrusion*

65 **1. Introduction**

Global warming, environmental degradation and pollution are among the major 66 67 concerns for the decades to come. The construction sector, with its extensive need 68 of natural materials like sand or gravel for concrete production [1, 2], is responsible 69 for resources overconsumption and generation of large quantities of greenhouse 70 gases and wastes [3]. The production of cement-based materials, with high energy 71 consumption and carbon footprint is one of the main causes of pollution [4]. The 72 development of less polluting construction techniques and materials, using local 73 and sustainable resources, is now required to meet the growing need for housing 74 and equipment of our societies (United Nations, Department of Economic and 75 Social Affairs, World population prospects Highlights, 2019). In this context, 76 earthen construction could be one of the solutions. Earthen construction is a 77 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 78 79 development of steel and concrete building that ensures better mechanical 80 performance, production rate and reproducibility [5]. Yet this material presents 81 some advantages: it has a low environmental impact, it is recyclable and available 82 locally [6] and presents good hygrothermal [7] and sound insulation properties. 83 However, its water sensitivity is often quoted as its main weakness related to 84 durability because humidity can alter the material and strongly reduce its 85 mechanical properties [8]. However, the ability of this material to adsorb and 86 release moisture from the atmosphere of a building and regulate its indoor 87 temperature and humidity is a strong asset. Nowadays, the development of earthen 88 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 fastprocessing and sufficient strength at dry state [9].

91 An often-quotes method to improve the mechanical and water durability properties 92 of raw earth is its stabilization with cement or lime [10, 11]. But these stabilisers 93 are non-renewable, present large carbon footprint and require high energy 94 consumption. New alternatives to these stabilisers inspired from vernacular earthen 95 construction techniques must be developed, that offer more environmentally 96 friendly solutions. Several organic additives have been used historically in the 97 production of earthen buildings, depending on what was locally available, such as 98 fibres, seaweed, barks, fruits, oil [12]. With the purpose to optimize mechanical 99 properties, to reduce the water sensitivity and to improve existing or develop new 100 and more efficient processing methods such as 3D printing, extrusion or poured 101 earth, several bio-based additives such as xanthan gum, linseed oil, ovalbumin, 102 casein, alginates or tannins have been already studied [9] [13].

Over the past few decades, various macroalgae have been introduced in Brittany. 103 104 Among these species, Polyopes lancifolius and Sargassum muticum, both native 105 from Asia, were probably introduced in Brittany via the imports of Pacific oysters 106 (Crassostrea gigas). P. lancifolius red algae (Halymeniales) has been first observed 107 in the gulf of Morbihan during the summer of 2008 [14] and S. muticum brown 108 algae (Fucales) has been first observed in France in 1980 at Brest and Port Blanc 109 [15]. Ulva sp. and Solieria chordalis native macroalgae have developed 110 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 111 112 beaches. Ulva sp. green seaweeds (Ulvales) mass blooms have been frequently 113 reported during spring and summer in semi-enclosed lagoons since 1970 but also 114 along beaches largely open to the sea and subject to a strong tidal movement [16]. 115 100 000 tons of green stranded seaweeds are collected each year in Brittany. S. 116 chordalis red seaweed (Gigartinales) appears every year from June to November 117 in south Brittany, on the peninsula of Rhuys [17]. In Morbihan, up to 15 000 tons

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

119 Worldwide, seaweeds have been increasingly exploited for their ability to produce 120 compounds of interest. The use of invasive species to obtain natural compounds 121 presents therefore a two-folded opportunity: a high availability of the biological 122 material and through specimen collection, mitigation of negative effects caused by 123 invasive species, contributing for ecosystem integrity and sustainability. Among all 124 these compounds of interest, cell wall polysaccharides are used in a wide range of 125 applications, particularly in the food industry [18] and pharmaceutical fields [19, 126 20], for their capacity to hold water, form gels and stabilize emulsions. They have 127 a biological function similar to that of hemicellulose in terrestrial plants, but with 128 higher flexibility that can withstand strong ocean waves and currents. 129 Polysaccharides also prevent seaweed desiccation and allow ion-exchange function 130 [21]. Above all, they are non-toxic and biodegradable. Cell wall polysaccharides 131 have also been used in recent years for the production of eco-materials, such as 132 bioplastics [22], aerogels for insulation boards [23] or bioasphalts [24].

133 Red algae cell walls are known to be composed of galactans generally built on 134 repeated alternating 1,3 linked alpha-D-galactopyranose and 1,4 linked beta-D-135 galactopyranose units, and differ in their level and pattern of sulfation, in 136 substitution by methoxyl and/or pyruvate groups and by other sugar residues 137 (anhydrogalactose, glucose, xylose). There are also differences in 3,6-138 anhydrogalactose content and the configuration of 1,3-linked ol-galactopyranose 139 residues (L for agars and D for carrageenans) [25]. The genus Solieria is 140 acknowledged to contain mainly 1-carrageenan disaccharide repeating units (beta-141 D-galactose-4-sulfate linked to 3,6-anhydro-alpha-D-galactose-2-sulfate) [26] [17]. 142 P. lancifolius matricial cell wall contains mainly κ-carrageenan (beta-D-galactose-143 4-sulfate linked to 3,6-anhydro-alpha-D-galactose) with potential presence of agar 144 [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, 146 alginate is present as a mixed sodium and/or potassium, calcium and magnesium 147 salt. Ulvan is a cell wall polysaccharide of green seaweed and is mainly composed 148 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.

155 In our study, the research is focused on the field of building materials, in particular 156 the incorporation of polysaccharides in raw earth constructions. The objective is 157 mainly to increase mechanical properties and water resistance of this natural but 158 still sensitive material, with the ultimate goal to replace highly polluting cements 159 and concretes. Several studies have demonstrated a stabilizing effect of alginates 160 extracted from brown seaweeds on raw earth construction [33], attributed to the 161 ionic bonding between the alginate polymer and the soil's divalent calcium cations 162 [34], [32]. Even if previous studies have already shown the positive effects of 163 carrageenan extracted from red seaweeds on water durability and mechanical 164 strength of earth material [3], this type of mechanism is not precisely described for 165 agar and ulvan extracted respectively from red and green seaweeds. This paper 166 describes an experimental study aimed at investigating the potential of 167 ingredients/products from invasive Brittany seaweeds to fine-tune its fresh-state 168 properties and to increase mechanical properties of raw earth-based building 169 materials. We propose to evaluate three ingredients/products: 1) at very low cost 170 whole dried seaweed milled, 2) at low cost hot aqueous/water extract that has been 171 lyophilized, 3) at a higher cost purified polysaccharide. Four different species of 172 Brittany seaweeds are studied. The objective is twofold: on the one hand, the 173 development of a low-polluting eco material for building construction, and on the

other hand, the valorisation of invasive algae, an available material with negativeimpacts today.

176 **2. Materials and methods**

177 **2.1. Materials**

178 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.

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

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

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

186 47°31'39''N, longitude: 2°46'09''O, France).

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

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

(% dry algae)	Ash	Neutral sugars	Proteins	Lipids
Ulva sp.	$15.9\pm1.20*$	$23.2 \pm 1.40*$	$24.4\pm0.10^*$	$0.6 \pm 0.0*$
Sargassum muticum	$25.4 \pm 1.00 *$	$5.2\pm1.10^{*}$	$24.3\pm4.30^{\ast}$	$1.0 \pm 0.10^{*}$
Solieria chordalis	39.5 ± 1.10*	$30.2 \pm 1.20*$	$16.2 \pm 0.60*$	$0.9 \pm 0.10^{*}$
Polyopes lancifolium	$12.6\% \pm 0.03$	$25.1\%\pm1.09$	15.0% ± 1.03	0.3% ± 1.10

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

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

191

192 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 μ m), fine sand (63-200 μ m) and normalised sand (0-4 mm). The 196 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) 198 of 64.6%, a methylene blue value (MBV) of 2.1 and 67.8% of its particles finer than 199 20 µm (PSD laser diffraction analysis). Fine sand and normalised sand are supplied 200 by Société Nouvelle du Littoral (Leucate, France). 201 The two reformulated soils present the following compositions: Soil n°1 is

202 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.
- 204 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].

211 **2.2. Methods**

212 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 purified polysaccharides (PP) (Fig. 1).



220

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*)

224 **Raw material (RM)**

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

227 Freeze-dried hot water extract (FDE)

228 Freeze-dried hot water extract corresponds to an hot aqueous/water extract that has 229 been lyophilized. The method of preparation of the aqueous extract is specific to 230 each type of alga wall. Polysaccharides from dried seaweed powder (< 5 mm 231 particle sire) were extracted in hot distilled water under agitation, with an initial dry 232 matter content of 5% for S.chordalis, S. muticum and Ulva sp. and 3.5% for P. 233 *lancifolius*. For S. chordalis the heating temperature was 85°C during 4h [26], for 234 P. lancifolius it was 80°C for 4h, for Ulva sp. It was 90°C for 2h [38] and for S. 235 *muticum* it was 80°C for 4h with the addition of a reagent (Na₂CO₃ 3%) [39]. The 236 total hot water extract was then freeze-dried and the dry extract was crushed in a 237 mixer.

238 **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 =
$$\frac{extracted polysaccharide weight (dry)}{initial seaweed weight (dry)} \times 100$$
 (3)

251 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.* 253 And 29.3 (% w/w) for S. muticum. The extraction yield for S. chordalis is consistent 254 255 with the results obtained by Bondu et al. [26] who reported a yield of 14,6%. Kidgell 256 et al. [29] have compiled on their side median extraction yields of 40% for Ulva 257 armoricana and 16,6% for Ulva lactuca. Mohamed et al. [28] obtained a yield of 258 20% for alginate extraction from S. muticum at 50°C. It must be noted that real 259 extraction yields may be slightly lower than those found as final purification steps 260 were not performed during the extraction procedure and some compounds like 261 pigments, phenols and/or fucoidans must be still present. It was then estimated, for 262 the specimens' preparation used in the different tests on earth, that the concentration 263 of free polysaccharides in the freeze-dried extracts (FDE) and the concentration of 264 polysaccharides present in the seaweed walls in raw seaweed extracts (RM) were 265 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 266 0.38% of RM or FDE ($\frac{Aimed \ concentration \ (0.25\% \ or \ 0.5\%)}{polysaccharide \ extraction \ yield}$). 267

268 2.2.2. Preparation of earth material specimens and testing procedure

269 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 275 2). The materials were then homogenized in a mortar mixer and hand compacted in 276 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 278 performed on each sample were dry density measurement, compressive strength at 279 dry state and after a five-minutes immersion in water (water durability). Density 280 and compressive strength were determined on one half of each specimen, after 281 breaking them in a three-point bending device, whereas water durability was tested 282 on the second half of each specimen after immersing them in water during 5 283 minutes. Density of dry specimens was determined by using a hydrostatic balance 284 and compressive strength on dry and wet specimens was determined using a 50 kN 285 loading frame and controlled at a constant displacement rate of 1 mm/min. Tests 286 were also carried out on reference specimens made with soil and different amounts 287 of water. All of the compressive tests were carried out on samples with an aspect 288 ratio of 1 following an adopted procedure in agreement with different French 289 compressive test procedures (AFNOR [NF EN 196-1], AFNOR [XP P 13-901] and 290 AFNOR [NF EN ISO 17892-7]). For the second part of the study, four specimens 291 containing 0.5% of S. chordalis polysaccharides and four specimens with S. 292 *muticum* freeze-dried extract containing a polysaccharide equivalent of 0.5 % were 293 prepared using the same methodology as for the preliminary study. Four reference 294 soil specimens were also prepared with 18% of water. After a prior drying phase, 295 specimens were broken in a three-point bending tester. Two halves of specimen 296 were kept in the oven, one half was kept during 5 days at room temperature and 297 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 299 in an atmosphere saturated in moisture. Compressive strength tests were performed 300 on each sample. For samples kept in saturated atmosphere, tests were performed 301 after 24h, 48h, 72h and 7 days as in a previous study [9] in order to see the impact 302 of the water uptake due to environmental ambiance on the material compressive 303 strength.

Sample	Soowood overact typo	Soil n°1	Seaweed	Water
reference	Seaweeu extract type	(%)	extract (%)	content (%)
T13	-	100	-	13
T15	-	100	-	15
T16,5	-	100	-	16,5

T18	-	100	-	18
T20	-	100	-	20
T22	-	100	-	22
T25	-	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
P10.5	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
SI0.25	S. chordalis FDE	100	1.25	21.9
S10.5	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
Ul0.25	Ulva sp. FDE	100	0.71	21.9
Ul0.5	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:

317
$$\tau_0 = \frac{wg \sin \alpha/2}{\pi (h \tan \alpha/2)^2} \tag{1}$$

318 Extrusion tests

319 Extrusion is an efficient industrial process that is able to industrially shape building 320 blocks as done for fired blocks [42, 43]. However, extrudability depends on earth 321 materials fresh properties that could not suit the process requirements [44, 45]. 322 Therefore, it is interesting to study the improvement of extrudability of an earth-323 based material using algae extracts. Extrusion tests were conducted using a ram 324 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 50 325 326 mm and a total length of 200 mm. Two die orifice diameters were tested (16 mm 327 and 24 mm). The material is pushed inside the barrel with a Teflon ram. The total 328 extrusion force (F) required to overcome the friction force on the extruder barrel 329 and the shaping force at die outlet is measured. Curves representing the evolution 330 of the total extrusion force (F) versus the remaining billet length (LB) are plotted. 331 In their study, Perrot et al. [46] highlight an example of the curve obtained for a 332 material with a good formulation to be extruded that remains homogeneous during 333 the process. Three different parts are visible on the curve they obtained. The first 334 part corresponds to the flow initiation. During this moment, when the ram begins 335 to move, the material is compacted in the barrel. The extrusion total force increases 336 very strongly and reaches a maximum which corresponds to the beginning of the 337 extrusion process. In the second part of the curve, the extrusion force linearly 338 decreases with the ram movement. As the billet length reduces, the surface of 339 friction between the material and the extruder barrel wall linearly decreases. It is 340 worth noting that if the earth does not show sufficient water retaining properties, 341 the material inside the barrel will consolidate and the extrusion force increase. Such

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:

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

345 where F (N) is the total extrusion force, LB (m) the remaining billet length and D 346 is the extruder barrel inlet diameter (m). The third part of the curve corresponds to 347 the end of the extrusion process, when the ram approaches the die orifice. The 348 recorded force can be constant or increases [46]. The experimental methodology to 349 prepare the samples is based on the preparation of different mixes of soil, water, 350 and specific seaweed extracts (freeze-dried extract and polysaccharides). Mix 351 proportions were adapted for each product to ensure that each batch contained 352 approximatively a polysaccharide equivalent of 0.5% of dry material content and 353 that its shear yield stress, which reflects the material consistency, was equal to 10 354 kPa, 15 kPa or 20 kPa (controlled by a fall cone penetrometer before the beginning 355 of the extrusion test). The materials were then homogenized in a mortar mixer and 356 the extruder barrel was filled by hand. The material billet length was determined at 357 the beginning of each test. Tests were performed twice on each mixture and for each 358 die orifice diameter.

359 3. Effect of seaweeds extracts on compressive 360 strength

361 **3.1. Preliminary study**

362 3.1.1. Tests on dry specimen

363 The obtained results during for the compressive strength test in the preliminary 364 study are shown in Fig. 2. Each value represents the strength measured on a single 365 specimen. The dry density of the specimens ranges between 1500 and 2000 kg/m3, 366 which corresponds to the expected range. Variations could be caused by variations 367 in hand compaction during the specimens' production and by the amount of water 368 required to obtain a workable mixture. Compressive strength results on dry 369 specimens show that the addition of raw seaweed extracts does not increase the 370 mechanical resistance for any species of seaweed, the compressive strength 371 remaining between 0.5 MPa and 1.5 MPa, which is similar to soil reference 372 specimens, which display an average compressive strength around 1 MPa. For P. 373 lancifolius, freeze-dried extract and polysaccharides (k-carrageenan/agar) have no 374 positive effect on mechanical resistance increase. For Ulva sp. a moderate 375 improvement of mechanical resistance is observed for the freeze-dried extract and 376 polysaccharides (ulvan), with a compressive strength between 1.5 MPa and 2.5 377 MPa. Best results are observed with the addition of polysaccharides of S. muticum 378 (alginate) and S. chordalis (1-carrageenan), which improve significantly the 379 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 380 381 observed in the same range for S. muticum freeze-dried extract whereas S. chordalis 382 freeze-dried extract does not allow to increase compressive strength. This could be 383 explained by the very low carrageenan concentration in the S. chordalis freeze-384 dried extract. For S. muticum and S. chordalis, the compressive strength seems to 385 increase with the polysaccharides' concentration in the mixture. Several studies 386 have demonstrated a stabilizing effect of alginates on raw earth construction [33, 387 47] attributed to the ionic bringing which takes place between the alginate polymer 388 and divalent calcium cations contained in the soil. A soluble form of alginate is 389 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 390 391 involved cooperative binding in water where interactions between the G blocks of 392 the negatively charged alginate polymer and the positively charged ions create 393 chain to chain associations. This is due to the formation of junction zones between 394 two or more chains where the cations sit within the buckled parts of the molecule, 395 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 396 397 continuous network [34]. This network could act like a secondary network that 398 would reinforce the structure created by the clay particles arrangement and their 399 interactions with water molecules and could explain the efficiency of S. muticum to 400 increase the mechanical strength. Some measurements still must be conducted to 401 prove the presence of divalent metal cations in the studied quarry waste that 402 composes the clayey part of the studied earth to confirm this assumption.

403



405 **Fig.2:** Compressive strength as a function of the dry density for raw earth dry specimen with and 406 without seaweed extract additives (- = Soil; \bullet = PP - purified polysaccharides 0.25%; \Box = PP-407 purified polysaccharides 0.5%; \blacklozenge = FDE - freeze dried hot water extract 0.25% eq.; \diamondsuit = FDE -408 freeze dried hot water extract 0.5% eq.; \blacktriangle = RM - raw material 0.25% eq.; \bigtriangleup = RM -raw material 409 0.5% eq.)

410 ι -carrageenan and κ -carrageenan also have the ability to create interaction and 411 binding with metal cations. ι -carrageenan forms a threefold, parallel double helix 412 in the presence of calcium ions [49]. Calcium ions and water molecules, connected 413 to peripheral sulfate groups of ι -carrageenan are holding the helices tight. 414 Rheological studies on ι -carrageenan, gels suggest that calcium is more effective 415 compared to monovalent ions like potassium or sodium.



417 Fig. 3: Formation of an alginate gel: Egg-box model: Ca²⁺ attaches itself into the G bloc
 418 structure[48]

416

419 On the contrary, K+, Cs+ and Rb+ are much more effective in stabilizing κ -420 carrageenan helices than monovalent cations and divalent cations such as Ca2+ and 421 Mg2+. As calcium ions are often present in large quantity in earthen materials, this 422 could explain the good efficiency of S. chordalis extracts on compressive strength 423 increase, by its capacity to create a strong and tight secondary network. In 424 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, 425 426 electrostatic or redox reactions but the affinity is less important with Ca2+ than 427 other metal cations such as Cr3+ or Cu2+ [30]. Ulvan demonstrates different 428 affinities toward various ions, such as Al>Cu>Pb>Zn>Cd=Mn>Sr>Mg=Ca [50]. 429 Thus, the efficiency of *Ulva sp.* extracts on compressive strength improvement 430 could be slightly lower than the efficiency of S. muticum or S. chordalis extracts.

431 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
S10.5	S. chordalis FDE	0.02	0.015
Up0.5	Ulva sp. PP	0.09	0.04
Ul0.25	Ulva sp. FDE	0.08	0.05
Ul0.5	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
SA10.5	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

440 The core of the specimen remained dry for S. chordalis and S. muticum extracts 441 (polysaccharides and freeze-dried extracts) but was totally wet for P. lancifolius 442 and Ulva sp. Compressive strength tests were done on the bricks which have kept 443 their shape. The results are summarized in table 3. Due to loss of shape and sample 444 disintegration, no compressive strength test could be performed on wet reference 445 soil specimens. Their compressive strength after 5 minutes immersion in water is 446 therefore considered to be zero. Only S. muticum freeze-dried extract and 447 polysaccharide and S. chordalis polysaccharide allowed to obtain significant results 448 with compressive strength higher than 1 MPa. S. muticum and S. chordalis 449 polysaccharides acted as water repellents, with a sort of waterproofing effect that 450 prevented water to penetrate in the core of the specimen. This effect is particularly 451 visible on specimens containing S. muticum extracts. On the contrary, P. lancifolius 452 and Ulva sp. extracts have accelerated water diffusion in the center of the specimen 453 compared to soil reference specimen. This could be due to the gel formation kinetic 454 or by the different binding behaviour between polysaccharides and water. The 455 hypothesis can also be made that the formation in a first step of a gel at the specimen 456 surface, with a specific network structure allows to maintain the shape of the

457 specimen and prevents its disintegration. But a much longer immersion in water458 could lead also to specimen disintegration.

True of	Type of extract				
seaweed	Raw material RM	Freeze dried hot water extract FDE	Purified polysaccharide PP		
P. lancifolius					
S. chordalis					
Ulva sp.					
S. muticum					
No addition					

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 (ι-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.

- 471 Water content increases more rapidly for specimen containing S. muticum freeze-
- 472 dried extract to reach 4.5% after 7 days.



474 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
476 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)

477

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 highwater 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.

485 After 7 days in the room at 80% relative humidity, reference soil specimen and 486 specimen containing S. chordalis polysaccharide reach a water content of 487 approximately 0.5%. The water content of specimen with S. muticum freeze- dried 488 extract is 1.3% (Fig. 5b). Again, the difference of behavior between S. chordalis 489 and S. muticum specimens could be due to S. muticum extract form. The evolution 490 of the compressive strength with specimen water content for reference soil, earth 491 containing S. chordalis polysaccharide and S. muticum freeze-dried extract are 492 plotted in Fig. 5c. At dry state, specimens with S. chordalis polysaccharide and S. 493 muticum freeze dried extract present much higher compressive strength than the 494 reference soil (4 MPa against 1.7 MPa), that confirms the previously obtained 495 results.

496 Even if compressive strength rapidly decreases with water content for specimens 497 containing seaweed extract, seaweed extract addition allows to maintain a higher 498 compressive strength for a water content lower than 1%. It means that addition of 499 S. chordalis and S. muticum extracts allows to increase compressive strength in 500 indoor conditions and that S. chordalis polysaccharide (1-carrageenan) allows also 501 to increase the mechanical resistance in an atmosphere having a relative humidity 502 of 80%. Additional test should be done on S. muticum polysaccharide (alginate) to 503 check if pure alginate allows also to increase the compressive strength in an 504 atmosphere having a relative humidity of 80%.

505 4. Structural build-up test: influence of seaweed 506 extracts

507 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 508 509 sustain weight on top, the faster it will be possible to stack the layers and build a 510 wall. Construction time can then be reduced. This is valid for vernacular 511 construction techniques such as rammed earth or cob, but also for new processes 512 such as poured earth or 3D printing. This parameter is particularly important for 3D 513 printing where layers of material are stacked quickly. A compromise should be 514 found between the printing speed and the structural build-up of the deposited layer 515 to sustain its own weight and the weight of the layers above [51]. The evolutions of 516 the apparent yield stress with time of earth without seaweed extract and earth 517 containing 0.25% of different seaweed polysaccharides are plotted in Fig. 6a, as 518 well as the stress induced by a wall of 1 m high [52]. The evolution of yield stress 519 for the mix soil-HMP was quite linear, mainly due to drying, whereas the evolution 520 for the mixtures containing polysaccharides were highly non-linear, with a strong 521 increase of yield stress during the first 20 minutes. S. chordalis, P. lancifolius and 522 Ulva sp. polysaccharides were the most efficient to obtain a fast-structural build-up 523 of the earth, with a yield stress at 20 minutes around 100 kPa, which is similar to 524 earth after 160 minutes. The structural build-up was therefore 8 times faster with 525 polysaccharides addition. After only 5 minutes, earth containing these 526 polysaccharides reached sufficient strength to support the weight of a 1 m high wall, 527 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 528 529 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)

533

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).

539 Results show that a low concentration of seaweed extract is sufficient to have a 540 good efficiency and increase the build-up rate. The seaweed extracts incorporation 541 procedure was important to obtain significant results. The dry seaweed extracts in 542 powder form were added to the mixture "soil + water" at the last moment. It can be 543 of interest to develop processes where seaweed extracts are added when it is needed 544 like accelerators at the level of printing head for 3D printed concrete [53]. The aim 545 was that the gelation of the polysaccharides occurred directly in the material in the 546 mould and not during the preparation phase. Some tests were carried out by first 547 mixing the seaweed extracts with water, waiting for gelation and then mixing this 548 sirup with the soil. But on one hand this procedure required a larger amount of water 549 to get a workable mixture, and on the other hand the results were not significant. 550 As the gelation process occurred in the water prior to mixing, no mechanism except 551 drying allowed to reduce the structural build-up time once the mixture was in placed 552 in the mould. The formation of a gel in situ, with the creation of bonds between the 553 polysaccharides and water molecules and metal ions already present in the mixture, 554 allows to obtain quickly a harder mixture with high yield stress. Once the gelation 555 process is complete, the yield stress of the mixture increases slowly, mainly due to 556 drying.

557

5. Extrusion: effects of seaweed extracts

558 Extrusion is a manufacturing process in which a plastic material is compressed and 559 forced through a die whose cross-section has the shape of the part to be supplied. 560 The extrudate is continuously formed. Extrusion is used in particular for the 561 production of fired earth bricks. 3D printing is also based on the extrusion process. 562 The development of this technique on raw earth requires precise rheological properties to have a smooth extrudate, without asperities, and to avoid the 563 564 phenomena of drainage and consolidation of the material [44]. All the tested 565 seaweed extracts allowed to reduce the required force to begin extrusion process 566 compared to the reference soil (Table 4), and this for both die orifice diameters. The 567 seaweed extract that allowed to obtain the minimal force to start the extrusion 568 process is Ulva sp. freeze-dried extract, with a required force divided by 2 compared 569 to the soil reference. S. muticum freeze-dried extract allowed also to greatly reduce 570 the force required for extrusion. A low force to start extrusion means less stress on 571 the material to be extruded and on the tools. It could be noted that the extrusion 572 force is the combination of the friction force at the interface between the material 573 and the extruder wall and the shaping force that is needed to change the diameter 574 of the extruder in the die area and is proportional to the shear yield stress [45, 46]. 575 It could be assumed that the seaweed extracts act as lubricants and help to reduce 576 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 577 578 force to start the extrusion process for reference soil and mixtures with S. muticum 579 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)	15.1	14.5	15.1	14.4	16.6
Force (N) D24	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

581





582

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

585 The required force to start the extrusion process strongly increases with the yield 586 stress for the reference soil, in particular for the 16 mm die orifice, whereas it grows 587 more slowly for mixture with S. muticum freeze-dried extract (Fig. 7). The addition 588 of S. muticum freeze-dried extract helps to maintain some ease of extrusion for 589 different consistencies, especially when the mixture contains less water. A figure is 590 available in supplementary material and presents the evolution of the total extrusion 591 force versus the remaining billet length for reference soil and mixtures containing 592 seaweed extract on the first 60 mmm extruded. On each curve, the strong increase 593 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. 596 This could indicate the presence of drainage and consolidation phenomena in the 597 material, and friction force remain important despite the frictional surface reduction 598 during the extrusion process. These observations lead to the conclusion that it is 599 impossible to have a correct extrusion with the reference soil. This phenomenon 600 can also be observed for mixture containing Ulva sp. freeze-dried extract. Even if 601 Ulva sp. freeze-dried extract allows to reduce the initial force required to start the 602 extrusion, it does not allow to have a correct extrusion behaviour over time. For 603 mixture containing S. muticum freeze-dried extract, a first decrease can also be 604 observed then the required force for extrusion remains almost constant. For mixture 605 containing P. lancifolius polysaccharide, for both die orifices, the curves are quite 606 smooth and decrease regularly, even if for die orifice of 24 mm, an increase of the 607 require force is observed at 65 mm.

	Ref.	P. lancifolius	S. chordalis	Ulva sp.	S. muticum
	soil	PP 0.5%	PP 0.5%	FDE 0.5%	FDE 0.5%
K _w (kPa) D24	-	9.17	2.60	12.37	9.13
K _w (kPa) D16	-	4.54	3.82	13.43	14.58

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

608

609 The profile of the curves suggests that the addition of *P. lancifolius* polysaccharide 610 could improve the ability to extrude the material. For mixture containing S. 611 chordalis, the curves decrease very slowly on the first 60 mm extruded. Table 5 612 summarizes the friction stress values Kw obtained with equation (2) for a yield 613 stress of 15 kPa. It was not possible to determine a friction stress value for the 614 reference soil. Friction stress values vary with the die orifice diameter. Friction 615 stress values are higher for the 16 mm die orifice, except for mixture containing P. 616 lancifolius polysaccharide. The mixture containing S. chordalis polysaccharide has 617 the lowest friction stress value, whereas mixtures with *Ulva sp.* freeze-dried extract 618 and S. muticum freeze-dried extract have higher friction stress values. To conclude, 619 some seaweed extracts seem to have a real impact on the ability to extrude earth 620 material. But some additional tests are necessary to better understand the 621 parameters affected.

622 **6. Conclusion**

623 The results obtained in this study demonstrate a certain effectiveness of parietal 624 polysaccharides extracted from certain invasive Brittany seaweeds in improving the 625 mechanical and rheological properties of raw earth-based material. The 1-626 carrageenan extracted from S. chordalis and the alginate extracted from S. muticum 627 thus allowed to increase the compressive strength of raw earth specimens in dry 628 conditions and in wet conditions until a relative humidity of 80%. All the tested 629 polysaccharides were able to significantly accelerate the structural build-up rate, 630 thus allowing to reduce processing times during building erection or the 631 development of 3D printing with raw earth. And visual observations on the impact 632 of the alginate extracted from S. muticum shows that this extract seems to improve 633 the rheological properties of the raw earth material to obtain a material which is 634 more easily extrudable than raw earth alone. These results represent a base, 635 additional tests must be conducted to have a better understanding of the mode of 636 action of these polysaccharides and to determine the best procedure for adding these 637 compounds to the mix soil and water. Additional tests must also be conducted on 638 other types of soil, with different clay content and calcium content.

639 In order to industrialize the process in the future, the polysaccharide extractions 640 were carried out with as few steps as possible. Some results with freeze-dried 641 extracts containing other molecules than polysaccharides showed that high purity 642 is not necessary. However, the polysaccharides precipitation required the use of 643 absolute ethanol, and the freeze-dried extracts used during these tests have three 644 main disadvantages, they require higher water additions to obtain a good 645 consistency, are less concentrated in polysaccharides as they still contained the 646 algal residues and the freeze-drying process is a rather high energy consumer 647 process and operates in batch. Other production processes could be considered to 648 obtain an extract with a high polysaccharide concentration. After the first step of 649 polysaccharide extraction with hot water, a second filtration step to separate the 650 solid residues could be carried out, followed by a atomization drying step. The final 651 goal would be to obtain an algae extract by the cleanest and most-efficient process.

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