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Elaboration of light composite materials based on alginate and algal biomass for flame retardancy: preliminary tests

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ABSTRACT

Alginate-based composites prepared by incorporation of bentonite into alginate or algal hydrogels show promising properties in terms of thermal degradation (mass-loss rate curves under epi-radiator irradiation). They can be used as coating agent or as structured materials. Alginates characterized by high guluronic acid content are more efficient for retarding the ignition of tested materials after calcium gelation. Brown seaweed can be directly used for preparing composite blocks with clay; a pretreatment for partial extraction of alginate was introduced in the preparation of the composite material. In order to achieve a better control of drying procedures (with low apparent density, limited shrinking), another kind of composite was successfully elaborated by the incorporation of freeze-dried alginate/bentonite beads into an alginate matrix. Algal biomass (a renewable resource, which requires less processing than when using pure alginate) can be used for the green manufacturing of promising flame-retardant materials (associated to bentonite). Freeze-dried alginate/bentonite beads incorporated in alginate hydrogels show interesting thermal degradation properties allied to low-density characteristics.

Introduction

Alginate is a natural and renewable resource obtained from brown seaweed (*Laminaria* and *Fucus* are emblematic examples). This is a linear copolymer constituted of guluronic (G) and mannuronic (M) acids (with different and variable fractions depending on the type and part of algal biomass, growing conditions, and seasons) linked by $\beta(1-4)$

bonds. This biopolymer can be used for many applications from environment (removal of metal ions and dyes from wastewater) to food and biomedical industry (encapsulation of flavors, drugs, cells, etc.). The interactions of carboxylic groups with metal ions (through chelation or ion-exchange) have been used for binding metal ions [1, 2], but also for structuring these materials and preparing hydrogels (ionotropic gelation) for applications in encapsulation of solid or liquid compounds. These encapsulation

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properties are generally based on the ionotropic gelation of guluronic and mannuronic acid with divalent metal cations (though gelation can be also obtained with acidic solutions or in the presence of trivalent metal cations). Encapsulation by alginate was developed for the immobilization of cells [3], enzymes [4], drugs [5] but also for the entrapment of ion-exchangers (solid or liquid ion-exchangers) for designing new sorbents [6–9].

The regulations concerning the fire-retardant properties of materials have gained over the recent decades the increased attentions of researchers for developing new materials with high thermal stability properties [10–16]. The incorporations of acid and carbon sources, nanoparticles, or intumescent agents in polymer-based composites are conventional processes used for improving their flame retardancy [17–19]. More recently the use of bio-based renewable supports has been investigated [20]. Alginate fibers have very attractive flame-retardancy properties: they are characterized by limited oxygen index (LOI) close to 48 %; this means higher than the relevant value of viscose (i.e., 20 %) [21]. Extensive studies on the flame-retardancy properties of alginate-based fibers and films have been reported considering the impact of divalent metal ions [22, 23]. For example, the Heat-Release Rate (HRR) and Total Heat Release (THR) of zinc-alginate fibers were determined by cone calorimetry: HRR and THR were significantly reduced with increasing the amount of zinc immobilized on the fibers (Zn(II) being immobilized by adsorption of alginate films by immersion in a Zn(II) solution). The incorporation of zinc increases char formation and reduces the maximum mass-loss rate. The type of metal bound to alginate strongly affects the thermal degradation of alginate-based films and its flame-retardancy properties through effects such as decreased release of combustible gaseous products (low HRR at low relative temperature) and catalytic acceleration of thermal degradation [16]. These beneficial effects are associated to the production of zinc carbonate and to the covering of the surface of the fibers [24]. Indeed, Tian et al. [24] report that the partial destruction of the glycosidic bound concomitantly to water desorption during the first phase of thermal degradation (in the range 50–200 °C) contributes to the formation of zinc carbonate, which in a second step of the process is degraded and produces some residues that contribute to form a coherent flame and heat barrier that limits the diffusion of the gases (oxygen and pyrolytic gases) and

the heat transfer. On the other hand, other studies suggest that zinc ions catalyze the alginate to form residues and zinc oxide [23]. In the case of Ca-alginate fibers, Zhang et al. [21] report that thick and consistent residues are formed during pyrolysis that effectively inhibit heat transfer. The condensed phase contributes to inhibit smoke release. The LOI values for metal/alginate fibers were ranked according to: Alg/Ca (48 %) > Alg/Ba (45 %) > Al/Zn (42 %) \gg Al/Cu (30 %) \gg Alginic acid (24 %) [21, 25]. However, the thermal degradation properties and/or flame-retardancy properties can be also enhanced by preparing composites associating, e.g., alginate-based matrix with clay materials [26–28], or metal oxides [29, 30]. The incorporation of montmorillonite into alginate scaffolds was investigated in terms of mechanical and flammability properties [26]: the heat release decreased, and the compressive modulus increased with the increasing amount of clay in the composite material.

The processing of alginate hydrogels allowed developing a wide range of different shapes including usual alginate beads, but also fibers, tubes, foams, and sponges (scaffolds) [2, 22, 23, 25–27]. These alternative shapes are opening new perspectives for the use of these materials: light materials having highly permeable properties (macroporous). Foams and sponges are generally manufactured through a freeze-drying procedure followed by post-crosslinking treatment [27].

In this work, a series of preliminary tests has been carried out for testing the flame-retardancy properties of alginate-based materials used as (a) a coating agent (surface impregnation of a flammable substrate; i.e., wood-based materials such as Masonite and balsa), or (b) as a structuring material designed under the form of foams using a very simple methodology based on the mass loss of target objects submitted to heat flux using an epiradiator. Two alginate samples have been tested (with different G/M ratios; i.e., inversed guluronic acid/mannuronic acid proportions) in order to verify, in a first step, the impact of structural properties of the biopolymer on the properties of coating layer regarding mass-loss rate (tests performed on wood-based surfaces). The incorporation of bentonite in alginate coating was also initially carried out on wood-based surfaces to verify the improvement of thermal stability of alginate/bentonite coating.

In a second step, structured materials have been produced under the form of biopolymer blocks, algal

block, and algal or alginate/bentonite blocks. The objective of testing algal biomass is to substitute partially or totally alginate with a less-expensive material by a one-pot process (which consists in alginate extraction and shaping of the material). This modification in the manufacturing procedure is supposed to contribute to the greener production of biopolymer or algal biomass/bentonite materials by one-pot extraction of alginate (from algal biomass) and shaping of the composite material.

The last series of material was produced by the incorporation of preformed alginate beads into the alginate foam (with the objective of increasing the physical/morphological stability of the foams when air-dried). This work must be considered a simple prescreening of the flame-retardancy potential of this wide portfolio of algal/alginate-based materials. The objective of this last part consisted of the manufacturing of materials with improved thermal degradation properties, having enhanced morphological stability (during the drying step by preventing material shrinkage), and with decreased apparent density: light green materials with enhanced thermal degradation properties from renewable resources.

Materials and methods

Materials

Two samples of alginate were supplied by FMC (Norway), referenced Protanal LF 240D (Alginate M) and Protanal LF 200S (Alginate G) with mannuronic acid–guluronic acid (M–G) distribution ratios of 67–33 and 34–66, respectively. Bentonite (clay), CaCl_2 , NaHCO_3 , CaCO_3 , and δ -gluconolactone were supplied by Sigma–Aldrich (Switzerland). Soluble wheat starch and ethanol were provided by Fluka AG (Switzerland). *Laminaria digitata* (brown seaweed) was purchased from SETALG (France) and used as supplied. Masonite panels (steam-cooked and pressure-molded wood fibers; thickness 2.9 ± 0.4 mm) were supplied by Isorel (France). Balsa wood (thickness: 3 ± 0.3 mm) was supplied by a local model-maker shop.

Synthesis of materials

Alginate solutions (2.5 and 5 % w/w) were prepared by dissolving the biopolymer in water under

agitation for at least 2 h. Solutions were stored in a refrigerator to prevent bacterial or fungal contamination and hydrolysis. The suspension of calcium carbonate was prepared by dispersion of the salt in water (10 %, w/w); samples taken from this stock solution were processed under agitation (homogeneous suspension). δ -gluconolactone is an additive (used in food industry, for example) that partially and progressively hydrolyzes in water to produce lactone and gluconic acid. When alginate is mixed with calcium carbonate and δ -gluconolactone, the reaction of gluconic acid with calcium carbonate enhances the release of calcium ions that, in turn, contribute to the in situ ionotropic gelation of alginate. This method favors the controlled gelation of alginate (in the whole volume of the “object” contrary to the shrinking gelation process occurring when alginate is ionotropically gelled by external contact with calcium chloride solution, the standard method). This method is also relatively slow and allows managing the gelling process when the mixture is used, e.g., for the surface impregnation of substrates.

Coating of wood-based surfaces

Masonite coating by the alginate/ CaCO_3 / δ -gluconolactone mixture was processed by means of the brush and the coating of both the surfaces and the edges of the squared panel (45-mm length). After biopolymer deposition, the coated panels were dried at 60 °C for a minimum of 2 h.

Tests on the coating of balsa wood followed the same procedure; however, in this case, bentonite or starch was added to the alginate/ CaCO_3 / δ -gluconolactone mixture before processing the surface coating. It is noteworthy that in the case of bentonite incorporation, ethanol was used for wetting the clay and for preventing its agglomeration. In addition, in this case, the coating was operated on each side of balsa panel, and two coating layers were successively deposited.

Preparation of alginate and algal biomass blocks

Algal dispersion was processed by mixing *Laminaria digitata* (finely crushed, 5 % w/w) with NaCO_3 (1 %, w/w) in water, for 1 h at 50 °C, and 1 h at 20 °C. For preparing blocks of structured materials (foams and dense blocks), this algal dispersion was mixed with

different compounds such as bentonite (with ethanol) and the gelling medium (i.e., $\text{CaCO}_3 + \delta$ -gluconolactone). The homogeneous mixture was poured into a silicon mold. After their homogeneous gelation, the blocks were removed from the molds and air-dried or freeze-dried. Freeze-drying is the best method for drying the blocks and maintaining the shape and structure of the material: air-drying strongly deformed the 3D rectangular shape of the structured materials. Alternative blocks of structured materials were prepared using directly alginate as the embedding material and adding algal biomass as an additive.

Preparation of alginate/bentonite beads incorporated in alginate blocks

Other variants of the composite blocks of structured materials were prepared using preformed alginate beads (which were air-dried or freeze-dried) in a mixture of alginate (2.5 % w/w), CaCO_3 and δ -gluconolactone. The alginate beads were prepared in the presence of starch or bentonite (+ethanol). Calcium carbonate (5 mL of suspension) was added to 90 mL of alginate solution (Alginate G, 2.5 % w/w), adding 10 g of bentonite (+8 g of ethanol) or 10 g of starch. The mixture was pumped through a thin nozzle into a gelation solution (2 % formic acid (85 % w/w), 2 % $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$). In some cases (i.e., samples A4 and A6), NaHCO_3 was added to the alginate solution for the preparation of alginate beads in order to create internal porosity (production of CO_2) and reduce the apparent density of the beads. Table 1 reports the

composition of the different batches. The objective of these alternative materials consisted in maintaining the shape of the blocks (shrinking effect) using a simple air-drying and reducing the apparent density of the blocks.

Fire tests

A combustion chamber was built with protection panels (aluminum walls) to prevent air currents that could affect the burning of the samples and reduce the reproducibility of the tests (See Figure AM1, Additional Material Section). The epiradiator (Power: 500 W) was placed at the top of the chamber with an adjustable platform to maintain a constant heat flux (measured by fluxmeter to approximately $17 \pm 1 \text{ kW m}^{-2}$). A distance of 8.5 cm between the surface of the epiradiator and the surface of the sample was systematically applied to maintain this constant heat flux. Although this is not a standard value, the system allowed maintaining reproducible irradiation. The piece of material to be irradiated was placed in a rectangular deck (50 × 50 mm) connected to a mass balance (Kern 572–33, France, precision: 0.01 g) by a deported arm (and protected from heat transfer by insulation) for following mass loss during the burning process. The balance is connected to a computer for online data acquisition. The chamber was pre-equilibrated in temperature (controlled to $100 \pm 10 \text{ }^\circ\text{C}$) by pre-irradiation; the protecting cap was removed just at the beginning of specimen irradiation. No spark igniter was used to force ignition. Figure AM1 (see Additional Material Section) shows

Table 1 Experimental conditions for the preparation of alginate beads/alginate composites and testing for thermal degradation

Reference	Composite alginate beads (2.5 % w/w, dry weight)				Composite alginate beads/alginate blocks			
	Drying ^a	Bentonite ^b	Starch	NaHCO_3	Alginate (2.5 %, w/w) (mass solution, g)	Alginate beads (dry weight, g)	CaCO_3 (g, suspension)	δ -Gluconolactone (g)
A1	F	10 % d.w.	–	–	20	2.5	1	0.5
A5	A	10 % d.w.	–	–	20	12	1	0.5
A3	F	–	10 % d.w.	–	20	2.5	1	0.5
A2	A	–	10 % d.w.	–	20	12	1	0.5
A4 ^c	F	–	–	1 %, d.w. ^d	20	1.5	1	0.5
A6 ^c	F	–	–	1 %, d.w. ^d	20	1.5	1	0.5

^a Drying: A for air-dried, F for freeze-dried

^b (including ethanol)

^c A4 small beads ($0.8 \pm 0.15 \text{ mm}$), A6 large beads ($1.7 \pm 0.3 \text{ mm}$)

^d sodium hydrogen carbonate was added with the objective of creating internal porosity (by internal production of CO_2)

a simplified scheme of experimental setup. Experimental data were obtained as the average of 3 or 4 tests processed under identical heating conditions and same sample batch. When relevant, the time to ignition was recorded.

Obviously this experimental procedure is not standardized and could not be considered as substitute to the existing standard methods using cone calorimeter test, but this is a fast and efficient tool for the pre-screening of this portfolio of materials. The experiments were specifically designed for prescreening the materials; although inspired from NF P 92 501 standard procedure, the experimental protocol is different, and data cannot be directly correlated.

Pyrolysis combustion flow calorimetry (PCFC)

Flammability was investigated using a pyrolysis combustion flow calorimeter (PCFC) which was developed by Lyon and Walters [31]. The sample (3 ± 1 mg) was first heated from 80 to 750 °C at 1 °C/s in a pyrolyzer under nitrogen flow, and the degradation products were sent to a combustor where they are mixed with oxygen in excess at 900 °C. Under such conditions, these products were fully oxidized. Heat-release rate (HRR) was then calculated by oxygen depletion according to Huggett's relation (1 kg of consumed oxygen corresponds to 13.1 MJ of released energy) [32]. Sample weights were measured before and after tests to calculate the residue amount.

Results and discussion

Preliminary tests on alginate-coated masonite supports

The first series of experiments was performed on Masonite panels impregnated with two types of alginate (rich in guluronic acid or in mannuronic acid) as a simple biopolymer coating (Alginate G or Alginate M) or as a calcium ionotropically gelled layer (Alginate G/M-Ca, using CaCO_3 and δ -gluconolactone). Figure 1 compares the mass-loss profiles of these different materials (using raw Masonite as the reference material). Three sections can be identified on these mass-loss profiles: (a) a first phase with a weak slope associated to the dehydration of the material, followed by (b) the mass loss due to the

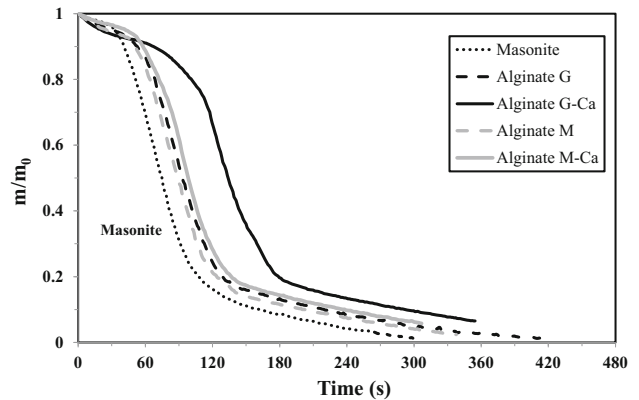


Figure 1 Effects of the type of alginate and the ionotropic gelation on the relative mass loss (m/m_0) for impregnated Masonite materials (reference: Masonite; G guluronic acid-rich alginate; M mannuronic acid-rich alginate; 2.5 % alginate solution; Ca ionotropic gelation with CaCO_3 and δ -gluconolactone).

ignition of the material (the slope is almost vertical), and (c) a third phase that represents the thermo-oxidation of the char after flame out (weak slope). The first phase represents a mass loss of approximately 10 % and lasts for 30 s for raw Masonite and 50–70 s for coated materials. This step also includes the beginning of the pyrolysis of the material but the heat flux being relatively low (i.e., 17 kW m^{-2}) the slope is significantly lower than the slope observed at the second step (where the heat flux is the combination of both the heat of the flame and the heat flux of the epi-radiator). The ionotropic gelation improves the flame-retardancy properties of the coated surface, and this beneficial effect is especially marked for materials based on Alginate G (i.e., Alginate G-Ca) : the time to ignition is shifted by biopolymer coating and more specifically when the biopolymer is gelled by calcium cations (Table 2). The simple coating of Masonite panels slightly delays the ignition probably because the coating layer limits gas exchanges. Guluronic-rich alginates have been reported to form more stable hydrogels with calcium in gastrointestinal conditions (corresponding to pH 1.2 and 7), especially when the ionotropic gelation occurs in the whole mass of the hydrogel (internal coagulation *vs.* external gelation into a gelation solution) [33]. External gelation is obtained by dropping the alginate material in a calcium-gelling solution. In the case of internal ionotropic gelation, a source of calcium (e.g., calcium carbonate) is introduced in the alginate solution in the presence of δ -gluconolactone. The slow release of protons due to gluconolactone

Table 2 Effect of coating treatment on time to ignition for masonite panels

Support	Gelation	Layers	Time to ignition (s)
Masonite (reference)	–	–	40 ± 6
Alginate G	No	1	54 ± 8
Alginate G	No	2	69 ± 6
Alginate G	Yes	1	113 ± 9
Alginate G	Yes	2	115 ± 3
Alginate M	No	1	63 ± 6
Alginate M	No	2	54 ± 7
Alginate M	Yes	1	92 ± 17
Alginate M	Yes	2	85 ± 3

dissociation contributes to the progressive release of calcium (neutralization of carbonates with production of carbon dioxide), which, in turn, leads to homogeneous gelation in the core of the alginate matrix. It was also reported by several studies that guluronic sequences form densely crosslinked structures while mannuronic sequences tend to retain larger amount of water in the network [34]. The calcium ionotropic gelation of guluronic-rich alginate favors the formation of deformable gels contrary to mannuronic-rich alginate [35]. The internal ionotropic gelation of alginate was reported to be strongly controlled by the amount of CaCO_3 used and the relative G/M fraction of the biopolymer: this affects the elasticity of the hydrogels but poorly influences the amount of Ca(II) bound to the hydrogel [36]. Guluronic-rich alginates have been shown to be less sensitive to shrinking and to have higher permeability and mechanical resistance than guluronic-low alginates [37]. High guluronic content contributes to increase the compressive modulus and strength of calcium alginate gels [38]. This may be very important for preparing structured materials (see below).

Figure 2 shows experiments performed on Masonite panels coated with one or two layers of calcium-gelated alginate G and Alginate M. This second series of experiments clearly confirms previous conclusions obtained from Fig. 1 with a single biopolymer coating. It is noteworthy that the second coating layer is not significantly enhancing the fire properties for coated Masonite; and times to ignition are even slightly reduced in the case of Alginate M coating (Table 2; in any case, the variation is not significant under the criterion of experimental uncertainty). This may be due to a loss of flexibility of the biopolymer layer deposited at the surface of the substrate and the

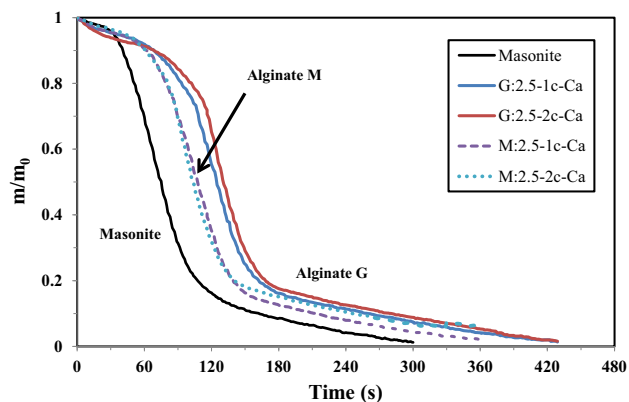


Figure 2 Effects of the type of alginate and the number of coating layers (1c: 1 layer; 2c: 2 layers) on the relative mass loss (m/m_0) for impregnated masonite materials (reference: free masonite; Guluronic acid-rich alginate; 2.5 % w/w alginate solution; ionotropic gelation with Ca(II) and δ -gluconolactone).

formation of cracking at the surface of the biopolymer layer. Under the hypothesis that the biopolymer layer minimizes the transfer of gas (oxygen, pyrolysis gases) [24], the deposition of a second layer is not expected to significantly improve fire retardancy, and a one-layer coating is sufficient.

Alginate, especially under the form of calcium-gelated layer with high guluronic acid fraction is assumed to limit gas diffusion, facilitates the accumulation of calcium, which, in turn, may enhance the formation of a residue during the combustion process. The testing of thermal properties by PCFC did not show significant differences between Alginate G and Alginate M. Figure AM2 (see Additional Material Section) shows the HRR curves obtained for alginates and algal biomass (with and without bentonite). The decomposition pathway is complex with several peaks and shoulders in the range of 150–550 °C. Both alginates and algal biomass exhibit mainly a first peak at 200 °C and a second one at 450 °C. There is not significant difference between these materials. The curves are noisy due to the very low intensity of the peaks. Indeed, the peak of heat-release rate (pHRR) is 10–12 W/g, and the total heat release is systematically lower than 3 kJ/g. These values are very low in comparison to usual polymers or other polysaccharides. For example, cellulose exhibits pHRR and THR values close to 141 W/g and 8.6 kJ/g, respectively [39].

The residue amount is in the range 35–38 wt% for these three materials in good agreement with the

literature [21] for calcium alginate. As a consequence, the differences observed in the times to ignition are not directly correlated to the thermal stability of coating layers; the beneficial interest of Alginate G is thus indirect and could be associated to the ionotropic gelation mode and to its effect as gas barrier. The incorporation of inert bentonite decreases the heat-release rate and total heat release and increases the residue amount up to 68 wt%. The heat-release rate is so low that it is difficult to interpret some changes in comparison to algal biomass without bentonite as the appearance of an additional small peak at 320 °C.

Tian et al. (2013) reported the limitation of gas transfer in the case of ionotropic gelation of alginate with Zn(II) [24]. This limitation of gas diffusion may explain the shift in the mass-loss profiles. It is noteworthy that no thermally stable char remains at the end of the test, due to a thermo-oxidation step at the end of the test. With associated to a thermo-oxidation phenomenon. Alginate G has been selected for subsequent experiments due to improved properties after homogeneous calcium ionotropic gelation.

Preliminary tests on alginate/bentonite-coated balsa wood

Alginate layer (prepared with the internal ionotropic gelation) was deposited at the surface of balsa wood. In an attempt to verify the possible beneficial effect of additives on the thermal degradation, starch and bentonite have also been incorporated in the coating layers. Figure 3 shows that coating the piece of balsa wood with alginate alone, or alginate combined with starch does not significantly affect the mass-loss profile. It is necessary to incorporate bentonite (inorganic fraction in the composite is close to 20 %, w/w) for observing a shift in the mass-loss curve. The addition of inorganic particles, layered oxides, or clays has been reported to promote (a) the formation of chars and thermal insulator layers, (b) the trapping of decomposition products, and (c) the formation of mass transport barriers to oxygen and other flammable volatile compounds [27]. In the present case, the ignition time is shifted, while the weight of final residue remains constant (Fig. 3). This preliminary test confirms the interest in incorporating the clay in the composite materials for the protection efficiency of the coating: the ignition time was increased from 10 to 17 s when using alginate/bentonite as a coating agent. Statistical analysis of data confirms that the shift in time to ignition is significant.

Tests on structured materials—algal blocks

The next step in the design of morphologically stable materials with high thermal stability consisted of the preparation of alginate/algal materials incorporating bentonite clay. Blocks of algal biomass (pretreated with sodium carbonate for partial extraction of alginate; this alginate fraction will be acting as the structuring material, while the cellulose fibers will be acting as mechanical reinforcement) were prepared with increasing amounts of clay. *Laminaria digitata* is reported to contain about 30 % of alginate (in dry weight) [40, 41]. Figure 4 shows the mass-loss curves: the reference curve is the algal suspension shaped as foam blocks with internal ionotropic gelation ($\text{CaCO}_3 + \delta\text{-gluconolactone}$). The incorporation of increasing amounts of bentonite induces a series of changes in the profiles of the mass-loss curves: (a) a slight increase in the initial phase (preceding the ignition), especially at high bentonite loading, (b) a decrease in initial slope of mass-loss curve, and (c) an increase in the mass of the residue at the end of the combustion. In the initial phase, the plateau lasts for increasing times with the amount of bentonite incorporated in the material. The largest variations were observed in the range of 1–3 g of bentonite addition (i.e., 20–60 % of algal mass, w/w dry basis); increasing the amount of bentonite to 5 g (i.e., adding as much bentonite as the dry amount of algal biomass) had a much limited effect and most of

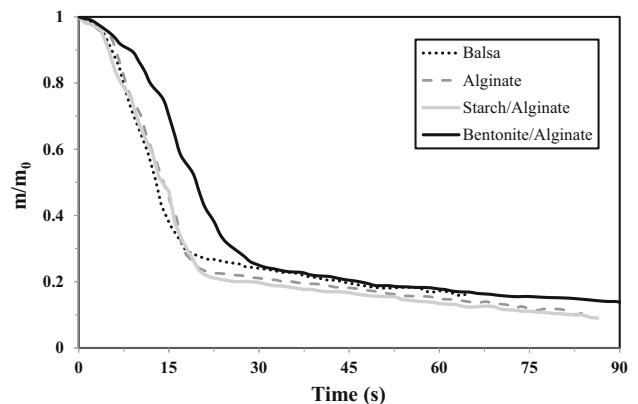


Figure 3 Effects of the incorporation of starch and bentonite in alginate coating of balsa wood on the relative mass loss (m/m_0) for composite materials (reference: Balsa; G guluronic acid-rich alginate; 2.5 % w/w alginate solution; ionotropic gelled with Ca(II) and $\delta\text{-gluconolactone}$; additive/alginate: 1/5, w/w, dry basis).

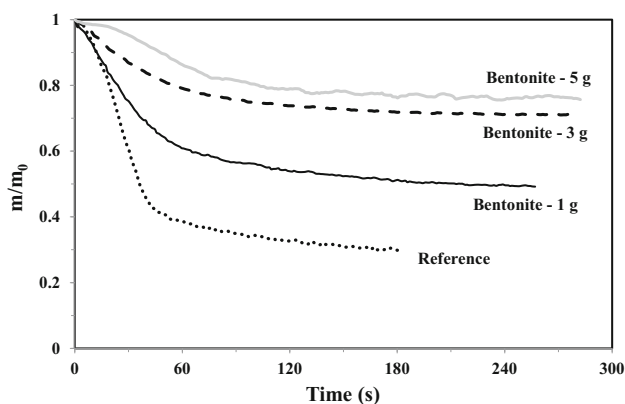


Figure 4 Effects of the incorporation of increasing amounts of bentonite (+ethanol) in algal blocks on the relative mass loss (m/m_0) for composite materials (reference: algal biomass; ionotropic gelation with CaCO_3 and δ -gluconolactone; proportions: 15 g Algal suspension (2.5 % w/w), m g bentonite (+ m g ethanol), 1 g CaCO_3 , 0.5 g δ -gluconolactone).

the impact consisted of increasing the duration of the initial phase. The analysis of the slope (in the linear section of the relative mass-loss curves; i.e., 15–30 s; or 25–40 s for the material with the highest bentonite loading) shows a progressive decrease when increasing the amount of bentonite: 0.018 s^{-1} for reference material (without bentonite), while the slope is successively halved when bentonite is added: 0.0084 s^{-1} for 1 g addition and 0.0040 s^{-1} for 3 g addition; however, a greater addition (i.e., 5 g) slightly affects the slope (i.e., 0.003 s^{-1}). Figure 5a correlates the fraction of residue produced after burning the composite blocks with the weight content of bentonite in the material. Figure 5b plots the mass-loss rates (MLR) as a function of bentonite weight fraction: MLR continuously decreased when increasing the amount of bentonite in the composite. However, when normalizing this MLR in function of the actual fraction of the organic content of the composite, the curve shows that when the bentonite addition is set to 5 g (i.e., 61 % weight fraction, and 70 % taking into account all mineral compounds) the MLR tended to stabilize close to 0.014 s^{-1} . The progressive decrease in the MLR could be explained by the accumulation of bentonite at the surface of the composite, which, in turn, contributes to form an insulating barrier. The duration of initial phase is significantly increased in the case of the 5-g addition of bentonite; this is probably due to the more dispersed distribution of the algal fraction in the composite and to the fact that the combustible fraction in

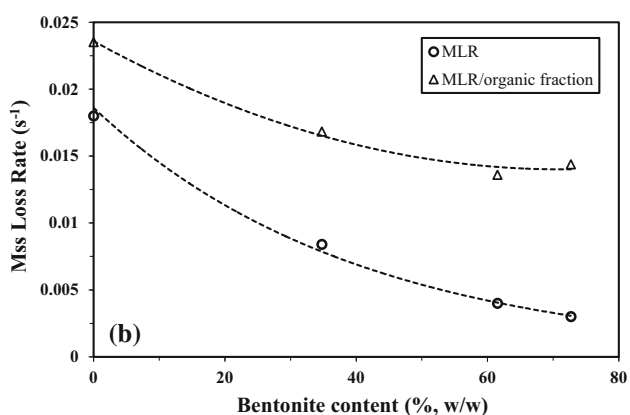
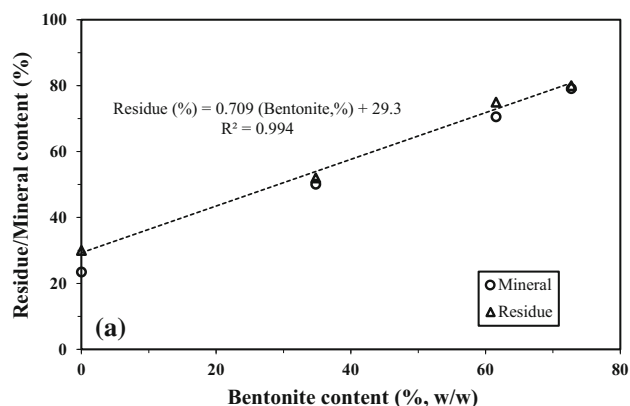


Figure 5 Effects of bentonite content on the formation of residue (a) and mass-loss rate (b) in the burning of algal biomass/bentonite composite blocks (mineral fraction was calculated taking into account the amounts of mineral compounds such as calcium carbonate, bentonite, etc.) (data from Fig. 4).

the composite is too low to produce a sufficient amount of inflammable gas at the surface of the solid: the auto-ignition is then more difficult.

Figure 6 shows the aspect of the residue obtained at the end of combustion testing with algal/bentonite blocks. It is important to observe that the char maintains a good morphological stability, at least compared with other systems that did not contain bentonite load.

Encapsulated alginate beads/alginate blocks

A large portfolio of composite blocks was prepared; the morphological aspect of dried materials is summarized in Table AM1 (See Additional Material Section). The materials that best maintained their shape and size were obtained by the incorporation of alginate beads within alginate blocks or by the incorporation of bentonite in algal blocks.

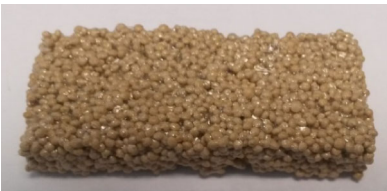





Figure 6 Example of char obtained after burning of algal/bentonite block (dimensions of the block after thermal degradation: 51 × 26 × 4.5 mm).

The positive effect of bentonite on the flame retardancy of the composite blocks led to investigate more deeply the properties of alginate/clay composite blocks taking into account the processing of the blocks (drying procedures and relative effect on the morphology of the blocks: deformation, shrinking, and apparent density). Alginate beads have been produced as biopolymer hydrogels or composite hydrogels (associated with wheat starch, bentonite or sodium hydrogen carbonate (for producing internal bubbles)). These beads were air-dried or freeze-dried

and then incorporated in alginate blocks (Table 1). Table 3 summarizes the morphological aspect of dried blocks. Figure 7 reports the mass-loss curves for the different materials. The conditions for the preparation of composite blocks strongly influence the mass-loss curves: amount of residue at the end of the combustion, duration of the initial phase, and initial slope of the curves. The most favorable profiles were obtained with the samples A1 and A5, which incorporated bentonite: the residues were significantly higher than with other materials. This is consistent with the results obtained in previous sections. This is also consistent with the nonflammability of these two blocks; indeed no ignition was observed on these two samples (Table 4). The nonflammability of these samples means that the heat flux applied to the blocks is only due to epiradiator heat flux (there is no additional contribution from the flame as observed with other samples); this contributes to reducing the degradation kinetics. The sample A2 (which does not contain bentonite) shows a singular behavior with mass-loss curve quite close to the profile observed with the sample A5 (within the first 40 s of testing); however, after ignition (at 36 s), the mass loss is very

Table 3 Composites based on alginate beads encapsulated in alginate blocks (dimensions of the blocks: 56 × 28 × 5 mm)

Drying of composite alginate beads		
Filling	Air-dried	Freeze-dried
Bentonite		
Starch		

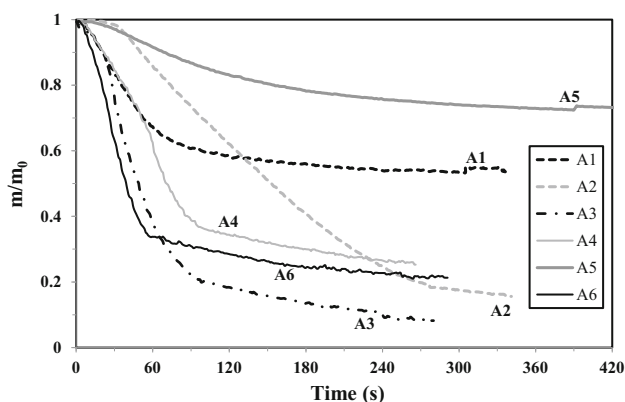


Figure 7 Effects of the incorporation of composite alginate beads (dried or freeze-dried) in alginate blocks on the relative mass loss (m/m_0) for hybrid materials (detailed compositions are appearing in Table 1).

Table 4 Properties of alginate beads/alginate blocks

Reference	Shrinking percentage (%)	Apparent density (g L^{-1})	Time to ignition (s)
A1	58	317	No
A2	53	755	36
A3	50	306	23
A4	60	308	58
A5	43	832	No
A6	34	164	25

No: no ignition

fast. Other materials showed less interesting properties in terms of mass-loss curves and time to ignition (Fig. 7, Table 4).

The shrinking properties at drying, and the apparent density of dried blocks were recorded, together with the time to ignition (Table 4). Figure 8a shows that the time to ignition increases with the apparent density of the blocks; however, the response strongly depends on the composition of the composite material. Indeed, in the case of NaHCO_3 material, even with the large increase in the apparent density the time to ignition increases by only a few minutes. On the other hand a limited increase in the apparent density causes a strong increase in the time to ignition. This means that the “compactness” of the biopolymer block is not the critical parameter, and the properties of the organic/inorganic load have a strong influence. Actually, the behavior of these materials is controlled by both the apparent density and the composition of the blocks (Table 4). Indeed, increasing the apparent density delays the time to

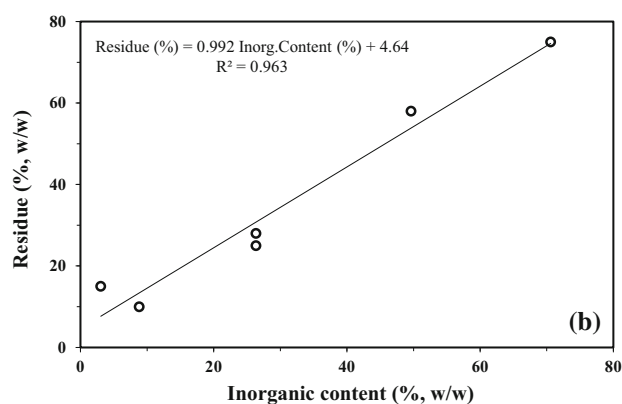
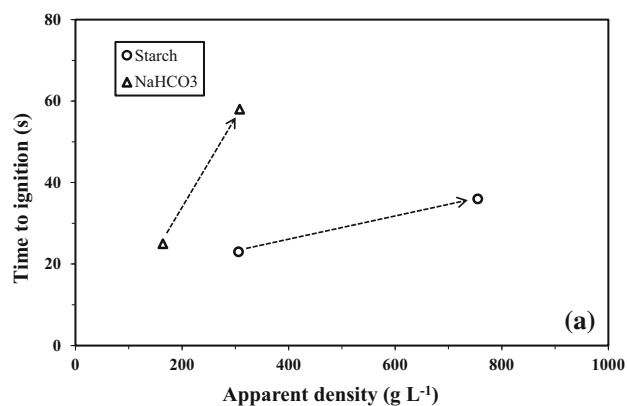


Figure 8 Fire tests on hybrid alginate beads encapsulated in alginate blocks: **a** correlation between time to ignition and apparent density, and **b** correlation of residue production to inorganic content (data from Fig. 7).

ignition, and decreases the slope (kinetics) of the mass-loss rate. Starch contributes to maintain the structural shape of the materials during the drying step but at the expense of poor fire-retardancy properties: (a) limited amount of residue, and (b) relatively fast ignition. On the other hand, bentonite incorporation slows down the mass-loss rate.

Figure 8b shows a clear correlation between the production of residue with the inorganic content in the composite material. The ordinate intercept is close to 5 % (w/w): this means that the char is rather limited.

Based on these results, the best compromise for preparing thermally stable composites with good stability at drying and low apparent density consists of using sample A1: apparent density is strongly decreased compared with sample A5, although the shrinking of the material at drying was higher (58 vs. 43 %). The lower apparent density is obviously associated to the use of freeze-dried alginate beads. Shrinking of beads at freeze-drying is much lower

than that with air-drying; this means that after the incorporation of the alginate beads, the mass density of additive is much larger than that with expanded freeze-dried alginate beads.

Conclusion

Guluronic-rich alginate is more favorable than manuronic-rich alginate, and homogeneous ionotropic gelation (by controlled release of calcium ions) allows preparing promising materials for coating surfaces (e.g., balsa wood, Masonite). The properties of thermal degradation are considerably increased by bentonite incorporation: increase in residue, in time to ignition, and lower flammability. Blocks made of algal/bentonite or freeze-dried alginate/bentonite beads encapsulated in alginate hydrogel show a good compromise between thermal stability properties and morphological characteristics (relatively low volumetric density). These preliminary tests require complementary investigation with standardized procedures for the quantification of flame-retardancy properties in comparison with conventional insulating materials; however, this screening of manufacturing processes demonstrates the promising perspectives of these new materials.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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