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New alginate foams: Box-Behnken design of their manufacturing; fire retardant and thermal insulating properties

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ABSTRACT: A new method for preparing alginate foams with progressive release of copper in the presence of sodium lauryl sulfate (SLS, foaming agent) has been designed. Copper acts as the ionotropic gelling agent through the reaction of copper carbonate with gluconolactone. The process does not require freeze-drying contrarily to the conventional method used for preparing macroporous alginate foams. The new materials investigated in this study have remarkable thermal properties, including thermal conductivity lower than $0.041 \text{ W m}^{-1} \text{ K}^{-1}$ and low heat release (below 2 kJ g^{-1}), which allows labeling these foams self-extinguishing materials. An experimental design methodology, based on a Box-Behnken plan with three parameters and three levels, is successfully used for evaluating the impact of the amounts of alginate, SLS, and copper carbonate on the productivity, apparent density, and shrinking at air-drying. It yielded an optimization of the process for the manufacturing of light, and stable/rigid insulating and thermally stable materials.

KEYWORDS: biopolymers and renewable polymers; foams; manufacturing; polysaccharides; thermal properties

INTRODUCTION

The increasing demand for alternative materials produced from renewable resources is driving an intense research for substituting oil-based products with agriculture or marine subproducts. For example, in environmental applications biosorbents are being investigated for replacing synthetic resins for the removal and/or recovery of metal ions from dilute solutions. Biomass can be also used for binding metals and then used for supported catalysis. In the field of safety and fire protection, materials of biological origin have also received a great attention for the last decades.^{1–4} Synthetic materials, especially chlorine and aromatic-containing ones as poly(vinyl chloride) and polystyrene, may produce toxic subproducts such as volatile organic compounds during combustion (even in well-ventilated conditions),^{5,6} while the thermal degradation of agriculture waste or marine resources is generally more environmentally friendly.⁷ Recently, alginate, a polysaccharide extracted from brown algal biomass has also retained a great attention due to its promising properties in terms of fire retardancy.^{8–13} Alginate is a heteropolymer constituted of guluronic acid and mannuronic units; this biopolymer rich in carboxylic acid is ionotropically gelled with divalent or trivalent metal cations to form stable hydrogels. The properties of the hydrogels strongly depend on the metal cations used for gelling.^{14–16} Zhang *et al.* investigated the flame retardancy properties and pyrolysis

products of calcium alginate¹⁰: they highlighted the relatively high value of the limiting oxygen index, close to 34, and the fact that alginate fibers do not show combustion in air. The heat release rate (HRR), effective heat of combustion, and total heat release (THR) are even lower than the relevant values of most of synthetic or natural polymers. The gelling of alginate with cobalt and manganese allows reducing HRR⁸: the presence of these metal ions is supposed to decrease the release of combustible gases. Similar trends were previously reported in the case of nickel- and copper-gelled alginate.⁹ Zinc was also successfully used for preparing alginate-based materials with enhanced fire retardancy properties.^{17–19} Kong *et al.* observed that the shape of calcium alginate fibers remained stable after limit oxygen index test (LOI) and that the rigid char contributes to form a barrier between the flame or heat and the material.²⁰ The incorporation of clay also contributes to improve thermal degradation properties.¹¹ The HR values are decreased when the proportion of clay increases in the composite.²¹ The freeze-drying procedure of alginate-based hydrogel leads to the formation of foam-like materials with good fire properties. While increasing clay proportion the apparent density of the composite obviously increases.

Foams, which are constituted by a continuous polymeric phase and a gaseous phase (as dispersed bubbles) have several advantages in comparison with unfoamed polymers: lightweight, high

strength to weight ratio, thermal insulation property, and high thermal stability.²² Apart synthetic industrial foams made of polypropylene (PP), polyethylene, or polystyrene base matrices, alternative materials have been used for preparing bio-based foams, for example poly(lactic acid).²³ Pantani *et al.* reported the combination of foaming agent with physical and temperature variations for elaborating biopolymer foams.²⁴ The elaboration of porous biopolymer scaffold has focused abundant research for the last decade using chitosan,²⁵ alginate,^{26,27} or starch-based materials for biomedical application although the concept is now expanding to other applications, such as environmental use for metal recovery,^{28–30} or manufacturing of fire retardant materials.³¹ Usually sophisticated or expensive drying methods are required using, for example, freeze-drying²¹ or drying under supercritical CO₂ conditions.^{28,31} An alternative method has been developed for preparing alginate-based foams without freeze-drying process, for lower cost. The foaming of the alginate-based material is improved using a foaming agent, such as sodium lauryl sulfate (SLS) to produce lighter foam with improved properties of fire retardancy, lower thermal conductivity. The *in situ* gelling of the foam is operated in the presence of copper ions and gluconolactone; the slow dissociation of gluconolactone produces protons that react with copper carbonate, which, in turn, release copper ions in the core of the solutions and causes the progressive ionotropic gelation of the biopolymer. The copper-gelling allows producing more stable and rigid structure than conventional calcium gelling.^{14–16} Despite, other metal cations can be used for alginate gelation, such as barium, zinc, which are very efficient for improving fire retardant properties of alginate (see above), the copper-alginate system is one of the most frequently used, and it is characterized by a high strength and rigidity. Calcium is even more frequently employed for manufacturing alginate-based gels; however, testing the selected procedure with calcium salt did not allow elaborating rigid gels; at air-drying (oven-drying) the porous structure irreversibly collapsed and the materials lose their morphology and shape limiting the possibility to use these materials for target applications. Another advantage at using copper salts is that copper bring bactericide properties that could contribute to prevent the early degradation of the foams.

The principal novelty brought by this study consists of the combined use of a foaming agent, the homogeneous ionotropic copper-based gelation mode, and the cost-effective air-drying method. The drying at 50 °C allows producing dried foams with stable structure that were characterized in terms of foam productivity, measured as the volume of dried foam produced with a given volume of preparation, apparent density and processing efficiency, qualified as the shrinking percentage at drying. A Box-Behnken (B-B) experimental design was designed for optimizing the synthesis procedure of alginate-based foams using copper carbonate, SLS: the concentration of alginate, SLS, and copper carbonate have been varied at three levels (–1, 0, and +1, see below) and the target characteristics are systematically determined in order to design the surface responses that fit experimental data. The processing equations (characterized by 10 specific coefficients, reflecting the individual impact and the cross-effects of experimental parameters) for the different

responses are established, on the basis of a quadratic model equation. The iso-response curves are plotted to illustrate the effects of these parameters and suggest optimum conditions for highest production of light and stable alginate-foams. The discussion of these curves helps in identifying the relative importance of these experimental parameters on the different responses. The main criteria for evaluating thermal insulating foams are characterized by low thermal conductivity, low density, and low flammability.³² Selected samples are also tested for thermal conductivity, thermal degradation, and mechanical stability. Scanning electron microscopy (SEM) is also used for characterizing the opening of foam cells.

EXPERIMENTAL

Materials

Alginate (Manugel DMB, sodium alginate) was supplied by FMC (Cork, Ireland). The commercial characterization of this material corresponds to a viscosity of 263 mPa s (for 1% w/w concentration at 20 °C). Calcium chloride (CaCl₂·2H₂O) was obtained from Chem-Lab (Zedelgem, Belgium). Calcium carbonate, gluconolactone, copper chloride (CuCl₂·2H₂O) were supplied by Sigma-Aldrich Chemie GmbH (Steinheim, Germany). SLS was purchased from Carlo Erba (Milano, Italy). Sodium carbonate was supplied by VWR Prolabo (Fontenay-Sous-Bois, France). The extruded polystyrene foam (EPS) tested as a reference material is commercialized by Raja France (Roissy, France) as a packing material (reference PSE50C).

Preparation of Copper Carbonate

Copper carbonate was synthesized by reaction between CuCl₂·2H₂O and Na₂CO₃ under pH control using the following procedure: 14 g of copper chloride were dissolved in 300 mL of demineralized water; the pH was adjusted to 10 using a 10% (w/w) solution of sodium carbonate. The solution was aged for 2 h before controlling the pH to 8 with 0.25 M HCl solution. The solution maintained under agitation and pH control for 3 h was finally adjusted to a final volume of 400 mL with demineralized water. Copper being in excess compared to carbonate the suspension contains copper carbonate and free copper: free copper will contribute to partial external ionotropic gelation of alginate while CuCO₃ will contribute to the delayed in-core ionotropic gelation (gluconolactone dissociation releases protons that will react with copper carbonate, see below). This suspension will be called CuCO₃ suspension in the next sections. It is noteworthy that commercial copper carbonate is not stable: it is rapidly dissociated in presence of moisture to form the so-called basic copper carbonate associating copper, carbonate, and hydroxide. In addition, the dried product appeared to be non-operable when mixed with alginate; instantaneous precipitation, and agglomeration make impossible the processing of the mixture. The actual fraction of solid precipitate in the suspension has been quantified to 20 g L^{–1} by weight loss at 105 °C.

Manufacturing of Alginate Foams

The principle of the synthesis of alginate foams consists in the homogeneous ionotropic gelation of foamed alginate.^{11,21,33} Foaming was facilitated by the addition under strong agitation of SLS. The slow release of copper (for ionotropic gelation) was operated by the introduction of copper carbonate and

Table I. Levels of Selected Parameters for Box-Behnken (B-B) Design

Variable	Symbol	Coded variable level		
		Low	Center	High
		−1	0	+1
Alginate (amount, g)	x_1	140 (2800)	150 (3000)	160 (3200)
SLS (volume, mL)	x_2	3.5 (35)	6.5 (65)	9.5 (95)
CuCO_3 (volume, mL)	x_3	2.5 (50)	5 (100)	7.5 (150)

Into brackets: amounts in mg for alginate biopolymer, SLS salt and CuCO_3 “equivalent” solid for a total volume of preparation of 200 mL.

gluconolactone in the alginate solution by analogy with the calcium carbonate/gluconolactone procedure of gelation: the progressive dissociation of gluconolactone releases protons that will interact with carbonate and, in turn, induces the release of copper and carbon dioxide, contributes to the internal ionotropic gelation of alginate in its expanded form (foamed suspension). Copper carbonate was preferred to calcium carbonate since the copper gelation of alginate gives stronger and more rigid hydrogels.¹⁵

Sodium alginate was first dissolved in demineralized water (4%, w/w) under agitation using a mixer/kneader (velocity: 150 rpm) for 12 h (until complete dissolution). SLS solution (1%, w/w) was added to a variable amount of the alginate solution (i.e., 140, 150, or 160 g): the volume of SLS (3.5, 6.5, and 9.5 mL; i.e., 35, 65, and 95 mg of SLS, respectively) and the amount of alginate solution (140, 150, and 160 g; corresponding to alginate dry weights of 5.6, 6, and 6.4 g, respectively) were varied for preparing different series of materials. Homogeneous copper carbonate suspension (10%, w/w; agitated) was introduced in the reactor varying the volume of suspension (i.e., 2.5, 5, and 7.5 mL, that corresponds to amounts of precipitates of 50, 10, and 150 mg of CuCO_3 , respectively). Demineralized water was added to a final volume of 200 mL. The suspension was maintained under agitation for 30 min. Then, 2 mL of CaCO_3 suspension (10%, w/w) were added to the mixture under agitation for 1 min and 3 g of gluconolactone were introduced under strong agitation (300–400 rpm) for 30 s and the wet foam was dropped into a rectangular mold (110 × 145 mm). This excess of carbonate (added as CaCO_3) serves to improve the fire retardant properties: the thermal degradation of carbonate produces carbon dioxide through endothermic reaction that may help in controlling fire behavior³⁴; or by heat absorption that increases to time to reach high temperatures around 500 °C.³⁵ The molds were finally dried for 72 h in an oven at 50 °C.

The slow release of copper, mediated by the weak organic acid, is important for preventing the formation of aggregates, the heterogeneous gelation of the biopolymer. Weak acid promotes the slow release and lightly delayed gelation, which, in turn, allows processing the preparation for dipping in the molds. Adding a stronger acid would not allow getting the desired homogeneous structure for the foams and would make the processing of the materials complex with a partial gelation of the mixture before it is dropped in the mold. The protons (released during gluconolactone dissociation) convert carbonate anions in carbonic acid and carbon dioxide, which contributes to a kind of

porogen effect in addition to the foaming effect of SLS during the strong agitation phase.

Preliminary tests allowed identifying three critical parameters for the manufacturing of alginate foams: the amounts of the biopolymer, the foaming agent (SLS), and ionotropic agent (copper carbonate). In order to optimize the manufacturing of the foam an experimental design methodology has been used: B-B design with three variables and three levels (see Table I). Fifteen formulations were prepared, including three replicates of the centered point; they are reported in Table II.

Several criteria were used for qualifying the production of the alginate foams: the volume of foam generated, both wet and dry, the density (kg m^{-3}), and the shrinking percentage (%). The responses to variable parameters are also reported in Table II.

A first B-B experimental design was carried out with wider ranges of values; it served to focus on more precise selected values.

The model follows the equation³⁶:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \quad (1)$$

where y is the predicted response vector, x_i are the independent variables, β_i are the linear coefficients, β_{ij} are the cross product coefficients, and β_{ii} are the quadratic coefficients. The units of these parameters depend on the tested parameter (apparent density, volume, shrinking percentage), since in the equation the centered coded values are dimensionless. The values of the parameters have been estimated by matrix calculation³⁶:

$$\hat{\beta} = (X^t X)^{-1} X^t Y \quad (2)$$

where $\hat{\beta}$ is the vector of coefficients (β_b , β_{ij} , β_{ii}), X is the so-called experimental matrix (15,10) (see Supporting Information section), X^t is the transposed experimental matrix.

It is noteworthy that a specific set of parameters (β_b , β_{ij} , β_{ii}) was established for each vector of response; that is, dry volume, apparent density, and shrinking percentage.

The central point, repeated three times (runs 13, 14, and 15), shows a relatively good reproducibility for apparent density (i.e., $24.9 \pm 1.8 \text{ kg m}^{-3}$; variation percentage: 7%), dry volume (i.e., $405 \pm 20 \text{ mL}$; variation percentage: 5%), and wet volume (i.e., $490 \pm 9 \text{ mL}$; variation percentage: 2%). On the other hand, for the shrinking percentage the variation is much

Table II. Box-Behnken (B-B) Design with Actual Values of Variables and Experimental Corresponding Results (for a Total Volume of Preparation of 200 mL)

Run #	Actual values of variables			Experimental results			
	x_1 (alginate) (mL)	x_2 (SLS) (mL)	x_3 (CuCO ₃) (mL)	Apparent density (kg m ⁻³)	Dry volume (mL)	Shrinking percentage (%)	Wet volume (mL)
1	140	3.5	5	50.5	251	26.1	339
2	160	3.5	5	145.7	168	38.8	275
3	140	9.5	5	31.6	425	43.1	748
4	160	9.5	5	22.0	408	37.7	654
5	140	6.5	2.5	18.9	504	12.8	578
6	140	6.5	7.5	20.0	441	17	531
7	160	6.5	2.5	22.4	294	24.3	388
8	160	6.5	7.5	28.4	289	25.4	388
9	150	3.5	2.5	71.0	176	42.7	307
10	150	9.5	2.5	31.6	404	40.7	681
11	150	3.5	7.5	95.0	148	45.9	275
12	150	9.5	7.5	23.8	431	30	616
13	150	6.5	5	22.5	434	11.7	492
14	150	6.5	5	25.4	390	20.2	500
15	150	6.5	5	26.9	392	18	478

greater (i.e., $16\% \pm 4\%$; variation percentage: 27%): surface deformation makes difficult the accurate determination of this parameter.

Characterization of Materials

The volumes of the foams were measured before and after drying for 72 h in an oven at 50 °C and the shrinking percentage was calculated by the volume loss after drying (in percentage). The apparent volumetric density was calculated by the measurements of weight and volume of dried foams. Obviously the shrinking during the drying step may cause, under certain conditions, a deformation of the surface of the dried foams; especially the surface that was in contact with the atmosphere; that is, not in contact with the mold. As a consequence the volumes may be determined with a certain “inaccuracy”; the maximum error is evaluated to 10%.

In addition, the macroporous structure (cell opening) of the foam has been characterized using SEM. Inner structure of foams was observed with a SEM (FEI Quanta 200 SEM). All images were obtained under high vacuum at a voltage of 10 kV and a working distance of 9–12 mm.

The analysis of the viscosity of alginate solutions was performed on a Visco Plus viscometer (Fungi Lab, Sant Feliu de Llobregat, Spain), changing both the mobile and the rotation speed with measured viscosity, in order to remain in the range of linearity of the equipment (scale 15%–90% of measurement range, as supplied for each mobile).

Fire Retardant Characterization

Fire behavior was assessed using UL94 vertical burning test.³⁷ Sample dimensions were $100 \times 10 \times e$ mm³, where e is the thickness of the foam. The pyrolysis combustion flow

calorimetry (PCFC) was also used to measure the flammability of samples at microscale (2–3 mg). This device was developed by Lyon and Walters.³⁸ The sample was first heated from 80 to 750 °C at 1 °C/s in a pyrolyzer under nitrogen flow (anaerobic pyrolysis—method A according to the standard ASTM D7309) and the degradation products were sent to a combustor where they were mixed with oxygen in excess at 900 °C. Under selected conditions, all gases were fully oxidized. 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.³⁹

Mechanical Characterization

Compression properties were measured using a Zwick TH010 apparatus at 5 mm/min. 16 mm diameter samples were carefully cut from foams. The dimensions of the foams (including their thickness) depend on the conditions used for the preparation of the materials due to different shrinking percentages. The actual thickness of the sample was systematically measured and used for the determination of mechanical properties. Three to six samples were tested for each formulation.

Thermal Conductivity Analysis

Among the remarkable properties of EPS, which is extensively used as insulating material, its low thermal conductivity can be considered an appropriate reference for testing the alginate-foams produced in this study. Making profit of the equipment available in our research center some preliminary tests have been carried out for comparison with the reference material but also for evaluating the potential impact of foam density. Thermal conductivity was measured at room temperature using a thermal conductivimeter based on hot wire method (FP2C from Neotim).

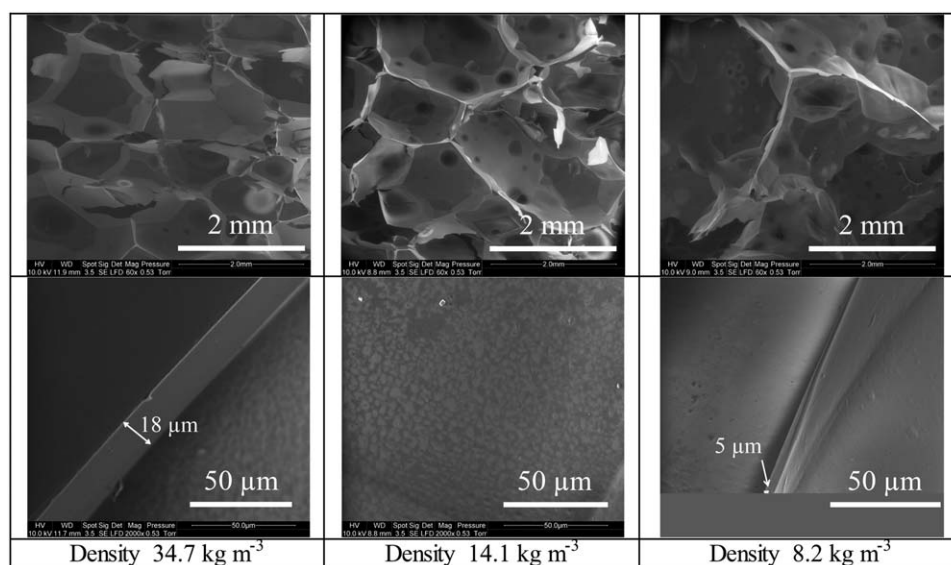


Figure 1. SEM observations of three foams. Effect of density on cell observation [top row, general morphology of foams at the lowest magnification ($\times 60$); bottom row, view focused on the thickness of cell walls, and fine surface aspect of the scaffold at highest magnification ($\times 2000$); pressure in the SEM chamber: 0.53 Torr; accelerating voltage: 10.0 kV].

RESULTS AND DISCUSSION

Morphology of Alginate Foams—SEM Analysis

Due to their brittleness, foams were damaged to a certain extent during cutting and preparation for SEM observations. Figure 1 shows the inner structure of three foams with various densities. These cells can be roughly considered as having a closed-cell structure.²³ The air-drying process is favoring the formation of closed-cells compared to freeze-drying process that forms more open cells. Actually, the freeze-drying was especially used for preparing macroporous alginate foams that were used as highly-percolating materials for the sorption of metal ions.²⁹ The freeze-drying conditions improve the release of the gas dissolved in the gel and the breaking of the bubbles leads to the formation of an interconnected porous network. This effect is even reinforced when using a blowing agent as SLS. With air-drying the interconnected porous network is not formed and the cells mainly remain closed. The open/closed cell structure may have a strong impact on (a) thermal insulating/fire retardancy properties by controlling the diffusion of gases and heat, but also on (b) mechanical properties.⁴⁰

It is noteworthy that the denser foams exhibit smaller cells. For the foams of lower density (8.2 kg m^{-3}) the order of magnitude of the cell size is higher than 4 mm while for intermediary density (i.e., 14.1 kg m^{-3}) the cells have size between $1 \times 1.5 \text{ mm}$ and $1.5 \times 3 \text{ mm}$. The smallest cells are obtained at the highest density; for density of 34.7 kg m^{-3} the cells are more regular with a size close to $1 \times 1.5 \text{ mm}$. Mohebbi *et al.* classified, in the case of PP foams, the materials in several types depending on the cell size and the cell density²²; by analogy with PP foams and based on their size the cells can be qualified as conventional close cells (cell size being greater than $300 \mu\text{m}$ and the cell density being obviously lower than 10^6 cells/cm^3).

The thickness of the cell walls also increases when density increases. This is particularly obvious when comparing the densest foam to the least dense one. This may be related to the

higher mechanical properties of denser foams (thickness from about $5 \mu\text{m}$ up to $18 \mu\text{m}$); however, the actual mechanical behavior of the foams is controlled by both the changes in the thickness of the walls and the cell size (cross section). This would deserve a more complete study for optimizing these mechanical properties. Holes can be also found into cell walls (see top row of Figure 1). Higher magnification highlights the roughness of the scaffold (see for example, pictures for the foam with intermediate density).

Photographs of the size face of the foams (vertical cut) shows that the structure is globally homogeneous; however, for certain formulations, a thin layer of the foams appears less expanded at the center of the block (Figure S1, see Supporting Information section).

Characterization of Thermal Conductivity, Mechanical, and Fire Retardant Properties of Foams

Fire Retardant Properties. The main benefit of alginate-based foams compared to expanded polystyrene foams is their low flammability. The flammability of alginate foams, fibers, or films has been already addressed. Depending on the divalent or trivalent cation used for gelation, V0 rating in UL94 test and LOI higher than 50 can be reached.^{8,9,17,41,42} High char contents ($>30 \text{ wt } \%$) both in air and nitrogen were also measured using thermogravimetric analysis. Gelation with calcium and barium cations was found as very effective for flame retardancy.^{43–45} Lyon *et al.* have studied correlations between PCFC and various fire tests from a large set of polymers.⁴⁶ For example, the probability to obtain V0 rating in UL94 test is high for THR and heat release capacity (HRC); that are lower than 17.8 kJ g^{-1} and $340 \text{ J g}^{-1} \text{ K}^{-1}$, respectively. The HRC is the peak HRR divided by the heating rate.

The measured properties in PCFC for alginate are much lower than the threshold values determined by the authors to pass UL94 test. HRR curve measured in PCFC is shown in Figure 2 for raw

alginate powder (the analytical procedure is independent of the shape and size of the sample). There is no influence of the physical state (powder vs. film vs. foam) on the data measured by PCFC. Probably the exact composition (presence of SLS or other components) may have an influence. But, it must be noted that the HRR is very low and the very small differences from one sample to another one cannot be interpreted. Then a change from 10 to 20 W g^{-1} appears nonsignificant. Two main peaks are observed. Other small peaks can be considered as noise. Keep in mind that peak of HRR for common polymers for which PCFC was designed is generally comprised between 200 and 1200 W g^{-1} ,⁴⁷ this means 10 to 50 times the value measured here. First peak is observed at 240 °C and the second one occurs at 440 °C. These two peaks correspond to two different steps in the thermal degradation profile as it would appear on TGA analysis. The first step consists of the thermal degradation of the material with simultaneous formation of a poorly stable residue, which will be degraded in a second step. However, it is noteworthy that an important fraction of carbon-based product remains in the residue that will be only thermally degraded under aerobic pyrolysis (with a heat release that may exceed 10 kJ g^{-1}). Under anaerobic pyrolysis conditions, the THR is around 3 kJ g^{-1} and the weight loss does not exceed 70%. This means that the effective energy of combustion is close to 4 kJ g^{-1} . This value is very low; this means that released gases are highly oxidized even before the combustion. This is probably due to the presence of significant amounts of carbon dioxide and/or water (and possibly low amounts of carbon-containing gas poorly oxidized and that will be oxidized during combustion with supplementary heat release). Anyway, it is important to point out that the quantities of heat released during the anaerobic pyrolysis are very low; close to the detection limit, which makes the interpretation debatable. The THR (which represents the surface area under the curves) is below 2 kJ g^{-1} for the foams versus 15–44 kJ g^{-1} for common polymers,⁴⁷ and 8–9 kJ g^{-1} for cellulose.⁴⁸ For formulated foams, both peaks are also observed at similar temperature but their intensity is lower, especially for the second peak. The residue content is close to 70 wt %.

All foams exhibit self-extinguishing behavior according to UL94 test and are V0 ranked, irrespective to their thickness or density. In some cases, some parts of burnt materials fall but do not ignite the piece of cotton located below. Actually, the differences observed on different series were not considered sufficient for considering the fire retardant properties to be significantly affected; all the materials are characterized by V0 ranking (UL94) and low THR.

Actually, according literature, sodium alginate materials are not self-extinguishing (regardless of the form; i.e., foams or films) based on tests such as UL94 or LOI. The nature of the gelling agent (metal ion) affects this behavior, while copper and manganese cations do not bring self-extinguishable properties,⁸ metal ions such as Fe(III), Cr(III), Al(III),⁴¹ Co(II),⁸ Zn(II),¹⁷ Ni(II),⁹ or Ba(II)⁴⁵ allows converting alginate to self-extinguishable material after metal gelation.

Figure S2 (see Supporting Information section) shows the change in the aspects of a foam block subjected to three successive flame exposition (individual irradiation time: 10 s). Though

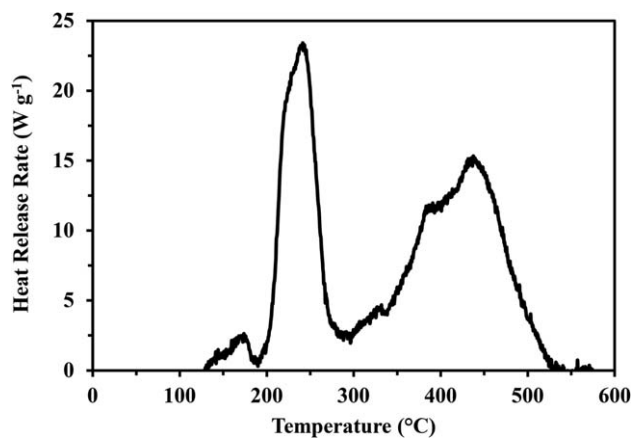


Figure 2. HRR curve for raw alginate in PCFC.

the block progressively degrades it appears that the material maintains its global structure compared to expanded polystyrene that melts and drips as soon as its temperature exceeds 100 °C.

Thermal Conductivity. Thermal conductivity is a key property of foams for insulating properties. Thermal conductivity was measured at room temperature for a set of foams exhibiting various densities. Values were measured in the range 0.028–0.039 $\text{W m}^{-1} \text{K}^{-1}$, corresponding to highly insulating materials. Similar value (0.041 $\text{W m}^{-1} \text{K}^{-1}$) was measured for commercial EPS foam with apparent density of 10 kg m^{-3} . The analytical procedure used for the characterization of thermal conductivity does not allow detecting significant differences below 0.005 $\text{W m}^{-1} \text{K}^{-1}$. As a consequence, the differences observed between the different samples cannot be considered representative. However, it is important to remind that the objective of this test consisted of demonstrating that the thermal conductivity is of the same order of magnitude than the values obtained with a conventional commercial sample. These data are sufficient to confirm the interest of these foams in terms of insulating properties: thermal conductivities are comparable to the values of a critical reference material like expanded polystyrene foam.

Mechanical Properties. Mechanical properties are also important properties for foams. Among the different tests existing for characterizing the mechanical properties of polymer foams,⁴⁰ the uniaxial compression test is a relatively simple test that can be readily used with appropriate reproducibility for the preliminary testing of mechanical strength and comparison of selected foams. Obviously more complete tests would be necessary for standard qualification of the materials.^{40,49,50} However, this simple test is sufficient for evaluating the relative impact of operating parameters through the correlation of the compression properties with the apparent density of the foams. Compression tests were carried out on a set of foams with apparent density ranging from 7 to 35 kg m^{-3} . Typical “stress–displacement” curves are shown in Figure 3. Curves for alginate foams are characterized by several peaks due to the brittle behavior of the foams. On the contrary, expanded polystyrene shows a smooth curve. Both maximum stress and modulus (measured typically

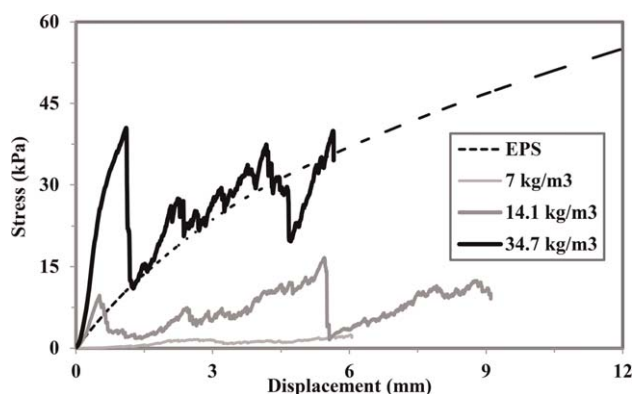


Figure 3. Stress–displacement curve for several alginate foams and EPS (dimensions of the samples mechanically tested: fixed diameter of 16 mm; variable thickness: 12.1, 19.4, and 14.4 mm, for the samples of apparent density close to 7, 14.1, and 34.7 kg m⁻³, respectively).

when the force is between 0.04 and 0.4 N) increase with apparent density increase. This expected result gives an indication on the importance of optimizing the density of the foams taking into account mechanical resistance in addition to the apparent density of the materials; for the next step in the optimization of foam production see Optimization of Foam Manufacturing section.

Figures 4 and 5 show the change in modulus and maximal stress with apparent density. Modulus is low for low-density foams (<200 kPa). A significant increase is observed for denser foams. For 15 and 35 kg m⁻³, modulus is 430 and 840 kPa, respectively. In the case of EPS, the modulus is slightly higher (around 300 kPa) than corresponding alginate foams with similar density.

Linear increase of maximum stress with apparent density is more obvious for alginate foams. The maximum stress increases from 2 to 45 kPa when density increases from 7 to 35 kg m⁻³. Nevertheless, EPS exhibits a much higher maximum stress: at least 62 kPa versus 5 kPa for comparable foams (data not shown because the maximum stress for EPS was not reached at the end of the test). This critical issue is currently investigated with both the incorporation of cellulose-based fibers and the

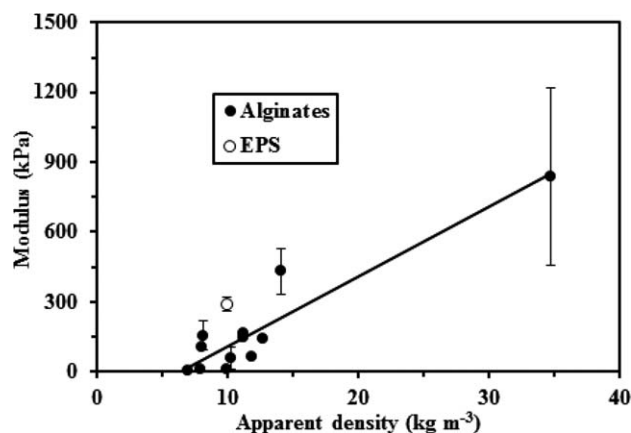


Figure 4. Modulus versus apparent density for several alginate foams and EPS (the solid line shows the linear regression plot of modulus vs. apparent density for alginate-based foams).

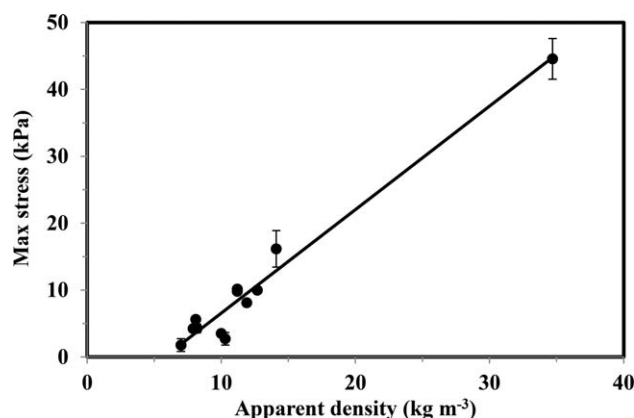


Figure 5. Max stress versus apparent density for several alginate foams (the solid line shows the linear regression plot of max stress vs. apparent density for alginate-based foams).

optimization of alginate concentration with the objective to increase mechanical resistance of composite material.

Optimization of Foam Manufacturing

B-B Design. Table II summarizes the main results obtained in the morphological characterization of alginate foams in relation with the variation of experimental parameters (B-B design).

The coefficients of the model for the four responses are reported in Table III. In addition, the predicted and experimental values are compared in Figures S3–S6 (see Supporting Information section) for the density of the foam, the dry volume, the shrinking percentage, and the wet volume, respectively. The calculated equations fit relatively well experimental data, especially for the apparent density and the volume of production of wet foams: the determination coefficients are close to 0.986 and 0.991, respectively; much better than for the shrinking percentage ($R^2 = 0.885$).

The main objectives for processing optimized foam, in terms of practical characteristics, concern the apparent density of the foam and the shrinking percentage that should be as low as possible and the volume of dried foam produced that should be the highest possible. Obviously, the experimental parameters should take into account, in a second step, criteria such as the mechanical properties of elaborated materials, as well as fire retardant properties and insulating performance. Ongoing research will consider the incorporation of additives (fibers, fire retardant compounds) to improve relevant properties, based on the optimization of foam production.

In order to get a better visualization and understanding of the effect of individual parameters on these three criteria a series of iso-response curves has been plotted using the general equations (β_{ij}) for the three parameters at the three levels (−1, 0, and +1). In addition, Figures S7–S15 (see Supporting Information section) show the three-dimensional curves at centered values of the third circular parameter.

Evaluation of Processing Parameters on Apparent Density.

Decreasing the apparent density below 20 kg m⁻³ (i.e., comparable to usual EPS materials; the tested EPS herein has a density of 10 kg m⁻³) requires using low amounts of alginate and

Table III. Coefficients of the Model [eq. (1)] for the Four Responses (Apparent Density, Dry Volume, Shrinking Percentage, and Wet Volume)

Coefficient	Apparent density	Dry volume	Shrinking percentage	Wet volume
β_0	24.93	408.33	16.63	490.00
β_1	12.19	-57.75	3.40	-61.43
β_2	-31.65	115.63	-0.25	187.91
β_3	2.91	-8.63	-0.28	-17.96
β_{12}	-26.20	16.50	-4.53	-7.35
β_{13}	1.23	14.50	-0.78	11.80
β_{23}	-7.95	13.75	-3.48	-7.98
β_{11}	2.30	-1.54	-0.08	7.71
β_{22}	35.22	-93.79	19.87	6.34
β_{33}	-4.81	-24.79	3.32	-26.71
R^2	0.954	0.938	0.885	0.985

intermediary amounts of SLS, regardless of the amount of copper carbonate introduced in the composition of the production batch (Figure 6). When increasing the alginate concentration the amount of SLS should be increased to reach target objective.

These results mean that a key parameter for the design of “light” materials is strongly controlled by the critical parameter alginate/SLS, while the relative value of copper carbonate has a limited effect on this parameter.

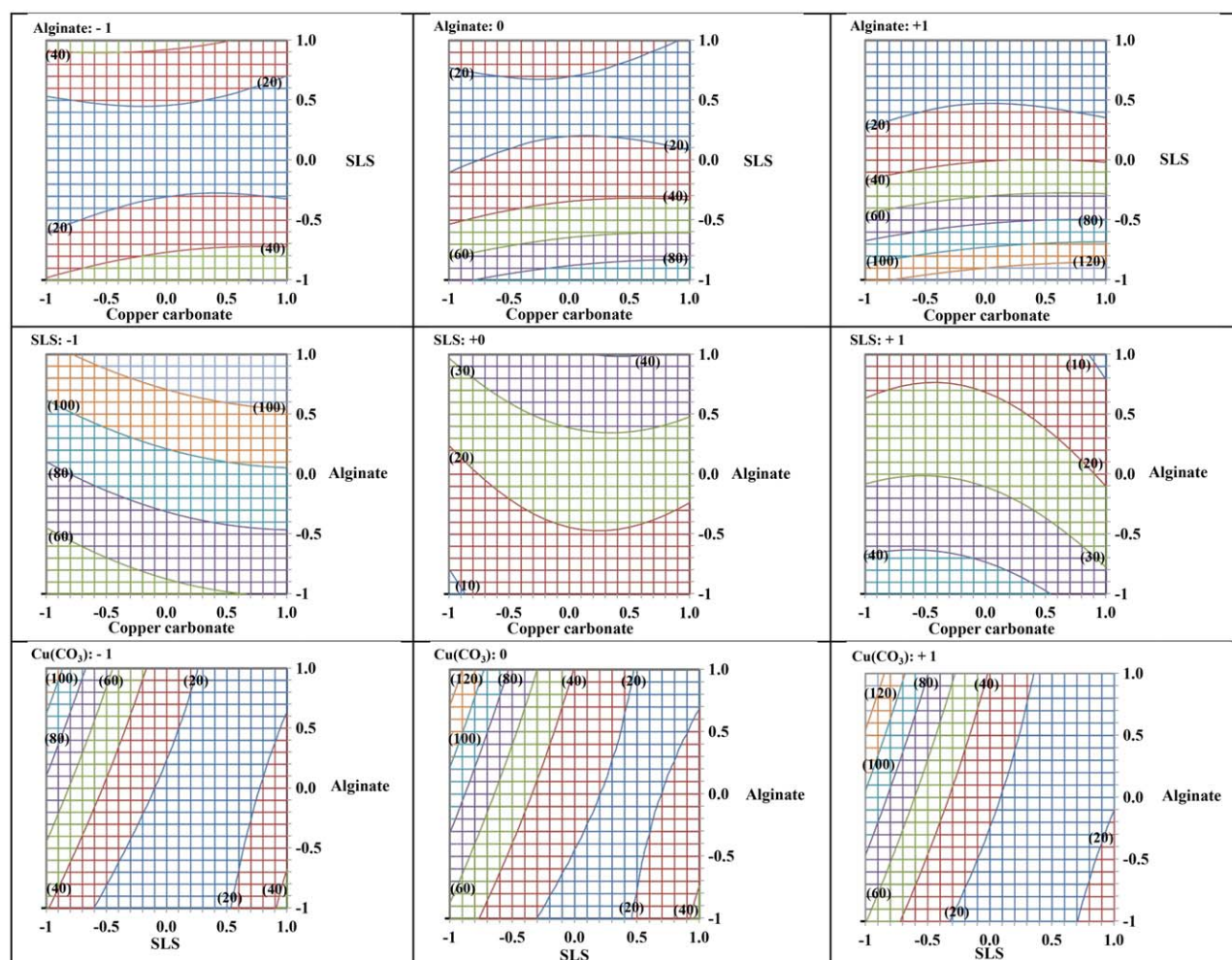


Figure 6. Isoresponse curves for the effect of experimental parameters (coded variables) on the volume of apparent density (kg m^{-3}) (−1/0/+1 levels: alginate: 2800/3000/3200 mg; SLS 35/65/95 mg; CuCO_3 equivalent solid: 50/100/150 mg for the preparation of a volume of 200 mL wet foam). [Color figure can be viewed at wileyonlinelibrary.com]

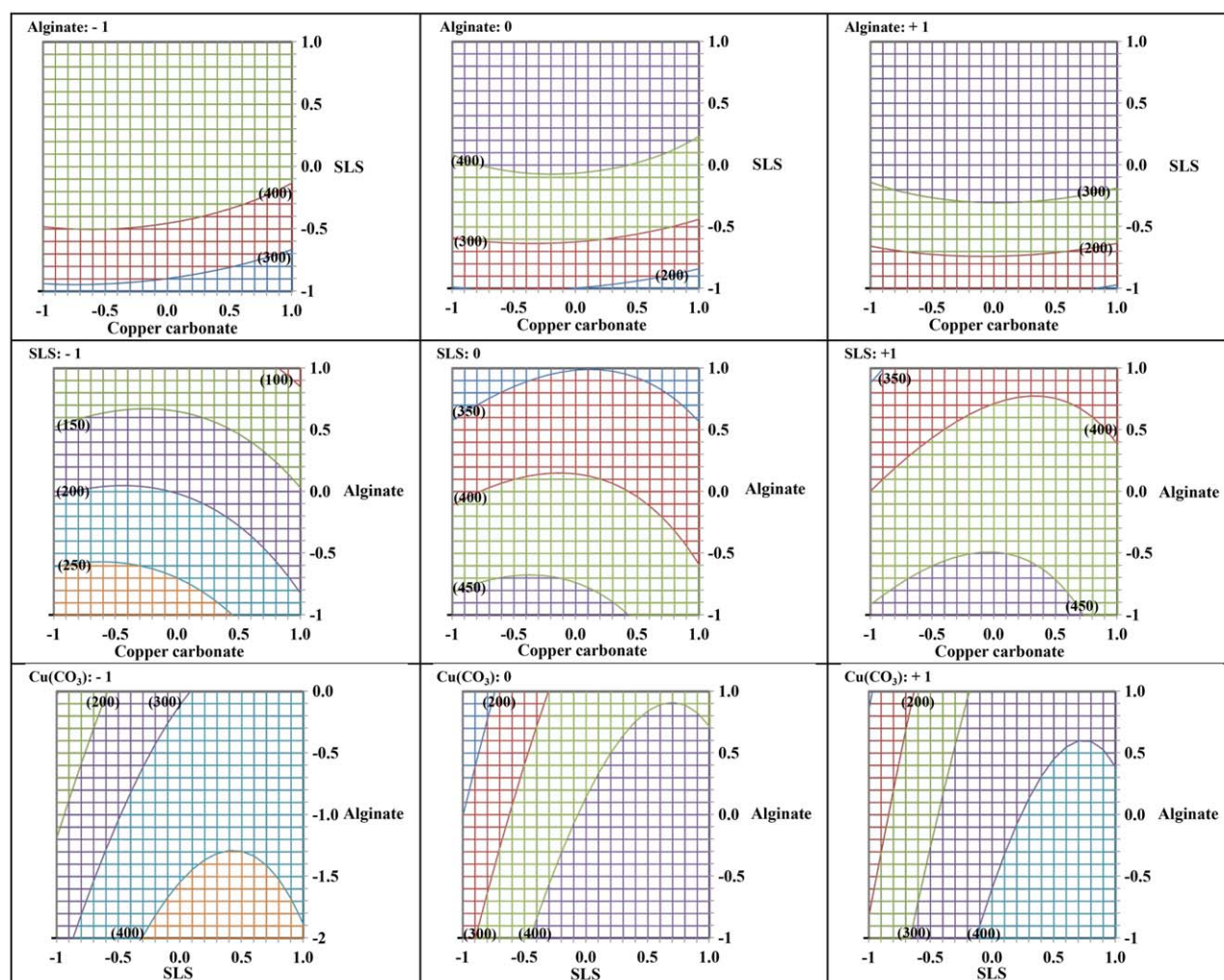


Figure 7. Isoresponse curves for the effect of experimental parameters (coded variables) on the volume of foam produced (dry volume, mL) (−1/0/+1 levels: alginate: 2800/3000/3200 mg; SLS 35/65/95 mg; CuCO₃ equivalent solid: 50/100/150 mg for the preparation of a volume of 200 mL wet foam). [Color figure can be viewed at wileyonlinelibrary.com]

At low SLS level (i.e., 3.5 mL, 35 mg/200 mL of preparation) whatever the amounts of alginate and copper the materials are very compact and the apparent density largely exceeds target level. At intermediary SLS level, alginate should be set at low level below 150 mL for 200 mL of preparation. A reciprocal trend is observed at high SLS level where the amount of alginate should exceed 150 g for 200 mL of preparation.

The levels of copper carbonate have a limited impact on the apparent density; however, best results are obtained with SLS in the range 6.5–9.5 mL (or 35–95 mg) for 200 mL preparation. The amount of alginate is not critical. Nevertheless, the optimal surfaces for the three levels of copper carbonate delimit a median axis that shows a relatively stable slope that corresponds to a mass ratio between alginate and SLS close to 40.

With the target of maintaining apparent density below 20 kg m^{−3} the best conditions correspond to the following proportions for 200 mL of preparation:

- Alginate solution: 140 mL (4% w/w solution; i.e., 5.6 g)
- SLS solution: 6.5 mL (1%, w/w solution; i.e., 65 mg)

- CuCO₃ suspension: weak impact (centering on 5 mL of 10% w/w suspension; i.e., 100 mg).

Evaluation of Processing Parameters on Dry Volume of Obtained Foams. Figure 7 reports the iso-curves for the production of dry foams. This is also a critical parameter for optimizing the productivity of the process. Low levels of SLS are crippling: when SLS is set to 3.5 mL for 200 mL of preparation, whatever the levels of copper carbonate and Alginate the production of foams remains below 300 mL. At levels 0 and +1, (i.e., 6.5 and 9.5 mL of SLS) the production of foams increases with decreasing Alginate volume, while the amount of copper carbonate has a weaker impact.

When examining the effect of alginate amount at three levels it appears that the biopolymer should be below 150 mL (i.e., below 6 g) for SLS higher than 6.5 mL (i.e., 65 mg), while the amount of copper carbonate has a limited impact. This conclusion is corroborated by the last row of Figure 7 that examines the effect of copper carbonate: for the three levels, best results were obtained for amounts of alginate below 6 g and SLS higher than 65 mg.

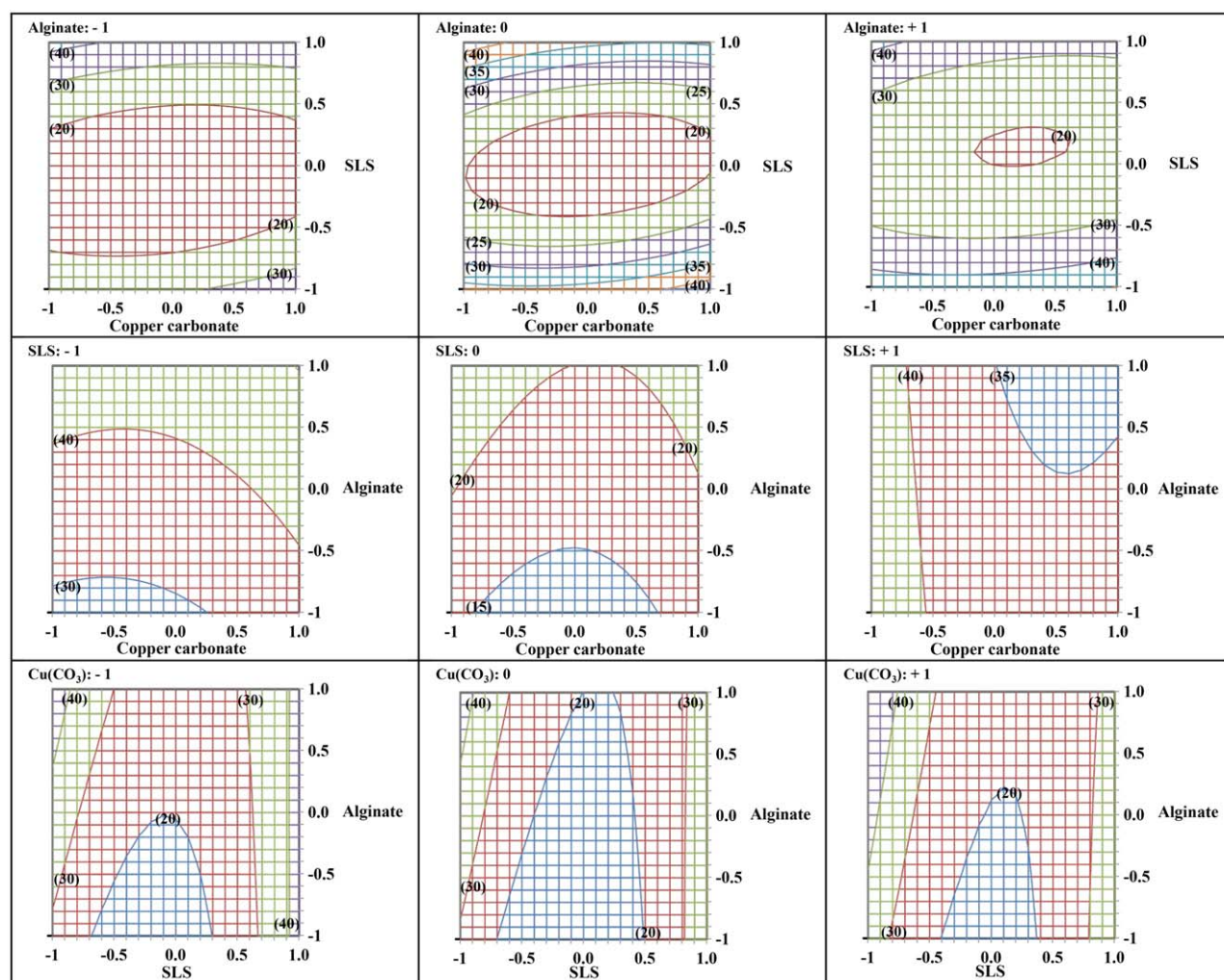


Figure 8. Iso-response curves for the effect of experimental parameters (coded variables) on the shrinking percentage (%) (−1/0/+1 levels; alginate: 2800/3000/3200 mg; SLS 35/65/95 mg; CuCO_3 equivalent solid: 50/100/150 mg for the preparation of a volume of 200 mL wet foam). [Color figure can be viewed at wileyonlinelibrary.com]

In the case of foam productivity the ratio alginate/SLS also sounds to be a crucial parameter. Best conditions correspond for 200 mL of preparation to:

- Alginate below 150 mL (4% w/w solution; i.e., 6 g of alginate)
- SLS above 6.5 mL (1% w/w solution; i.e., 65 mg)
- Copper carbonate (5 mL 10% w/w suspension; i.e., 100 mg).

Evaluation of Processing Parameters on Shrinking Percentage. The shrinking percentage is also an important criterion in terms of operability of the manufacturing. An important shrinking is frequently associated to a large deformation of the size and planarity of the foams that will make the material difficult to use for final application. In this section, the shrinking is roughly calculated as the reduction (in percentage) of the produced volume with reference to wet volume. Obviously, this parameter is not independent of the other parameters analyzed above but it seems interesting discussing the results under this

specific criterion. Figure 8 shows the iso-response curves for shrinking percentage; the objective being to maintain this shrinking percentage below 20%.

The first row of Figure 8 illustrates the effect of SLS and copper carbonate at three levels of alginate. The optimum for the reduction of shrinking is clearly located at the center of the figures with intermediary values for SLS and copper carbonate. The optimum surface is considerably reduced in size when increasing alginate amount; this requires a more drastic control of the other compounds. The shrinking decreases when alginate amount decreases.

When considering the effect of SLS level on shrinking it appears that SLS should be around 6.5 mL (1% solution; i.e., 65 mg) with copper carbonate close to 5 mL suspension (10% w/w; i.e., 100 mg); under these conditions the amount of alginate has a limited impact on shrinking. However, when the SLS amount moves from this central value the shrinking strongly increases regardless the values of the other parameters.

The third row of Figure 8 shows the iso-response curves for the three levels of copper carbonate amount; similar profiles are observed with a minimized shrinking obtained at the central value of SLS and with low levels of Alginate.

Optimal conditions are roughly found close to:

- Alginate: below 150 mL (4% w/w solution; i.e., 6 g)
- SLS: 6.5 mL (1% w/w solution; i.e., 65 mg)
- CuCO_3 : 5 mL (10% w/w suspension; i.e., 100 mg).

Effect of Alginate/SLS Ratio. The analysis of iso-response curves has demonstrated that the critical parameters are alginate and SLS levels, while copper carbonate has a lowest impact on the global productivity, apparent density, and morphological stability (shrinking). The macroscopic observation of the different series also subjectively identified a number of materials having “appropriate properties,” such as general aspect (correlated to shrinking), handling stability (correlated to mechanical stability), and apparent density. In Table II, the data in italics identify the experimental conditions that fit individual selected criteria; that is: Apparent density around (or below) 20 kg m^{-3} ; dry volume around (or higher) 400 mL; and shrinking percentage <20%. Data in bold correspond to conditions that satisfy all criteria. Actually, the best results correspond to the conditions for the preparation of 200 mL:

- Alginate: 140 mL (4% w/w solution; i.e., 5.6 g)
- SLS: 6.5 mL (1% solution; i.e., 65 mg)
- Copper carbonate: 2.5 mL (10% suspension; i.e., 50 mg)

Under these conditions, the three criteria are satisfied. Several other points also give relatively good manufacturing performance and stability properties as shown in Table II: including the central point: coded values (0, 0, 0) corresponding to alginate: 150 mL (i.e., 6 g), SLS: 6.5 mL (i.e., 65 mg), and CuCO_3 : 5 mL (i.e., 100 mg). The point (alginate: 140 mL; SLS: 6.5 mL, CuCO_3 : 7.5 mL) also gives good production parameters.

Copper carbonate appears to have a marginal effect on the synthesis and properties of produced foams (at least in the tested experimental range). Actually all the positive conditions correspond to a mass ratio between Alginate and SLS around 42–46. The capacity of the alginate-based system to form foam is obviously correlated to its viscosity: a highly viscous biopolymer solution (corresponding to high alginate concentration) has more difficulties to foam in the presence of the foaming agent (SLS) than a “fluid” solution. Figure S16 (see Supporting Information section) shows the evolution of viscosity with alginate concentration: the viscosity should be below 4000 cP. Other parameters such as the surface tension of the alginate/SLS solution are probably playing an important role on the foaming of the suspension and then the morphological properties of the foams.

CONCLUSIONS

The foaming of alginate solution using SLS (foaming agent) in the presence of copper carbonate and gluconolactone (ionotropic gelation system) allows preparing expanded macroporous structures that retain their shape after air-drying. The

production of foams, their apparent density, and their shrinking (during the drying step) are critical parameters in terms of productivity and processing. These materials have remarkable characteristics in terms of thermal conductivity (below the corresponding value of expanded polystyrene foam; i.e., $0.041 \text{ W m}^{-1} \text{ K}^{-1}$), and fire properties (self-extinguishing behavior according to UL94 test and classified as V0 ranked materials; THR below 2 kJ g^{-1}). The mechanical properties, roughly defined by compression tests but also by the shrinking percentage and the collapse of the foam structure during the drying step, are logically correlated to the apparent density and the operating conditions should be selected taking into account a compromise between the mechanical stability and the apparent density. The SEM characterization shows that the “opening” of the cells of the foams decreases with apparent density.

According to the criteria selected for the optimization of the synthesis, the best conditions were determined. For the preparation of 200 mL of suspension, alginate should be set below 6 g, SLS should be around 65 mg while copper carbonate should be around 500 mg (in mass of active product; i.e., 150 mL of 4% w/w alginate solution, 6.5 mL of 1% SLS solution, and 6.5 mL of 10% w/w CuCO_3 suspension). These conditions allow maintaining the shrinking below 20%, the apparent density below 20 kg m^{-3} , and the production of dry foam exceeds 400 mL (for an initial volume of preparation of 200 mL). The critical mass ratio between alginate and SLS is around 42–46.

Current development consists of incorporating fibers and other additives in these alginate foams in order to increase their mechanical and fire retardant properties. An effort will be made for using green products (PLA, natural fibers, bioplasticizer) for improving the mechanical properties of the foams but also their surface properties (with more specifically the objective of decreasing the wettability of the material). A special attention will be also focused on testing the acoustic properties of these foams. The mechanical properties of the gel, the manufacturing conditions are strongly controlled by intrinsic parameters associated to the biopolymer such as the viscosity of the solution. Playing with the type of alginate (G/M ratio) and the concentration is the key for appropriate processing; but a low concentration of the biopolymer would lead to a dramatically collapse of the foam structure during the drying step. The strength of the gel and the dried foam could be also controlled by the type of metal salt used for ionotropic gelation. These are parameters that could be tested with profit for improving the properties of the foams in addition to the incorporation of other adjuvants (as reported above).

REFERENCES

1. Wang, S.-Y.; Yang, T.-H.; Lin, L.-T.; Lin, C.-J.; Tsai, M.-J. *Bioresour. Technol.* **2008**, *99*, 2072.
2. Mngomezulu, M. E.; John, M. J.; Jacobs, V.; Luyt, A. S. *Carbohydr. Polym.* **2014**, *111*, 149.
3. Basak, S.; Samanta, K. K.; Chattopadhyay, S. K.; Narkar, R. *Cellulose* **2015**, *22*, 2767.

4. Garcia, M.; Garmendia, I.; Garcia, J. *J. Appl. Polym. Sci.* **2008**, *107*, 2994.
5. Rossi, M.; Camino, G.; Luda, M. *Polym. Degrad. Stab.* **2001**, *74*, 507.
6. Blomqvist, P.; Hertzberg, T.; Tuovinen, H.; Arrhenius, K.; Rosell, L. *Fire Mater.* **2007**, *31*, 495.
7. Idumah, C. I.; Hassan, A. *Rev. Chem. Eng.* **2016**, *32*, 115.
8. Liu, Y.; Zhao, J.-C.; Zhang, C.-J.; Guo, Y.; Zhu, P.; Wang, D.-Y. *J. Mater. Sci.* **2016**, *51*, 1052.
9. Liu, Y.; Zhao, J.-C.; Zhang, C.-J.; Guo, Y.; Cui, L.; Zhu, P.; Wang, D.-Y. *RSC Adv.* **2015**, *5*, 64125.
10. Zhang, C.; Zhu, P.; Zhao, J.; Zhang, N. In *Eco-Dyeing, Finishing and Green Chemistry*; Shao, J. H., Fan, Q. G., Eds.; Trans Tech Publications Ltd.: Zurich, Switzerland, **2012**.
11. Gady, O.; Poirson, M.; Vincent, T.; Sonnier, R.; Guibal, E. *J. Mater. Sci.* **2016**, *51*, 10035.
12. Palumbo, M.; Navarro, A.; Giraldo, P.; Lesar, B.; Lacasta, A. M. *Proceedings of the 1st International Conference on Bio-based Building Materials*, RILEM publications, PRO 99. **2015**, 751.
13. Palumbo, M.; Lacasta, A. M.; Navarro, A.; Giraldo, P.; Lesar, B. *Constr. Build. Mater.* **2017**, *139*, 531.
14. Agulhon, P.; Markova, V.; Robitzer, M.; Quignard, F.; Mineva, T. *Biomacromolecules* **2012**, *13*, 1899.
15. Agulhon, P.; Robitzer, M.; David, L.; Quignard, F. *Biomacromolecules* **2012**, *13*, 215.
16. Agulhon, P.; Robitzer, M.; Habas, J. P.; Quignard, F. *Carbohydr. Polym.* **2014**, *112*, 525.
17. Liu, Y.; Zhao, X.-R.; Peng, Y.-L.; Wang, D.; Yang, L.; Peng, H.; Zhu, P.; Wang, D.-Y. *Polym. Degrad. Stab.* **2016**, *127*, 20.
18. Liu, Y.; Zhao, J.; Zhang, C.; Ji, H.; Zhu, P. *J. Macromol. Sci. Phys.* **2014**, *53*, 1074.
19. Tian, G.; Ji, Q.; Xu, D.; Tan, L.; Quan, F.; Xia, Y. *Fibers Polym.* **2013**, *14*, 767.
20. Kong, Q.-S.; Wang, B.-B.; Ji, Q.; Xia, Y.-Z.; Guo, Z.-X.; Yu, J. *Chin. J. Polym. Sci.* **2009**, *27*, 807.
21. Chen, H.-B.; Wang, Y.-Z.; Sánchez-Soto, M.; Schiraldi, D. A. *Polymer* **2012**, *53*, 5825.
22. Mohebbi, A.; Mighri, F.; Ajji, A.; Rodrigue, D. *Cell. Polym.* **2015**, *34*, 299.
23. Okolieocha, C.; Raps, D.; Subramaniam, K.; Altstadt, V. *Eur. Polym. J.* **2015**, *73*, 500.
24. Pantani, R.; Volpe, V.; Titomanlio, G. *J. Mater. Process. Technol.* **2014**, *214*, 3098.
25. Madhally, S. V.; Matthew, H. W. T. *Biomaterials* **1999**, *20*, 1133.
26. Sharma, C.; Dinda, A. K.; Mishra, N. C. *J. Appl. Polym. Sci.* **2013**, *127*, 3228.
27. Sharma, C.; Dinda, A. K.; Potdar, P. D.; Mishra, N. C. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.42743.
28. Wang, L.; Sánchez-Soto, M.; Abt, T.; Maspoch, M. L.; Santana, O. O. *Polym. Int.* **2016**, *65*, 899.
29. Wang, S.; Vincent, T.; Roux, J.-C.; Faur, C.; Guibal, E. *Chem. Eng. J.* **2017**, *325*, 521.
30. Sone, H.; Fugetsu, B.; Tanaka, S. *J. Hazard. Mater.* **2009**, *162*, 423.
31. Shang, K.; Liao, W.; Wang, J.; Wang, Y.-T.; Wang, Y.-Z.; Schiraldi, D. A. *ACS Appl. Mater. Interfaces* **2016**, *8*, 643.
32. Kim, B. G.; Lee, D. G. *J. Mater. Process. Technol.* **2008**, *201*, 716.
33. Poncelet, D.; Babak, V.; Dulieu, C.; Picot, A. *Colloids Surf. A* **1999**, *155*, 171.
34. Hull, T. R.; Witkowski, A.; Hollingbery, L. *Polym. Degrad. Stab.* **2011**, *96*, 1462.
35. Ciudad, A.; Haurie, L.; Lacasta, A. M. *Fire Mater.* **2015**, *39*, 14.
36. Goupy, J. *Plans D'expériences Pour Surfaces de Réponse*; Dunod: Paris, France, **1999**.
37. Xuan, S. Y.; Wang, X.; Song, L.; Xing, W. Y.; Lu, H. D.; Hu, Y. *Polym. Int.* **2011**, *60*, 1541.
38. Lyon, R. E.; Walters, R. N. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 27.
39. Huggett, C. *Fire Mater.* **1980**, *4*, 61.
40. de Vries, D. V. W. M. In *department of Mechanical Engineering, Mechanics of Materials*; Eindhoven University of Technology: Eindhoven, The Netherlands, **2009**; p 34.
41. Liu, Y.; Li, Z.; Wang, J.; Zhu, P.; Zhao, J.; Zhang, C.; Guo, Y.; Jin, X. *Polym. Degrad. Stab.* **2015**, *118*, 59.
42. Liu, Y.; Wang, J.-S.; Zhu, P.; Zhao, J.-C.; Zhang, C.-J.; Guo, Y.; Cui, L. *J. Anal. Appl. Pyrolysis* **2016**, *119*, 87.
43. Zhang, J.; Ji, Q.; Shen, X.; Xia, Y.; Tan, L.; Kong, Q. *Polym. Degrad. Stab.* **2011**, *96*, 936.
44. Zhang, J.; Ji, Q.; Wang, F.; Tan, L.; Xia, Y. *Polym. Degrad. Stab.* **2012**, *97*, 1034.
45. Liu, Y.; Zhang, C.-J.; Zhao, J.-C.; Guo, Y.; Zhu, P.; Wang, D.-Y. *Carbohydr. Polym.* **2016**, *139*, 106.
46. Lyon, R. E.; Safronava, N.; Quintiere, J. G.; Stoliarov, S. I.; Walters, R. N.; Crowley, S. *Fire Mater.* **2014**, *38*, 264.
47. Sonnier, R.; Otazaghine, B.; Iftene, F.; Negrell, C.; David, G.; Howell, B. A. *Polymer* **2016**, *86*, 42.
48. Dorez, G.; Ferry, L.; Sonnier, R.; Taguet, A.; Lopez-Cuesta, J. M. *J. Anal. Appl. Pyrolysis* **2014**, *107*, 323.
49. Lu, W.-Y. Sandia National Laboratories, Mechanical Characterization of Rigid Polyurethane Foams, Document N° SAND2014-20708. *Mechanics of Materials*: Albuquerque, NM, **2014**; p 72.
50. Lee, S.-T.; Ramesh, N. S.; Park, C. B. *Polymeric Foams Science and Technology*; CRC Press: Boca Raton, FL, **2007**.