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Bio-based boards made of hazelnut shell and *A. donax* for indoor applications - A solution with good performance in case of fire

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ABSTRACT

The present study investigated the reaction to fire of bio-based boards for indoor applications made of *A. donax* and hazelnut shells as aggregates. A sodium silicate solution was employed as the adhesive due to its several advantages. Among others, the possibility of moderating some of the main drawbacks of bio-based building composites, such as the resistance to fire. The considered materials were analysed both individually, to test their inherent properties, and when integrated into the composites, ensuring considerations about materials' influence on the final products' properties. Two different test methods, using a cone calorimeter, were considered and performed. The results showed that the sodium silicate solution avoided flaming and smoking, in case of a constant heat application with and without an igniter (spark), demonstrating the benefit of its use in this type of bio-based composites. Overall, the particleboards demonstrated their ability to comply with fire behaviour consistent with the Class A1 requirements, while the bio-components on themselves were characterized by an intermediate fire risk propensity. Thus, the present study provided an effective solution to avoid one of the main drawbacks of bio-based composites. It demonstrated the feasibility of employing the proposed bio-based bio-

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Nomenclature, symbols and acronyms

А	A. donax	pHRR	Peak Heat Release Rate
Н	Hazelnut shells	THR	Total Heat Release
AH	A. donax + Hazelnut shells	TGA	Thermogravimetric analysis
S	Sodium silicate solution	SPR	Smoke Production Rate
AS	A. donax-based composite	TSP	Total Smoke Production
HS	Hazelnut shells-based composite	TTI	Time To Ignition
AHS	Mixture-based composite	FIGRA	Fire Growth Rate
FR	Flame Retardant	EHC	Effective Heat of Combustion
HRR	Heat Release Rate	SBI	Single Burning Item

1. Introduction

Due to the increasingly serious environmental problems, mainly caused by the construction sector, nowadays research is focused on proposing and evaluating the performance of sustainable solutions [1]. Several possibilities are being investigated, such as new building products, innovative construction practices, and environmentally friendly materials.

Particleboards present many advantages: easy on-site installation, flexibility of applications, and low costs [2,3]; they have a large diversity of applications, and a significant volume of production is required worldwide. Furthermore, they can be produced by using both wood chips and alternative materials, such as bio-fibres and wastes derived from agro-industrial practices and forest cleaning [4, 5]. As these materials are environmentally friendly [6], they have many benefits: they lower energy consumption [7] and the composites embodied energy, guarantee circular economy practices [8], and secure the disposal of bio-wastes as well, which could cause environmental problems [9–11]. Due to their several promising properties, studies on bio-based particleboards are more and more carried out [12,13].

Depending on the employed bio-based materials, different performances could be achieved. For example, Mati-Baouche et al. [14] considered a composite made of sunflower stalks bounded by chitosan that demonstrated promising acoustic absorption, guaranteed by porosity. Paiva et al. [15] evaluated the thermal insulation performance of corn cob particleboards and achieved advantageous values thanks to the raw material properties, as demonstrated also by Bovo et al. [16]. Nadhari et al. [17] assessed the mechanical properties of banana trunk waste binderless particleboards and reported encouraging results.

Bio-based particleboards, and bio-based composites in general, in indoor applications, could improve hygrothermal and acoustic comfort [18] passively contributing to indoor conditions and lowering operational costs [19]. The hygrothermal comfort is related to several factors, such as temperature and relative humidity [20]. The acoustic one is related to the protection against noise and is mainly guaranteed by adequate sound insulation [21], and proper distribution of the materials, as it may depend on both their layout and sound absorption capacity [22]. Both comforts are important to guarantee safe and healthy places for the users.

On the other side, bio-based particleboards can present some drawbacks due to their intrinsic organic (typically cellulosic) matrix [23]. They showed, indeed, low water resistance [24,25], they were prone to biological colonisation [26–28], such as mould growth, fungi development, and insect attack [29], and they displayed poor behaviour in case of fire [30,31]. The latter, in particular, posed a serious threat to the indoor applicability of bio-based particleboards, since cellulosic waste residues typically underwent decomposition at moderate temperatures, often below $300-400 \,^{\circ}$ C [32,33]. Thermal degradation resulted in the generation of heat, emission of smoke and soot, and the release of volatile substances able to ignite [34]. In response, Flame Retardant (FR) systems were frequently employed to mitigate or hamper the thermal decomposition and combustion processes inherent in combustible materials like polymer composites [35]. These systems were designed to intervene in various stages of polymer combustion [35], either physically or chemically, affecting the heating, pyrolysis, ignition, and propagation stages of thermal degradation processes.

Table 1

Past studies on fire retardants for boards and particleboards.

Type of board	Fire retardant	Ref.
Particleboards made of wood chips and urea-formal dehyde, produced by pressing at 160 bar and 130 $^\circ \rm C$ for 8 min	Wollastonite nanofibers	[42]
Particleboards made of wood chips, expandable polystyrene, a mixture of Polymethyl acrylic, expandable graphite, and melamine polyphosphate, produced at 130 °C for 55 min	A mixture of polymethyl acrylic emulsion, expandable graphite, and melamine polyphosphate	[43]
Particleboards made of walnut shells and urea–formaldehyde and phenol–formaldehyde binder, produced by a hydraulic press at 90 °C with 100 atm. for 19 min	Urea-formaldehyde blend	[44]
Particleboards made of hemp fibres, rice husk, ammonium dihydrogen phosphate and a mixture of water and starch, produced by pressing at 10Mpa, 140 °C for 6 min	Ammonium dihydrogen phosphate	[45]
Particleboards made of poplar wood powder treated with ammonium tris isocyanurate triphosphate, and urea-formaldehyde resin, produced in a hydraulic press at 165 °C and 2–3 MPa for 8 min	Ammonium tris isocyanurate triphosphate	[46]
Plywood boards made of a thin layer of wood, melamine formaldehyde resin and phosphate ester acid, produced at room temperature; the solution containing the flame retardant was directly applied on the boards	Montmorillonite polyphosphate	[47]
Plywood boards made of a thin layer of wood, melamine formaldehyde resin and phosphate ester acid, produced at room temperature by dispersing the solution containing the flame retardant directly on the plywood panels	Cyclic acid phosphate ester loaded with nano-silica	[48]

The enhancement of the behaviour in case of fire remains a critical challenge in contemporary industrial settings, prompting the application of several different approaches. Among these, the application of coatings with FR materials [36,37], the incorporation of FR materials into composites [38], or the utilization of inherently flame-resistant matrices can be chosen depending on the specific requirements. The application of traditionally formulated FR additives or coatings (based mainly on halogens), employing principles ranging from gas phase intervention to interrupt radicals chain reaction propagation, has recently faced scrutiny due to environmental concerns [39]. Hence, the exploration of alternative FR materials and systems has been required. Organometallic complexes, particularly ferrocene-based derivatives, emerged as a promising avenue, demonstrating catalytic properties in char formation that effectively suppress smoke [40,41]. Nanofillers were also positively utilized in FR systems, primarily to promote the formation of a protective intumescent layer in the condensed phase, hindering oxygen penetration, reducing the transfer of volatile gases to the flame, and, ultimately, extinguishing it.

However, for particleboards, these options have limited applicability due to the intrinsic heterogeneous nature of the products, which would imply the use of a dispersed matrix phase to be modified with these approaches. When dealing with heterogeneous aggregates for particleboards, the selection of inherently FR matrices represents a viable route to produce FR composites. Table 1 reports some past studies that assessed this possibility.

According to complementary past studies [49,50], sodium silicate showed interesting properties as a fire protector. It is known as "water glass", and it is a non-toxic and environment-friendly material [51,52]. It was employed in several sectors due to its benefits and economic convenience [53]: for detergents and cleaning compounds [53], for materials treatments [52] for ceramics and geopolymers [54,55], as a remediation tool for water [56], as binders in bio-based building boards [50,51]. As for this latter, the sodium silicate guaranteed both the feasibility of boards' production [49] and the reduction of some of the main bio-based materials' weaknesses, such as biological attack [57]. Hence, silicon-based composites could be an efficient possibility to explore. With this approach, the issue of flammability could be conveniently overcome, ensuring the production of sustainable particleboards made of agro-wastes and bio-resources. Differently from traditional FR, sodium silicate is a safe material that, when released into the environment, does not bring along specific concerns [51,52]. Thus, even in the aftermath of a potential fire, the discarded waste residue based on sodium silicate aggregate should not pose additional environmental safety concerns.

Considering this background, the present study investigated bio-based particleboards for indoor applications by using a sodium silicate solution as the binding matrix, for its several benefits. Among others, its good resistance to fire [49,50]. As for the aggregates, giant reed (*Arundo donax* L.) and hazelnut shells were considered according to past studies [18,58]. Besides the advantages of bio-based materials, both are widely available all over the year in the Euro-Mediterranean area [23], avoiding the problem of the seasonality of bio-wastes/bio-resources, which could discourage their use for building composites' production. Both hazelnut shells-based and giant reed-based composites demonstrated promising properties to improve indoor comfort, such as high hygroscopicity and interesting sound absorption capacity. Hence, they could be suitable and effective as indoor coating boards [18,58]. However, to guarantee their application as such, their performance in case of fire must be verified.

Although fire behaviour has not been widely investigated yet [59], some past studies considered this property by assessing ignition, incombustibility, and Heat Release Rate [60], as well as the smoke and toxic gas production, one of the most common causes of fire deaths [61]. Different test methods could be considered to evaluate the fire reaction of bio-based materials. For example, Palumbo et al. [62] described a small-scale flammability test, performed on a fire testing technology pyrolysis combustion flow calorimeter. The researchers considered a bio-based board made of corn pith and a natural gum (sodium alginate) and determined the Heat Release Rate (HRR) and the Total Heat Release (THR). They considered boric acid as a possible effective solution to improve the performance in case of fire. Rocha et al. [60] tested the fire reaction of bamboo, wood, and rice husk wastes by using a cone calorimeter. They analysed also their physical, chemical, and thermal properties, by performing the thermogravimetric analysis (TGA). The researchers determined the HRR and the THR and considered a possible treatment to improve the performance in case of fire of these bio-aggregates (e.g., alkali treatment, which could reduce heat release parameters for wood and bamboo). Antunes et al. [19] performed a non-standardised test to assess the performance of a rice husk-earth-gypsum-air lime composite in case of fire. They exposed the considered composite to a flame near a border with a resource to a torch. In all cases, the results of the fire-reaction tests allowed rating the materials according to their performance, verifying if they meet the standard requirements, and suggesting possible improvements if necessary (e.g., application of fire retardants). Nevertheless, further investigation on bio-based composites' performance in case of fire should be performed to improve this property [63].

Starting from these considerations and past studies, this research work addresses the fire reaction of the *A. donax*-based and hazelnut shells-based boards and a sodium silicate binding matrix by using a cone calorimeter. Some of the previously cited studies described in detail the research project that investigated and analysed the proposed bio-boards. First, bibliographic research was carried out to select some bio-aggregates [23], which were tested to provide their characterization as raw materials [64]. After that, different adhesives were considered and assessed [57], and the sodium silicate was selected. Then, the bio-based boards made of bio-aggregates and sodium silicate were produced and tested. The most suitable production process was investigated [65], and a horizontal analysis was performed, by assessing different properties, such as the hygrothermal, acoustic, and mechanical ones [18,58]. Finally, the influence of materials formulation was investigated by considering the hygroscopic properties [66]. The research project, described in the reported references, suggested that the hazelnut shell-based and the *A. donax*-based boards could be employed as indoor coatings. As it can be an important drawback for this type of application, the present study wants to complement their characterization, evaluating their performance in case of fire.

The aim is to evaluate the reaction to fire of the materials, considered individually (bio-aggregates and the dried sodium silicate solution), and the composites produced by using them. Hence, in addition to the reaction to fire, considerations on the influence of each material and the correlation between materials and composites will be made, supported by TGA characterization. Furthermore,

this study wants to assess, by laboratory experience, the sodium silicate's benefit, also when it is employed as an adhesive in bio-based boards.

2. Materials and samples production

2.1. Bio-aggregates and adhesive

Arundo donax L., known also as giant reed and giant cane, was provided by cultivations in Cadriano and Ozzano dell'Emilia, Bologna. Hazelnut shells were provided by Raccolti di Cin, Baldissero d'Alba, Cuneo, Italy. Both the aggregates were shredded, using a mechanical mill, to have grain sizes between 4 and 8 mm (Fig. 1), dried in an oven at T = 60 °C until constant mass (variation in mass ≤ 0.1 % after 24 h), and characterized as described by Cintura et al. [18,58].

A sodium silicate solution, Na₂O•n(SiO₂), with the properties reported in Table 2, was provided by Ingessil Srl, Montorio, Verona, Italy [67].

The bio-aggregates were placed in plastic boxes without any binder; they were tested individually (100 % of the considered volume of *A. donax* or hazelnut shells) and as a mixture (50 % of the considered volume of *A. donax* and 50 % of hazelnut shells). The sodium silicate solution was placed into three silicon moulds 10 cm \times 10 cm \times 4 cm, filled at a height varying between 2 and 4 mm and it was dried at laboratory conditions. The materials (both the aggregates and the sodium silicate) were stabilized at T = 20 °C and RH = 60 % in a conditioned room, and then tested. For the samples' designation, the first letter of the material was considered: A = A. *donax*; H = Hazelnut shells; AH = A. *donax* + Hazelnut shells; S = Sodium silicate solution.

2.2. Composite samples

The composite samples were produced as described by Cintura et al. [18,58], considering the same quantities of the materials, namely, 70 % aggregates - 30 % sodium silicate binder (percentages by volume). This ratio was selected after several practical tests, not reported for the sake of brevity, and detailed in previous studies [57,65] where other properties of the composites were assessed. The aim was to maximize the content of bio-wastes/bio-resources, minimize the sodium silicate solution, and guarantee enough mechanical resistance, avoiding the breaking of the samples.

Three composites were produced and consisted of.

- 70 % of A. donax and 30 % of sodium silicate solution
- 70 % of hazelnut shells and 30 % of sodium silicate solution
- 35 % of A. donax, 35 % of hazelnut shells, and 30 % of sodium silicate solution.

The bio-aggregates and the binder were mechanically mixed for 10 min, then placed into moulds, and levelled by a spatula without compaction. The production process was described in more detail in the reference studies [18,58]. The moulds were closed, placed at T = 60 °C for 3 h, then at laboratory conditions for 2 days, always rotated to secure a homogeneous distribution of the sodium silicate solution [65]. Finally, the samples were demoulded and cured at laboratory conditions for 28 days and dried at T = 50 °C until constant mass (variation in mass less than 0.5 % after 24 h) [50,68]. Three samples 10 cm × 10 cm × 4 cm and three cubic samples with 3.5 cm sides for each composite were produced. Then, they were stabilized at T = 20 °C and RH = 60 % in a conditioned room and tested.

Again, for the composite samples' designation, the first letters were considered: AS = A. *donax* + Sodium silicate solution; HS = Hazelnut shells + Sodium silicate solution; AHS = A. *donax* + Hazelnut shells + Sodium silicate solution. Fig. 2a, b and c show the produced samples adapted from Cintura et al. [66].

Table 3 reports the apparent density of the composite samples, evaluated in a past study [66].



Fig. 1. Bio-aggregates after shredding: (a) A. donax; (b) hazelnut shells (adapted from Refs. [18,58]).

Table 2

Characteristic of the sodium silicate solution provided by Ingessil Srl.

Property	Value
Weight ratio [-]	2.40
Density [°Bè]	46.45
Molar ratio [-]	2.48
Sodium silicate concentration [% p/p]	41.33
SiO ₂ [% p/p]	29.17
Na ₂ O [% p/p]	12.16
Density $[g/m]$ at T = 20 °C	1.471
pH (T = 20 °C)	12.40



Fig. 2. Composite samples 10 cm × 10 cm × 4 cm made of bio-aggregates and sodium silicate solution: a) A. donax-based; b) hazelnut shells-based; c) mixture-based.

Table 3

Characteristics of the obtained bio-composites: the apparent density of the composite samples adapted from Cintura et al. [66] and the inorganic residue evaluated via muffle oven treatment.

Composite	Apparent density [kg/m ³]	Inorganic residue [%]
A. donax-based composite – AS	470 ± 75	35
Hazelnut shells-based composite – HS	677 ± 47	23
Mixture-based composite – AHS	607 ± 52	34

3. Methods

The performed laboratory tests, and the number and size of the samples, were reported in the following sections.

3.1. Bio-aggregates and composites characterization

The thermal stability, water content, and the inorganic fraction composition of the considered bio-aggregates (i.e., *A. donax*, A, and hazelnut shells, H), were assessed by thermogravimetric analysis, TGA, using a TA Instruments TGA Q550 Discovery Series under a nitrogen atmosphere (flow rate 60 mL/min) at a 10 °C/min heating rate, from 25 °C to 800 °C using a Pt pan.



Fig. 3. Evaluation of the inorganic fraction of bio-aggregate composite cubic samples (3.5 cm): a) A. donax-based; b) hazelnut shells-based; c) mixture AH-based; d) samples into the muffle furnace.

As for the composite samples (AS, HS, AHS), the evaluation of their composition was carried out by thermal treatment. Three cubic samples for each composite, with 3.5 cm (Fig. 3a, b, and c) were weighed (m_0), placed in a muffle furnace at T = 900 °C (Fig. 3d) until the complete degradation, and then weighed again (m_F).

3.2. Reaction to fire

Reaction to fire was evaluated by using an oxygen consumption cone calorimeter (Fire Testing Technology Limiter FFT Cone Calorimeter) (Fig. 4a), according to ISO 5660-1 [69]. This method considers the correlation between the net heat of combustion and the required oxygen and consists of burning the samples in ambient conditions. The cone calorimeter is one of the most effective bench-scale methods for studying the flammability properties of materials [70].

The tests were carried out with a heat flow of 35 kW/m^2 (about 650 °C) which can be roughly compared to a small-scale fire. The instrument could work with a heat flow ranging between 5 and 100 kW/m². The higher irradiation levels led to better reproducibility, more clearly defined ignition time, and shorter measurement times. Furthermore, they also corresponded to more fully developed fire conditions. Hence, often a smaller irradiation level better fits the fire protection goals. Indeed, it accounts for the material behaviour in a condition close to the initial stage of a fire, showing its ability – or even better, inability – to ignite and propagate, and finally, to contribute to the fire expansion. This condition seems the most interesting for a preliminary evaluation of particleboards employed as building components which, as such, had an important role in fire safety conditions.

Among the several properties provided by the tests, the Heat Release Rate (HRR), the pHRR (Peak Heat Release Rate), the Total Heat Release (THR), the Smoke Production Rate (SPR) and Total Smoke Production (TSP) were considered. HRR is the heat released per unit area for samples under a constantly imposed heat flux; pHRR is the maximum value of the heat release rate profile. THR is the potential for thermal energy available for the combustion of the material, which increases the probability of fire [60]. As for the smoke production, described by SPR and TSP, it was analysed due to its dangerousness in case of fire [61,71,72].

Two different tests were performed and, in the present study, were identified as "Test Method A" (non-combustibility test) and "Test Method B" (Single Burning Item test, SBI). Both would require different equipment than the cone calorimeter. However, the results presented hereafter were intended for a preliminary evaluation of the potential of the proposed composites in terms of performance in case of fire.

3.2.1. Test method A (simulating non-combustibility test)

Test Method A requires that the samples are subjected to a heat flow for 30 min, in the absence of ignition, simulating as much as possible what is specified in EN ISO 13501 [73] and EN ISO 1182 [74]. The lack of an external sparkle ignition is applied to highlight the intrinsic risk of fire of a material or composite, trying to assess its potentially non-combustible behaviour. The latter, indeed, accounts for the safest class of products to be used in building and construction.

One sample for each material (A_01, H_01, AH_01, S_01) was placed into a metal standardized mould $10 \text{ cm} \times 10 \text{ cm} \times 4 \text{ cm}$. For the bio-aggregates, the mould was filled until the top (Fig. 4b and c). For the dried sodium silicate solution, the sample was placed up to non-flammable support and then into the mould. This allowed it to reach the top since the upper surface of the sample should be at a standardized distance from the cone. A metallic net was used to retain the samples during the test (Fig. 4d) avoiding expansion which would diminish the distance from the heat source in the cone. As for the composites, one sample for each one (AS_01, HS_01, AHS_01), 10 \text{ cm} \times 10 \text{ cm} \times 4 \text{ cm}, was placed into the metal mould (Fig. 4e, f, and g). The mould was, then, placed under the cone heater at a



Fig. 4. Test to evaluate the fire reaction by exposing the materials to a constant heat source. a) Cone calorimeter; samples into the metal mould (10 cm × 10 cm × 4 cm) before the test: b) hazelnut shells H, c) *A. donax* A; d) air-dried sodium silicate solution S; e) hazelnut shells-based composite HS; f) *A. donax*-based composite AS; g) mixture-based composites AHS.

constant distance of 25 mm. A constant heat flux of 35 kW/m² (corresponding to a temperature between 650 °C and 670 °C) was applied for 30 min (without an igniter). In addition to the previously reported properties, by Test Method A, the flashover index, evaluated as pHRR/TTI (where TTI represents the Time to Ignition), was determined.

3.2.2. Test method B (simulating single burning item)

Test Method B is a complementary testing condition to the previously presented Test Method A. It was designed to simulate the flame exposure that would be experienced by coatings on the walls of a room when a "wastepaper basket" ignites adjacent to the coatings itself. Then, to simulate these conditions, a sparkle ignition is presented, representing the threat of an adjacent fire which would surely set the volatiles on fire.

In Test Method B, samples were subjected to heat flow for 10 min in the presence of ignition, simulating as much as possible what is specified in EN ISO 13501 [73]. This should ensure the simulation and the achievement of data correlated to an analysis carried out according to EN ISO 13823 [75], namely the Single Burning Item (SBI) test. The remaining two replicas of each material (A_02–03, H_02–03, AH_02–03, S_02–03) and composite (AS_02–03, HS_02–03, AHS_02–03) were placed into the metal mould, as previously described. The composite samples, originally with a thickness of 4 cm, were sanded by a mechanical roller with sandpaper to reach a thickness of 2 cm. This ensured enough distance between the sample's surface and the source of the spark. The mould was placed under the cone shape (constant distance = 25 mm) and as previously anticipated, in addition to the constant heat flux of 35 kW/m², a spark (igniter) was generated. Besides the previously mentioned properties, by Test Method B, the Fire Growth Rate, FIGRA_{0,2MJ} index, was determined.

4. Results

4.1. Bio-aggregates and composites characterization

The curves obtained by the TGA test on the bio-aggregates are reported in Fig. 5a and b.

The results showed that, despite their different nature, size, and shape, the bio-aggregates were quite similar in terms of thermal stability, with an onset weight loss located around 260 °C. Although *A. donax*, *A*, appeared more in a fibrous arrangement than



b

Fig. 5. TGA thermograms of the bio-aggregate samples: a) A. donax; b) hazelnut shells.

hazelnut shells, H (Fig. 1), the water content was not significantly different. Furthermore, while working in a nitrogen atmosphere, the ability to leave a charred residue was slightly higher for H, with about 8 % wt char content at 800 °C vs. 5 % wt in the case of A. The charring ability is usually an indication of the fire-resisting ability of a material [76,77]. Comparing the results of the two bio-aggregates, a similar fire behaviour would be expected.

As for the composite samples, Table 3 shows the inorganic residue evaluated via muffle oven treatment. Owing to the macroscopic size of the bio-aggregates, it was not possible to run representative TGA tests of the composites to provide a reliable indication of their composition. The results showed that, overall, the binder fraction was slightly higher in the case of the two composites made of *A. donax*, AS and AHS, while the hazelnut-based composite samples, HS, had a lower inorganic residue fraction. This result could be determined by a higher capacity of *A. donax*, more fibrous, to retain the sodium silicate solution than the hazelnut shells, with a different, less fibrous surface in the exterior part of the shell. The significant difference in the inorganic fraction content might affect the overall flame response of the composites.

4.2. Reaction to fire

4.2.1. Test method a (simulating non-combustibility test)

The results of the test Method A, (application of constant heat, without generating any sparks, and analysing the fire reaction for 30 min), are reported in Table 4.

Fig. 6 shows the Heat Release Rate (HRR) for Test Method A of materials and composites (the type of the tested materials/composites instead of the samples' designation was reported).

The bio-aggregates curves presented an initial delay step, which represented the time required to reach the degradation temperature and start releasing ignitable volatiles. Then, both A and H curves increased sharply until a peak, reached between the first and the second minute of the test [60]. Both bio-aggregates were extremely fast in reaching the pHRR, with values of pHRR = 268.0 kW/m² (at 120 s) for hazelnut shells, pHRR = 217.3 kW/m² (at 51 s) for the mixture of the two aggregates, and pHRR = 200.8 kW/m² (at 42 s) for *A. donax* (Table 4).

These results were in line with the results of TGA (Section 4.1), with a slightly higher charring ability of H, which indeed, delays the peak in the HRR. Even when mixing A and H in a 50/50 vol ratio, the prevailing behaviour was determined by *A. donax* which first ignited and then sparked an anticipated combustion of the hazelnut shells fraction (TTI = 42 s for A, TTI = 52 s for AH). This observation, together with the testing conditions, accounted for the strong and inherent behaviour of the two different bio-aggregates: they were set on fire depending on their tendency to release volatiles upon thermal degradation.

Petrella [78] defined that the ratio of the peak HRR to time to ignition, namely pHRR/TTI, is an indication of the materials' propensity to flashover. Higher values of pHRR/TTI suggested a greater hazard, and a low tendency to flashover when below 0.1. In this study, all the bio-aggregates entered an intermediate risk region (pHRR/TTI in the 1–10 range). *A. donax* seemed to impart a higher hazard, even mixed with the hazelnut shells, having both A and AH similar flashover tendency, which doubled the one of H. However, the full hazard risk cannot be determined by considering only this parameter.

The Total Heat Release (THR) provides a full picture of the potential fire hazard behaviour since it represents the inherent energy in a material independent of environmental factors. As THR could be calculated by integrating the curve of HRR over time [30], its trend shows how fast the materials achieved the highest values of HRR. The results are represented in Fig. 7.

The hazelnut shells reached the highest values of HRR the fastest, followed by the mixture of the two aggregates and the *A. donax*. While A set to lower values of Heat Release after the first burst, H instead kept on releasing a higher amount of heat all over the test. Indeed, after the peak, the achieved minimum values are HRR = 46.1 kW/m² (at 1740 s) for hazelnut shells, HRR = 26.6 kW/m² (at 1746 s) for the mixture of the two aggregates, and HRR = 10.7 kW/m² (at 1227 s) for *A. donax*.

When the bio-aggregates were included in a composite structure with sodium silicate as a binder, the fire response was drastically modified. The trend observed for all the composites, regardless of their main component, was almost flat all over the test and the curves did not show any marked peak (Fig. 6).

In the absence of an external ignition source, as in the case of Test Method A, some random sparkle can occur during the 30-min test span. However, none of them could be considered as sustained flame which represented "*the existence of flame on or over the surface of the specimen for periods of over 10 s*" [69]. Hence, they cannot be used to define the flashover potential of the sample, which, consequently, was 0, and accounted for intrinsically safe composites in all the cases. This result was outstanding, since the application of such a convenient binder, which already demonstrated potential benefits in hygrothermal absorption [66] and also as a potential

Table 4	Ta	Ы	e	4
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Reaction to fire tested by Test Method A: results of bio-aggregates and composite samp
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Samples	Time to Ignition [s]	Peak Heat Release Rate (pHRR) [kW/m ²]	Heat Release Rate (HRR) [kW/m ²]	Total Heat Release (THR) [MJ/m ²]	Total Smoke Production (TSP) [m ²]	Flashover Index [kW/s.m ²]
A_01	33	200.8	10.5	64.4	1.5	6.1
H_01	108	268.0	81.5	145.6	4.9	2.5
AH_01	40	217.3	10.8	107.4	1.4	5.4
S_01	n.d. ^a	12.4	n.d. ^a	0.2	0.9	n.d. ^a
AS_01	n.d. ^a	11.7	5.8	10.4	0.5	n.d. ^a
HS_01	n.d. ^a	22.6	5.3	9.5	1.3	n.d. ^a
AHS_01	n.d. ^a	12.7	5.5	10.0	0.5	n.d. ^a

^a n.d. = not detectable.



Fig. 6. Heat Release Rate (HRR) of the materials and the composite samples determined by the cone calorimeter test: Test Method A simulating non-combustibility test (reporting the type of the tested materials/composites instead of the samples' designation).



Fig. 7. Total Heat Release (THR) of the materials and the composites determined by the cone calorimeter test: Test Method A simulating non-combustibility test (reporting the type of the tested materials/composites instead of the samples' designation).

barrier for fungi and moulding attacks [57], was able to fully hamper fire development. The performance in case of fire of the bio-aggregates was widely improved by the addition of the sodium silicate solution when producing the composites. Nonetheless, there was a correspondence between the materials and the composites. While not reporting any hazard, the highest values of HRR were achieved by hazelnut shells (both individually and in composites), possibly owing both to the intrinsic ability of H to release more heat but also to the lower sodium silicate content in the composite (both pointing at the same result). The addition of *A. donax* to hazelnut shells lowered the maximum values of the HRR both in the bio-aggregates and in the composite. Since the presence of sodium silicate



Fig. 8. Smoke Production Rate (SPR) of the materials and the composite samples determined by the cone calorimeter test: Test Method A simulating noncombustibility test (reporting the type of the tested materials/composites instead of the samples' designation).

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binder hampered completely the peak heat evolution, this mixed approach was beneficial in terms of fire protection, even in the case of fire development.

Another important parameter in fire protection is the prevention of smoke evolution. Indeed, smoke represents a significant threat to people exposed to fires, since hampers visibility slowing down escape, while also producing a significant amount of toxic and potentially lethal products. Fig. 8 reports the Smoke Production Rate (SPR) of the materials and the composite samples.

The principle of the smoke measurement is based on the observation that a volume of combustion products exponentially decreases the intensity of transmitted light as a function of distance from the observation point; hence in the present case, SPR is a measurement of the smoke obscuration ability.

The curves of the SPR were in line with the ones of the HRR for the aggregates, reaching a peak before the first 2 min – maximum values of SPR = $0.100 \text{ m}^2/\text{s}$ (at 87 s) for hazelnut shells, SPR = $0.038 \text{ m}^2/\text{s}$ (at 36 s) for the mixture of the two aggregates, SPR = $0.074 \text{ m}^2/\text{s}$ (at 30 s) for *A. donax*. It is interesting to observe that the smoke production peak significantly anticipated the heat release peak, supporting the hazard of this parameter that, even in the very initial stages of the fire development, represented an insidious threat to human life. The smoke production of the composites was practically insignificant throughout the test for *A. donax* containing composites and this behaviour was, in contrast, a very outstanding result in terms of fire safety and protection of the proposed particle-boards. When the hazelnut shells composite was analysed, a higher amount of smoke was released. However, it is worth pointing out that, differently from the aggregates, in the composite the smoke evolved all along the 30-min test, avoiding an intense fast smoke release, namely a lower threatening condition. Hence, in all cases, the great impact of the sodium silicate binder presence was evident, avoiding or strongly suppressing and diluting the production of smoke (Fig. 8).

Fig. 9 reports the Total Smoke Production (TSP) for Test Method A of materials and composites.

Analogously to THR and HRR, the TSP showed how fast the materials achieved the highest values of SPR, hence the fastness of the hazard evolution, demonstrating that the small quantities of smoke were released after minutes. The sodium silicate both protected the bio-based materials from burning and improved the smouldering effects, as these properties were closely related [30,60].

4.2.2. Test method B (simulating of single burning item)

The results of the test Method B, (application of constant heat, generating a spark, and analysing the fire reaction for 10 min), are reported in Table 5.

Fig. 10 reports the Heat Release Rate (HRR) for Test Method B of the materials and the composite samples (as for the designations, the type of the tested composites were reported instead of the samples).

The trends of the curves confirmed the results achieved by performing Test Method A, but the differences between the materials were more evident. Indeed, exposing the samples to a spark resulted in a quicker ignition, occurring when they reached the minimum flammability range due to the ignitable volatiles produced during thermal degradation. In Test Method B, *A. donax*, A, and the composite, AH, exhibited more distinct values compared to Test Method A. The presence of ignition indeed preceded the flame event, potentially aligning with the previously discussed higher charring ability of hazelnut shells under such conditions, thus delaying the contribution of the H component to flame generation.

Again, for HRR, hazelnut shells achieved the highest peak (pHRR = 412.5 kW/m², at 63 s), followed by the mixture of the two aggregates (pHRR = 242.6 kW/m², at 42 s), and *A. donax* (pHRR = 171.0 kW/m², at 24 s), considering the highest value between the two samples for each composite. In the presence of a spark, all the aggregates reached a peak before the first minute, faster than for Test Method A, due to the more critical conditions that aim at highlighting the very first flammability condition reached. Then, the curve decreased and achieved minimum values of HRR = 35.4 kW/m² (at 579 s) for the hazelnut shells, HRR = 61.7 kW/m² (at 417 s) for the mixture of the two aggregates and HRR = 5.4 kW/m² (at 552 s) for *A. donax*, considering the minimum value between the two samples for each composite. As for the Total Heat Release, THR, reported in Fig. 11, hazelnut shells reached an overall higher amount, followed by the mixture of the two aggregates and the *A. donax*, analogously to Test Method A.



Fig. 9. Total Smoke Production (TSP) of the materials and the composites determined by the cone calorimeter test: Test Method A simulating non-combustibility test (reporting the type of the tested materials/composites instead of the samples' designation).

Table 5

Reaction to fire tested by Test Method B: results of bio-aggregates and composite samples, reporting both tested samples.

Samples	Time to Ignition [s]	Peak Heat Release Rate (pHRR) [kW/m ²]	Heat Release Rate (HRR) [kW/m ²]	Total Heat Release (THR) [MJ/m ²]	Effective heat of combustion (EHC) [MJ/kg]	Total Smoke Production (TSP) [m ²]	Fire Growth Rate (FIGRA _{0,2MJ}) [W/s]
A_02	7	171.0	48.0	28.2	14.2	0.4	7855
A_03	8	164.3	33.3	19.6	13.5	0.2	6242
H_02	50	412.5	99.1	58.2	11.1	0.3	3947
H_03	51	400.1	88.9	52.2	11.8	0.3	3896
AH_02	26	242.6	83.5	50.0	7.3	0.1	4284
AH_03	27	241.5	82.5	52.2	7.4	0.2	4209
S_02	n.d. ^a	10.0	0.3	0.5	n.d. ^a	0.3	14
S_03	n.d. ^a	13.1	1.7	1.1	0.8	0.6	231
AS_02	n.d. ^a	n.d. ^a	n.d. ^a	1.4	1.4	0.4	n.d. ^a
AS_03	n.d. ^a	n.d. ^a	n.d. ^a	0.2	n.d. ^a	0.1	n.d. ^a
HS_02	n.d. ^a	n.d. ^a	n.d. ^a	0.3	n.d. ^a	0.2	n.d. ^a
HS_03	n.d. ^a	n.d. ^a	n.d. ^a	0.3	n.d. ^a	0.3	n.d. ^a
AHS_02	n.d. ^a	n.d. ^a	n.d. ^a	1.3	1.1	0.1	n.d. ^a
AHS_03	n.d. ^a	n.d. ^a	n.d. ^a	1.2	0.9	0.1	n.d. ^a

 a n.d. = not detectable.



Fig. 10. Heat Release Rate (HRR) of the materials and the composite samples determined by the cone calorimeter test: Test Method B simulating Single Burning Item (reporting the type of the tested materials/composites instead of the samples' designation).



Fig. 11. Total Heat Release (THR) of the materials and the composites determined by the cone calorimeter test: Test Method B simulating Single Burning Item (reporting the type of the tested materials/composites instead of the samples' designation).



Fig. 12. Smoke Production Rate (SPR) of the materials and the composite samples determined by the cone calorimeter test: Test Method B simulating Single Burning Item (reporting the type of the tested materials/composites instead of the samples' designation).

The addition of the sodium silicate, once again lowered the value of the HRR and THR (Figs. 10 and 11 respectively), in line with the results of Test Method A. Hence, the sodium silicate widely influenced the final performance and improved the fire reaction of the bio-aggregates. For the composites, the curves of HRR (Fig. 10) did not show a peak.

As reported in Table 5, by Test Method B, it was possible to evaluate FIGRA_{0,2MJ} index, namely the Fire Growth Rate index, which represents the maximum HRR throughout time. Then, it measures the heat contribution to developing fire from specific materials, allowing predicting the tendency for fire growth. Similarly, to the previous case in evaluating the flashover potential, FIGRA_{0,2MJ} showed that the bio-aggregates represented hazardous materials. The addition of sodium silicate widely changed the scenario, with the condition in which FIGRA cannot be evaluated, practically accounting for the negligible risk of fire growth.

Fig. 12 shows the Smoke Production Rate (SPR) of the materials and the composites.

Considering the aggregates, for Test Method B, the SPR was lower than for Test Method A. By generating a spark, the maximum values of SPR were 0.011 m²/s for hazelnut shells, 0.010 m²/s for the mixture and 0.006 m²/s for *A. donax*. Differently from the previous result, the *A. donax* showed the lowest value of the peak. In any case, in the presence of ignition, the smoke production was significantly lower, possibly owing to the flame production in the presence of a lower concentration of ignitable volatiles. As for the composites, again, the sodium silicate solution avoided smoke production and improved the fire reaction behaviour. The results of TSP are reported in Fig. 13.

Fig. 14 shows the samples after the test. The bio-aggregates burnt (Fig. 14a) due to the low resistance to fire typical of bio-based materials [30,31]; the sodium silicate swelled, alone (Fig. 14b) and in the composites (Fig. 14c). This reaction avoided composites' burning and smoke production, hence the sodium silicate created a sort of barrier which protected the bio-aggregates, as better discussed in the following section.

5. Discussion

5.1. Main findings of the research

The results of the reaction to fire of the bio-based composites were extremely promising and confirmed the sodium silicate's great influence [71]. Indeed it improved the performance in case of fire, lowering the values of the Heat Release Rate (HRR) and the Total Heat Release (THR) and significantly avoiding smoke production, one of the main problems in case of fire [71,72]. The sodium silicate created a silica-rich hybrid layer, which protected the bio-aggregates with an intumescent barrier, as explained by Li et al. [79]. Due to its inorganic characteristics, it shielded the organic bio-aggregates from burning [71].

The results of the fire reaction tests (Tables 4 and 5) suggested that the analysed composites could be considered as noncombustible products. Hence, they could be employed as indoor coating boards ensuring the minimization of the hazards due to smoke and toxic gases.

Comparing the two performed tests, some differences were evident. For the HRR of the bio-aggregates, higher values were achieved in Test Method B (Fig. 10), while the HRR curve decreased more evidently in Test Method A (Fig. 6). This was in line with the expectation, as for Test Method A, the samples were exposed to constant heat during the test, without any other source of ignition, differently from Test Method B, where a spark generation (igniter) was introduced. For this latter, the peak of the curve was achieved faster, as also represented by THR trends (Figs. 7 and 11). These two curves also showed some differences between the composites: in Test Method B their values were almost zero throughout the test, while in Test Method A they were a bit higher. As for the smoke production for bio-aggregates (as no significant smoke was produced by the composites bonded by sodium silicate), in Test Method B the Total Smoke Production (TSP) was lower than in Test Method A, coherently with the results of THR, as the two properties are related [30,60]. This result was caused by the different heat applications: more uniform heat radiation burnt more quantities of materials, thereby generating more smoke and heat [30].



Fig. 13. Total Smoke Production (TSP) of the materials and the composites determined by the cone calorimeter test: Test Method B simulating Single Burning Item (reporting the type of the tested materials/composites instead of the samples' designation).



Fig. 14. Samples after the assessment of fire reaction (Test Method B): a) mixture of *A. donax* and hazelnut shells AH; b) dried sodium silicate solution S; c) composite samples: hazelnut shells-based ones HS (left); *A. donax*-based ones AS (centre); mixture-based ones AHS (right).

The considerations on the two performed tests demonstrated as Test Method A and Test Method B, simulating two different conditions, produced different heat and smoke responses of the building materials. Thus, to assess the reaction to fire of building materials, both were significant.

The comparison with past studies that assessed the fire reaction of bio-aggregates, and the sodium silicate validated the achieved results.

Rocha et al. [60] considered rice husk, bamboo and wood shaving and carried out the same tests performed in the present study for the materials: TGA and reaction to fire by using a cone calorimeter and applying, however, a higher constant heat flux of 50 kW/m², representing an already well-developed fire. For TGA the researchers achieved similar results, highlighting a preliminary water loss and then a sequence of weight drops accounting for cellulosic base products' decomposition. A final higher weight loss was possibly referred to the decomposition of the aromatic lignin component which is the most stable fraction and possibly also responsible for the charring ability of the bio-based products. As for the fire reaction, the bio-aggregates showed similar HRR curves to the ones of the present study, namely an initial delay period, then a peak and a decrease. The achieved values of HRR were lower than the ones of the present study, especially for the hazelnut shells. This was caused potentially by a different material distribution that might alter the fire reaction, as well as by different heat flux applied. Moreover, while the actual values are not precisely stated by Rocha et al. [60], it seemed that the analysed materials displayed a higher water content than the ones of the present study. Thus, they produced not only a lower mass to burn but also a higher water fraction that helped smooth the fire evolution itself. However, the fire reaction behaviour (trend of HRR curves) was positively comparable.

Li et al. [71] assessed the reaction to fire of wood modified with a sodium silicate solution and provided the HRR, THR, SPR, and TSP. The results demonstrated that, by impregnating the wood with the sodium silicate, all the above cited properties were improved, as the values of all the curves lowered. This confirmed the promising performance in case of fire of the sodium silicate, which acted as a protection barrier for bio-based materials [79], in agreement with the present results.

While it is a difficult comparison to be carried out, since the manufacturing of the different products can be widely variable, it seems that a key point in boosting the fire resistance of the boards is a complete covering of the biomass with the intumescent sodium silicate binder. This feature, achieved in the present work, cannot be controlled, or compared with other literature data, but it should be a key point in developing a potential scale up of such particleboards.

5.2. Fire classification

The results of the present study indicated the composites' fire classification. Indeed, building materials are divided into six classes, from class A to F, plus related subclasses, based on their reaction to fire. Class A1, for example, includes those materials that do not contribute in any phase of the fire, including the fully developed fire phase, and can automatically fulfil all the requirements of the lower classes. Class F, the worst, labels all products for which their reaction to fire cannot be determined or cannot be classified in one of the previous classes. EN ISO 1182 [74], EN ISO 1716 [80] and EN 13823 [75] are useful standards to refer to for obtaining the A classification, according to ISO 13501 [73], and provide the use of different instrumentation and preparation of samples with a certain geometry.

Several different approaches were issued over the years to set fire classification. The cone calorimeter was initially discarded owing to the small sample size that can accommodate. However, in the present case, the cone calorimeter test carried out on particleboards was used as a mead of comparison with a more complex (and costly) technique that would imply the preparation of significantly bigger samples (such as a single burning item). Law et al. [81] analysed the evolution of such standards and reported that to comply with the A1 class – the non-combustible item class – in the Single Burning Item (SBI) condition, samples should show an Effective Heat of Combustion (EHC) below 2.0 MJ/kg (according to the German requirements [81]) and no flame whatsoever.

All the analysed bio-based composites were compliant with this requirement, and they also well complied with the A2 class requirement. This aspect, together with practically null Fire Growth Rate (FIGRA) and flashover index accounted all to the potential for the discussed formulations to undergo certification in the A2, as the minimum, but possibly also A1. It was not clear what should be the applied heat flux. In their discussion, Law et al. [81] reported that a Heat Flow of $20-40 \text{ kW/m}^2$ was acceptable for defining the SBI, with some hint at choosing 40 kW/m². While the present data refer to a heat flow of 35 kW/m^2 , corresponding at nearly $650 \degree C$, it seemed an acceptable situation to work for assigning class A parameters, being them A1 or A2. Consequently, the data on flame behaviour presented herein cannot be effectively utilized to ascertain the material's adherence to the standard. However, an inference may be drawn from the observed performance that, if tests were performed following the stipulated standard parameters, compliance with the specified constraints would likely be achieved.

5.3. Additional considerations and future studies

The analysed bio-based composites presented several benefits. First, being made of agro-industrial wastes and being bio-resources, they could be a suitable solution to reuse these wastes. Both the bio-aggregates were widely produced and available all over the year, thus overcoming the problem of seasonality. Furthermore, the materials employed in this study were locally produced, hence the energy requirement for both the production and the transport was minimized, boosting their sustainability.

Even if the selected adhesive was not bio-based, the sodium silicate has many advantages, as described in Section 1, as also confirmed further in the present study. Indeed, the performed laboratory tests showed that the sodium silicate solution eliminated one of the main drawbacks of bio-based products, namely the low fire resistance. This is an extremely promising result for this research field. Furthermore, the achieved results demonstrated that the proposed boards, which could be used as indoor coatings improving indoor comfort [18,58], possibly meet the A1 fire class.

On the other hand, according to past studies [18,58,66], the proposed boards showed some weaknesses that should be moderated or solved. For example, the mechanical performance appeared low, both for compressive and flexural strength. Cintura et al. [18,58] reported values of compressive strength of about $\sigma = 2.1 \text{ N/mm}^2$ and flexural strength of about $\sigma = 0.39 \text{ N/mm}^2$ for hazelnut shell-based composite. The *A. donax*-based boards did not achieve the breaking load, and they seemed more similar to straw bales, with value of compressive strength of about $\sigma = 0.9 \text{ N/mm}^2$ and flexural strength of about $\sigma = 0.35 \text{ N/mm}^2$. Hence, both the hazelnut shell-based and *A. donax*-based boards seemed inadequate as structural boards or masonry units [18], although the results were in line with past research [58].

The high hygroscopicity of the composites could be both a benefit and a drawback [66]. Indeed, despite it could be useful to control indoor conditions, it could also cause the degradation of the materials [62]. Some strategies could improve low moisture resistance, such as the addition of certain additives (i.e., phosphorus, boron, or silica fume [82]). However, this possibility should be demonstrated and better detailed to define if the benefits might be more than the drawbacks.

Finally, a great weakness could be the low resistance to biological colonisation of the bio-aggregates [64]. Nevertheless, according to past research [49,50] the sodium silicate solution could also avoid chemical decomposition and biological colonisation, but these properties should be further investigated.

Thus, the present study demonstrated that the use of sodium silicate as a binder is an efficient solution to produce boards made of eco-friendly materials, safe for human health from different points of view. Finally, the combination of these materials results in a building composite that could improve indoor conditions.

To provide further support to these considerations a qualitative cost-effectiveness analysis of the proposed bio-based boards was considered. As the employed bio-aggregates were by-products, their cost was derived only from the transport of the materials. Hence, the final cost of the boards will be mainly caused by the sodium silicate and the manufacturing process. Although sodium silicate production required some costs, it could be produced by innovative processes, which made it cheaper [83,84]. Furthermore, as previously reported, the quantities of the adhesive were minimized (only 30 %), and the production process avoided high temperatures, pressing and the use of specific treatments. Hence, a low production cost was expected. However, a more detailed analysis and a life cycle assessment (LCA) would better support these considerations, as well as quantify the sustainability of the proposed boards.

6. Conclusions

This study considered bio-based boards for indoor applications. The employed bio-aggregates were giant reed (*A. donax* L.) and hazelnut shells. A sodium silicate solution was employed as the adhesive. The thermal stability, water content, and the inorganic fraction composition of the raw materials and the composites and their reaction to fire were evaluated.

The following conclusions were achieved.

- The particleboards' composition strongly resented the quality of the employed agro-wastes and bio-resources under fire. Hazelnut shells determined significantly lower inorganic waste residue than *A. donax*.
- The two performed test methods were useful for carrying out considerations about the fire reaction of materials and composites. By a cone calorimeter method, it was possible to apply constant heat, with and without generating a spark (igniter), and to have different results for heat release and smoke production of the samples. These results allowed making different considerations, crucial to assess the possible hazards of the proposed composites.
- Considering the standard requirements for building products and the results of the fire reaction test, the considered bio-based composites could be classified as class A2 and potentially A1.
- The sodium silicate widely improved the fire reaction of the bio-aggregates, avoiding their burning and smoke production. Hence, the considered bio-based boards show a good performance in case of fire and could be employed as indoor panels without risks to humans.

An effective solution to improve the bio-based boards' behaviour in case of fire was, hence, described and validated. Future studies could further analyse boards' properties by changing some parameters (e.g., the grain size of the bio-aggregates, the percentages of the sodium silicate solution, and the additions of some additives) and investigate the possibility of using a sodium silicate solution as a superficial treatment in bio-based building products. Furthermore, the performance in case of fire of the considered boards could be further detailed by considering more replications, different conditions, and hence different test methods.

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CRediT authorship contribution statement

Eleonora Cintura: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Paulina Faria:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Luisa Molari:** Writing – review & editing, Supervision, Conceptualization. **Laura Mazzocchetti:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Conceptualization. **Matteo Dalle Donne:** Writing – review & editing, Visualization, Investigation. **Loris Giorgini:** Resources. **Lina Nunes:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Eleonora Cintura reports financial support was provided by Foundation for Science and Technology. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- M. Posani, M.D.R. Veiga, V. Peixoto de Freitas, K. Kompatscher, H. Schellen, Dynamic hygrothermal Models for monumental, historic buildings with HVAC systems: complexity shown through a case study, E3S Web of Conferences 172 (2020) 15007, https://doi.org/10.1051/e3sconf/202017215007.
- [2] A.A. Owodunni, J. Lamaming, R. Hashim, O.F.A. Taiwo, M.H. Hussin, M.H. Mohamad Kassim, Y. Bustami, O. Sulaiman, M.H.M. Amini, S. Hiziroglu, Adhesive application on particleboard from natural fibers: a review, Polym. Compos. 41 (2020) 4448–4460, https://doi.org/10.1002/pc.25749.
- [3] G.I. Mantanis, E.T. Athanassiadou, M.C. Barbu, K. Wijnendaele, Adhesive systems used in the European particleboard, MDF and OSB industries, Wood Mater. Sci. Eng. 13 (2018) 104–116, https://doi.org/10.1080/17480272.2017.1396622.
- [4] M. Gürü, A.F. Karabulut, M.Y. Aydın, İ. Bilici, Processing of fireproof and high temperature durable particleboard from rice husk, High Temp. Mater. Process. 34 (2015) 599–604, https://doi.org/10.1515/htmp-2014-0092.
- [5] F.G. Gonçalves, J.B. Paes, Y.M. Lopez, P.G. de A. Segundinho, R.G.E. de Oliveira, M.V. Fassarella, A.S. Brito, I.L.S. Chaves, R.S.F. Martins, Resistance of particleboards produced with ligno-cellulosic agro-industrial wastes to fungi and termites, Int. Biodeterior. Biodegrad. 157 (2021) 105159, https://doi.org/ 10.1016/j.ibiod.2020.105159.
- [6] M. Posani, R. Veiga, V.P. de Freitas, Thermal mortar-based insulation solutions for historic walls: an extensive hygrothermal characterization of materials and systems, Construct. Build. Mater. 315 (2022) 125640, https://doi.org/10.1016/j.conbuildmat.2021.125640.
- [7] M. Palumbo, A.M. Lacasta, N. Holcroft, A. Shea, P. Walker, Determination of hygrothermal parameters of experimental and commercial bio-based insulation materials, Construct. Build. Mater. 124 (2016) 269–275, https://doi.org/10.1016/j.conbuildmat.2016.07.106.
- [8] M. Duque-Acevedo, I. Lancellotti, F. Andreola, L. Barbieri, L.J. Belmonte-Ureña, F. Camacho-Ferre, Management of agricultural waste biomass as raw material for the construction sector: an analysis of sustainable and circular alternatives, Environ. Sci. Eur. 34 (2022) 70, https://doi.org/10.1186/s12302-022-00655-7.
- [9] M.M. Santos, M.A. Diez, M. Suárez, T.A. Centeno, Innovative particleboard material from the organic fraction of municipal solid waste, J. Build. Eng. 44 (2021) 103375, https://doi.org/10.1016/j.jobe.2021.103375.
- [10] M.T. Ferrandez-García, A. Ferrandez-Garcia, T. Garcia-Ortuño, C.E. Ferrandez-Garcia, M. Ferrandez-Villena, Assessment of the physical, mechanical and acoustic properties of Arundo donax L. biomass in low pressure and temperature particleboards, Polymers 12 (2020), https://doi.org/10.3390/ POLYM12061361.
- [11] H. Pirayesh, A. Khazaeian, Using almond (Prunus amygdalus L.) shell as a bio-waste resource in wood based composite, Compos. B Eng. 43 (2012) 1475–1479, https://doi.org/10.1016/j.compositesb.2011.06.008.
- [12] L. Nunes, R. Réh, M.C. Barbu, P. Walker, A. Thomson, D. Maskell, S. Knapic, A. Bajraktari, J.M. Greef, C. Brischke, E. Mansour, T. Ormondroyd, G.A. Teppand, M. Palumbo, A.M. Lacasta, Nonwood bio-based materials, in: Performance of Bio-Based Building Materials, Elsevier, 2017, pp. 97–186, https://doi.org/ 10.1016/B978-0-08-100982-6.00003-3.
- [13] S. Abdulkareem, A. Adeniyi, Production of particle boards using polystyrene and bamboo wastes, Nigerian Journal of Technology 36 (2017) 788–793, https:// doi.org/10.4314/njt.v36i3.18.
- [14] N. Mati-Baouche, H. de Baynast, P. Michaud, T. Dupont, P. Leclaire, Sound absorption properties of a sunflower composite made from crushed stem particles and from chitosan bio-binder, Appl. Acoust. 111 (2016) 179–187, https://doi.org/10.1016/j.apacoust.2016.04.021.
- [15] A. Paiva, S. Pereira, A. Sá, D. Cruz, H. Varum, J. Pinto, A contribution to the thermal insulation performance characterization of corn cob particleboards, Energy Build. 45 (2012) 274–279, https://doi.org/10.1016/j.enbuild.2011.11.019.
- [16] M. Bovo, N. Giani, A. Barbaresi, L. Mazzocchetti, L. Barbaresi, L. Giorgini, D. Torreggiani, P. Tassinari, Contribution to thermal and acoustic characterization of corn cob for bio-based building insulation applications, Energy Build. 262 (2022) 111994, https://doi.org/10.1016/j.enbuild.2022.111994.
- [17] W.N.A.W. Nadhari, M. Danish, M.S.R.M. Nasir, B.J. Geng, Mechanical properties and dimensional stability of particleboard fabricated from steam pre-treated banana trunk waste particles, J. Build. Eng. 26 (2019) 100848, https://doi.org/10.1016/j.jobe.2019.100848.
- [18] E. Cintura, P. Faria, L. Molari, L. Barbaresi, D. D'Orazio, L. Nunes, Characterization of an Arundo donax-based composite: a solution to improve indoor comfort, Ind. Crop. Prod. 208 (2024) 117756, https://doi.org/10.1016/j.indcrop.2023.117756.
- [19] A. Antunes, P. Faria, V. Silva, A. Brás, Rice husk-earth based composites: a novel bio-based panel for buildings refurbishment, Construct. Build. Mater. 221 (2019) 99–108, https://doi.org/10.1016/j.conbuildmat.2019.06.074.
- [20] M. Posani, R. Veiga, V. Freitas, Post-Insulating traditional massive walls in Southern Europe: a moderate thermal resistance can be more effective than you think, Energy Build. 295 (2023) 113299, https://doi.org/10.1016/j.enbuild.2023.113299.
- [21] S. Sakthivel, S. Senthil Kumar, B. Melese, S. Mekonnen, E. Solomon, A. Edae, F. Abedom, M. Gedilu, Development of nonwoven composites from recycled cotton/polyester apparel waste materials for sound absorbing and insulating properties, Appl. Acoust. 180 (2021) 108126, https://doi.org/10.1016/j. apacoust.2021.108126.
- [22] G. Fratoni, D. D'Orazio, L. Barbaresi, M. Garai, L. Cappellini, Mixing materials in false ceilings to increase sound diffusion in education spaces, INTER-NOISE and NOISE-CON Congress and Conference Proceedings 265 (2023) 5002–5006, https://doi.org/10.3397/IN 2022 0723.
- [23] E. Cintura, L. Nunes, B. Esteves, P. Faria, Agro-industrial wastes as building insulation materials: a review and challenges for Euro-Mediterranean countries, Ind. Crop. Prod. 171 (2021) 113833, https://doi.org/10.1016/j.indcrop.2021.113833.
- [24] L. Liu, H. Li, A. Lazzaretto, G. Manente, C. Tong, Q. Liu, N. Li, The development history and prospects of biomass-based insulation materials for buildings, Renew. Sustain. Energy Rev. 69 (2017) 912–932, https://doi.org/10.1016/j.rser.2016.11.140.
- [25] R. Muthuraj, C. Lacoste, P. Lacroix, A. Bergeret, Sustainable thermal insulation biocomposites from rice husk, wheat husk, wood fibers and textile waste fibers: elaboration and performances evaluation, Ind. Crop. Prod. 135 (2019) 238–245, https://doi.org/10.1016/j.indcrop.2019.04.053.
- [26] C.H. Koh, F. Gauvin, K. Schollbach, H.J.H. Brouwers, Upcycling wheat and barley straws into sustainable thermal insulation: assessment and treatment for durability, Resources, Conserv. Recycl. 198 (2023) 107161, https://doi.org/10.1016/j.resconrec.2023.107161.
- [27] A.M. Tobon, Y. Andres, N. Locoge, Impacts of test methods on the assessment of insulation materials' resistance against moulds, Build. Environ. 179 (2020) 106963, https://doi.org/10.1016/j.buildenv.2020.106963.
- [28] S. Ginestet, C. Aschan-Leygonie, T. Bayeux, M. Keirsbulck, Mould in indoor environments: the role of heating, ventilation and fuel poverty. A French perspective, Build. Environ. 169 (2020) 106577, https://doi.org/10.1016/j.buildenv.2019.106577.
- [29] S. Curling, Test methods for bio-based building materials, in: Performance of Bio-Based Building Materials, Elsevier, 2017, pp. 385–481, https://doi.org/ 10.1016/B978-0-08-100982-6.00007-0.
- [30] N.K. Kim, S. Dutta, D. Bhattacharyya, Heat and smoke production of flax fibre reinforced composites under horizontal and vertical orientations, Compos. B Eng. 178 (2019) 107467, https://doi.org/10.1016/j.compositesb.2019.107467.
- [31] T. Bhuvana, A. Tiwari, C. Chandraprakash, Green fabrication of cellulose-rich agricultural residues for scalable and biodegradable acoustic boards, Ind. Crop. Prod. 204 (2023) 117404, https://doi.org/10.1016/j.indcrop.2023.117404.
- [32] P. Rantuch, T. Chrebet, Thermal decomposition of cellulose insulation, Cellul. Chem. Technol. 48 (2014) 461-467.
- [33] J.A. Libra, K.S. Ro, C. Kammann, A. Funke, N.D. Berge, Y. Neubauer, M.M. Titirici, C. Fühner, O. Bens, J. Kern, K.H. Emmerich, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, Biofuels 2 (2011) 71–106, https://doi.org/ 10.4155/bfs.10.81.
- [34] A.P. Mouritz, A.G. Gibson, Fire Properties of Polymer Composite Materials, Springer Netherlands, Dordrecht, 2006, https://doi.org/10.1007/978-1-4020-5356-6_2.
- [35] A.P. Mouritz, A.G. Gibson, Flame retardant composites, in: Fire Properties of Polymer Composite Materials, Springer Netherlands, Dordrecht, 2006, pp. 237–286, https://doi.org/10.1007/978-1-4020-5356-6.
- [36] S. Merighi, L. Mazzocchetti, T. Benelli, E. Maccaferri, A. Zucchelli, A. D'Amore, L. Giorgini, A new wood surface flame-retardant based on poly- m -aramid electrospun nanofibers, Polym. Eng. Sci. 59 (2019) 2541–2549, https://doi.org/10.1002/pen.25235.

- [37] S. Scurti, J. Ortolani, A. Ghirri, E. Maccaferri, D. Caretti, L. Mazzocchetti, Phosphorylated poly(vinyl alcohol) surface coatings as intumescent flame inhibitor for polymer matrix composites, Prog. Org. Coating 177 (2023) 107457, https://doi.org/10.1016/j.porgcoat.2023.107457.
- [38] L. Mazzocchetti, T. Benelli, E. Maccaferri, S. Merighi, J. Belcari, A. Zucchelli, L. Giorgini, Poly-m-aramid electrospun nanofibrous mats as high-performance flame retardants for carbon fiber reinforced composites, Compos. B Eng. 145 (2018) 252–260, https://doi.org/10.1016/j.compositesb.2018.03.036.
- [39] A.M. Emsley, G.C. Stevens, 14 The risks and benefits of flame retardants in consumer products, in: A.R. Horrocks, D. Price (Eds.), Advances in Fire Retardant Materials, Woodhead Publishing, Guilford (UK), 2008, pp. 363–397.
- [40] L. Busetto, M.C. Cassani, R. Mazzoni, Procedure for the Preparation of Metal Complexes Containing Hydroxycarbonylcyclopentadienide Ligands, EP 1258487A1, 2002.
- [41] L. Busetto, M.C. Cassani, R. Mazzoni, V.G. Albano, P. Sabatino, P. Frediani, E. Rivalta, Coordination chemistry of ester-functionalized cp ligands. A versatile approach to the chiral hydroxyalkoxycarbonylcyclopentadienide [C₅H₄CO₂(CHMe)₂OH] - . Synthesis, structure, and catalytic activity of rhodium(I) and iron(II) complexes, Organometallics 21 (2002) 4993–4999, https://doi.org/10.1021/om0205492.
- [42] A. Esmailpour, H.R. Taghiyari, P. Nouri, A. Jahangiri, Fire-retarding properties of nanowollastonite in particleboard, Fire Mater. 42 (2018) 306–315, https:// doi.org/10.1002/fam.2493.
- [43] J. Lu, D. Wang, P. Jiang, S. Zhang, Z. Chen, S. Bourbigot, G. Fontaine, M. Wei, Design of fire resistant, sound-absorbing and thermal-insulated expandable
- polystyrene based lightweight particleboard composites, Construct. Build. Mater. 305 (2021) 124773, https://doi.org/10.1016/j.conbuildmat.2021.124773.
 [44] M. Gürü, M. Atar, R. Yildirim, Production of polymer matrix composite particleboard from walnut shell and improvement of its requirements, Mater. Des. 29 (2008) 284–287, https://doi.org/10.1016/j.matdes.2006.10.023.
- [45] D. Battegazzore, J. Alongi, D. Duraccio, A. Frache, Reuse and valorisation of hemp fibres and rice husk particles for fire resistant fibreboards and particleboards, J. Polym. Environ. 26 (2018) 3731–3744, https://doi.org/10.1007/s10924-018-1250-3.
- [46] D. Yan, D. Chen, J. Tan, L. Yuan, Z. Huang, D. Zou, P. Sun, Q. Tao, J. Deng, Y. Hu, Synergistic flame retardant effect of a new N-P flame retardant on poplar wood density board, Polym. Degrad. Stabil. 211 (2023) 110331, https://doi.org/10.1016/j.polymdegradstab.2023.110331.
- [47] L. Yan, Z. Xu, X. Wang, Synergistic effects of organically modified montmorillonite on the flame-retardant and smoke suppression properties of transparent intumescent fire-retardant coatings, Prog. Org. Coating 122 (2018) 107–118, https://doi.org/10.1016/j.porgcoat.2018.05.016.
- [48] L. Yan, Z. Xu, X. Wang, Influence of nano-silica on the flame retardancy and smoke suppression properties of transparent intumescent fire-retardant coatings, Prog. Org. Coating 112 (2017) 319–329, https://doi.org/10.1016/j.porgcoat.2017.07.017.
- [49] S.J. Lee, V. Thole, Investigation of modified water glass as adhesive for wood and particleboard: mechanical, thermal and flame retardant properties, European Journal of Wood and Wood Products 76 (2018) 1427–1434, https://doi.org/10.1007/s00107-018-1324-x.
- [50] S. Liuzzi, C. Rubino, F. Martellotta, P. Stefanizzi, C. Casavola, G. Pappalettera, Characterization of biomass-based materials for building applications: the case of straw and olive tree waste, Ind. Crop. Prod. 147 (2020) 112229, https://doi.org/10.1016/j.indcrop.2020.112229.
- [51] A. Bakatovich, F. Gaspar, N. Boltrushevich, Thermal insulation material based on reed and straw fibres bonded with sodium silicate and rosin, Construct. Build. Mater. 352 (2022) 129055, https://doi.org/10.1016/j.conbuildmat.2022.129055.
- [52] W. Chai, L. Zhang, W. Li, M. Zhang, J. Huang, W. Zhang, Preparation of plastics- and foaming agent-free and porous bamboo charcoal based composites using sodium silicate as adhesives, Materials 14 (2021) 2468, https://doi.org/10.3390/ma14102468.
- [53] S. Liu, W.K. Ott, Sodium silicate applications in oil, gas & geothermal well operations, J. Petrol. Sci. Eng. 195 (2020) 107693, https://doi.org/10.1016/j. petrol.2020.107693.
- [54] Z. Zhang, H. Chen, Y. Wang, G. Wang, L. Li, M. Zhong, H. Bai, Effect of sodium silicate binder on the performance of ceramic coatings on copper prepared by the slurry method, Surf. Coating. Technol. 448 (2022) 128868, https://doi.org/10.1016/j.surfcoat.2022.128868.
- [55] H.S. Rajan, P. Kathirvel, Sustainable development of geopolymer binder using sodium silicate synthesized from agricultural waste, J. Clean. Prod. 286 (2021) 124959, https://doi.org/10.1016/j.jclepro.2020.124959.
- [56] B. Li, B.F. Trueman, M.S. Rahman, Y. Gao, Y. Park, G.A. Gagnon, Understanding the impacts of sodium silicate on water quality and iron oxide particles, Environmental Science: Water Research & Technology 5 (2019) 1360–1370, https://doi.org/10.1039/C9EW00257J.
- [57] E. Cintura, P. Faria, M. Duarte, L. Nunes, Eco-efficient boards with agro-industrial wastes assessment of different adhesives, Construct. Build. Mater. 404
- (2023) 132665, https://doi.org/10.1016/j.conbuildmat.2023.132665.
 [58] E. Cintura, P. Faria, L. Molari, L. Barbaresi, D. D'Orazio, L. Nunes, A feasible re-use of an agro-industrial by-product: hazelnut shells as high-mass bio-aggregate in boards for indoor applications, J. Clean. Prod. 434 (2024) 140297, https://doi.org/10.1016/j.jclepro.2023.140297.
- [59] B. Arias-Cárdenas, A.M. Lacasta, L. Haurie, Bibliometric analysis of research on thermal, acoustic, and/or fire behaviour characteristics in bio-based building materials, Construct. Build. Mater. 432 (2024) 136569, https://doi.org/10.1016/j.conbuildmat.2024.136569.
- [60] M. Rocha, B. Gomes, A. Aguiar, A. Landesmann, N.P. Hasparyk, R. Toledo Filho, Fire reaction properties of bio-based aggregates used in thermally insulated building components, Fire Mater. 48 (2024) 62–78, https://doi.org/10.1002/fam.3166.
- [61] S. Schiavoni, F. D'Alessandro, F. Bianchi, F. Asdrubali, Insulation materials for the building sector: a review and comparative analysis, Renew. Sustain. Energy Rev. 62 (2016) 988–1011, https://doi.org/10.1016/j.rser.2016.05.045.
- [62] M. Palumbo, A.M. Lacasta, A. Navarro, M.P. Giraldo, B. Lesar, Improvement of fire reaction and mould growth resistance of a new bio-based thermal insulation material, Construct. Build. Mater. 139 (2017) 531–539, https://doi.org/10.1016/j.conbuildmat.2016.11.020.
- [63] Y. Yang, L. Haurie, D.Y. Wang, Bio-based materials for fire-retardant application in construction products: a review, Journal of Thermal Analysis and Calorimetry 147 (2022) 6563–6582, https://doi.org/10.1007/s10973-021-11009-5.
- [64] E. Cintura, P. Faria, M. Duarte, L. Nunes, Bio-wastes as aggregates for eco-efficient boards and panels: screening tests of physical properties and biosusceptibility, Infrastructures 7 (2022) 26, https://doi.org/10.3390/infrastructures7030026.
- [65] E. Cintura, P. Faria, L. Molari, L. Nunes, Optimisation of production parameters to develop innovative eco-efficient boards, in: S. Amziane, I. Merta, J. Page (Eds.), Bio-Based Building Materials Proceedings of ICBBM 2023, 2023, pp. 111–122, https://doi.org/10.1007/978-3-031-33465-8_10.
- [66] E. Cintura, L. Nunes, L. Molari, M. Bettuzzi, M.P. Morigi, R. Brancaccio, P. Faria, Hygroscopicity and morphology of bio-based boards the influence of the formulation, Appl. Sci. 14 (2024) 873, https://doi.org/10.3390/app14020873.
- [67] Ingessil, 2022. https://www.ingessil.com/it. (Accessed 30 November 2022).
- [68] S. Liuzzi, C. Rubino, P. Stefanizzi, F. Martellotta, Performance characterization of broad band sustainable sound absorbers made of almond skins, Materials 13 (2020) 5474, https://doi.org/10.3390/ma13235474.
- [69] ISO 5660-1:2015 + A1:2019 Reaction-To-Fire Tests Heat Release, Smoke Production and Mass Loss Rate. International Organization for Standardization, Geneva, Switzerland.
- [70] B. Schartel, T.R. Hull, Development of fire-retarded materials—interpretation of cone calorimeter data, Fire Mater. 31 (2007) 327–354, https://doi.org/ 10.1002/fam.949.
- [71] P. Li, Y. Zhang, Y. Zuo, J. Lu, G. Yuan, Y. Wu, Preparation and characterization of sodium silicate impregnated Chinese fir wood with high strength, water resistance, flame retardant and smoke suppression, J. Mater. Res. Technol. 9 (2020) 1043–1053, https://doi.org/10.1016/j.jmrt.2019.10.035.
- [72] R. Sonnier, H. Vahabi, C. Chivas-Joly, New insights into the investigation of smoke production using a cone calorimeter, Fire Technol. 55 (2019) 853–873, https://doi.org/10.1007/s10694-018-0806-z.
- [73] EN 13501-1:2007+A1 Fire Classification of Construction Products and Building Elements Part 1: Classification Using Data from Reaction to Fire Tests. European Committee for Standardization, Brussels, Belgium.
- [74] EN ISO 1182:2020 Reaction to Fire Tests for Products Non-combustibility Test. European Committee for Standardization, Brussels, Belgium.
- [75] EN 13823:2020+A1:2022 Reaction to Fire Tests for Building Products Building Products Excluding Floorings Exposed to the Thermal Attack by a Single Burning Item. European Committee for Standardization, Brussels, Belgium.
- [76] D.W. van Krevelen, Some basic aspects of flame resistance of polymeric materials, Polymer 16 (1975) 615–620, https://doi.org/10.1016/0032-3861(75)90157-3.

- [77] J. Dai, Y. Peng, N. Teng, Y. Liu, C. Liu, X. Shen, S. Mahmud, J. Zhu, X. Liu, High-performing and fire-resistant biobased epoxy resin from renewable sources, ACS Sustain. Chem. Eng. 6 (2018) 7589–7599, https://doi.org/10.1021/acssuschemeng.8b00439.
- [78] R.V. Petrella, The assessment of full-scale fire hazards from cone calorimeter data, J. Fire Sci. 12 (1994) 14–43, https://doi.org/10.1177/ 073490419401200102.
- [79] M.E. Li, S.X. Wang, L.X. Han, W.J. Yuan, J.B. Cheng, A.N. Zhang, H.B. Zhao, Y.Z. Wang, Hierarchically porous SiO₂/polyurethane foam composites towards excellent thermal insulating, flame-retardant and smoke-suppressant performances, J. Hazard Mater. 375 (2019) 61–69, https://doi.org/10.1016/j. ihazmat.2019.04.065.
- [80] EN ISO 1716:2010 Reaction to Fire Tests for Products Determination of the Gross Heat of Combustion (Calorific Value). European Committee for Standardization, Brussels, Belgium.
- [81] A. Law, G. Spinardi, L. Bisby, The rise of the Euroclass: inside the black box of fire test standardisation, Fire Saf. J. 135 (2023) 103712, https://doi.org/10.1016/ j.firesaf.2022.103712.
- [82] L. Song, W. Liu, F. Xin, Y. Li, Study of adhesion properties and mechanism of sodium silicate binder reinforced with silicate fume, Int. J. Adhesion Adhes. 106 (2021) 102820, https://doi.org/10.1016/j.ijadhadh.2021.102820.
- [83] F. Andreola, L. Barbieri, I. Lancellotti, The environmental friendly route to obtain sodium silicate solution from rice husk ash: a comparative study with commercial silicates deflocculating agents, Waste and Biomass Valorization 11 (2020) 6295–6305, https://doi.org/10.1007/s12649-019-00849-w.
- [84] E. Kamseu, L.M. Beleuk à Moungam, M. Cannio, N. Billong, D. Chaysuwan, U.C. Melo, C. Leonelli, Substitution of sodium silicate with rice husk ash-NaOH solution in metakaolin based geopolymer cement concerning reduction in global warming, J. Clean. Prod. 142 (2017) 3050–3060, https://doi.org/10.1016/j. jclepro.2016.10.164.