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1	Optimizing performance of insulation materials based on wheat straw, lime
2	and gypsum plaster composites using natural additives
3	
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19	Highlights
20	• The thermal conductivity of bio-composites is optimized using natural additives.
21	• The mechanical strength is sufficient to support the self-weight of bio-composites.
22	• Effect of additives on microstructural changes and carbonation-hydration mechanisms
23	• Changes in morphology of the binder's microstructure influence mechanical behaviour
24	Abstract

The aim of this study was to optimize the thermal performances of a bio-composite based on cereal straw and mineral binders. The purpose is to reduce its thermal conductivity by

decreasing the amount of mineral binder while maintaining sufficient mechanical properties to 27 ensure self-bearing. Three additives, namely hemoglobin, casein and gelatin, from a renewable 28 and biodegradable biomass source were used. Thermal and mechanical characterization of the 29 composites was carried out. The influence of the additives on the carbonation-hydration 30 mechanisms, microstructure changes and macroscopic properties was investigated. The 31 microstructure and the mineralogy of the binders without and with additives was investigated 32 through microstructural analysis (SEM, DRX and TGA). The optimized composites have an 33 interesting thermal conductivity with acceptable mechanical properties for use in building 34 insulation. 35

Keywords: Wheat Straw, Lime, Plaster, Gelatin, Hemoglobin, Casein, Mechanical properties,
Thermal conductivity, Carbonation rate.

38 1 Introduction

Faced with the challenging objectives of reducing energy consumption and the CO₂ emissions 39 40 from industry and the building sector and the depletion of raw materials, the development of new materials based on renewable resources and with a low environmental impact has become 41 a central issue in research and the economy. The use of vegetable fibers in building materials 42 43 is one solution to improve the hygrothermal behavior of buildings and reduce the use of raw materials by using agricultural products or even residues. Composites based on vegetable fibers 44 have been the subject of several studies in recent years. They have shown interesting thermal, 45 hydric and acoustic properties [1]. The performance of these materials depends on their 46 constituents and the elaboration process adopted, such as the nature of the binder [2], the 47 aggregate/binder ratio [3,4], the size of aggregates [2], the compaction [2,3,5–7] and curing 48 conditions (temperature and humidity) [2,8]. 49

In practice, as reported in the literature, most of the biobased materials developed use cement 50 51 [9–14] or lime [2,3,5,7,15–17] as the principal binder in order to obtain acceptable mechanical properties and satisfactory durability. Nevertheless, because of the poor adhesion of vegetal 52 aggregates with these binders, high aggregate fractions have to be used to obtain satisfactory 53 mechanical properties. In turn the use of a high fraction of these binders in biocomposites leads 54 to mediocre thermal conductivity of the composite, which is in most cases greater than that of 55 classic insulation materials (rockwool, polystyrene foam). On the other hand, the cement 56 manufacturing process generates a large amount of CO₂ [18–20]. In fact, the production of one 57 tonne of cement generates 900 kg of CO₂ [8]. The lime industry also has a significant CO₂ 58 59 emission rate [21,22]. Taking into account the amount of CO₂ fixed during the carbonation of lime, the CO₂ emission rate is estimated at between 335 and 415 kg/t [8]. 60

In order to ensure both a low environmental impact and an industrial use, various strategies
have been applied by many researchers consisting in using alterantive binders, using additives,
optimizing the surface of vegetal aggregates and so on.

64 Several benefits have been reported in the literature on the incorporation of vegetal aggregates in order to develop materials with different use criterions. On the thermal behaviour point of 65 view, the lowest thermal conductivity is the criterion for improving energy consumption. 66 Experimental investigations have proposed insulation materials and established the positive 67 effects of the vegetable fibers such as hemp [23] sunflower stalk [24]. In addition to the thermal 68 performance, bio-composites are an excellent regulator of air humidity with a better water 69 buffering capacity. Other researchers have also highlighted the use of other binder in order to 70 71 improve thermal, mechanical and hygric properties such as proteinic binder with flax shives developed by El Hajj et al [25], or hemp and straw extracted binder studied by Collet et al. [26]. 72 The present work aimed at optimizing the thermal performance of two composites based on 73 cereal straw mixed with lime or gypsum plaster. These composites were developed in our 74

previous work [27–29]. The goal was to reduce the thermal conductivity by decreasing the 75 76 amount of mineral binder while maintaining acceptable mechanical properties that allow the composites to support their self-weight during their implementation as thermal insulants. To do 77 this, three procedures are proposed by integrating additives from a renewable and biodegradable 78 source: in the first, a hemoglobin powder is added as an air entrainer to the constituents of the 79 material in order to create additional porosity in the matrix and thus to reduce the thermal 80 conductivity of the composite. The second consists on the one hand in increasing the porosity 81 of the material and on the other hand in improving the adhesion to the matrix-fibre interface by 82 replacing a certain percentage of binder with casein powder, which gives it adhesive qualities 83 84 [30,31]. The third aims to substitute a portion of the mineral binder with another binder based on a gelatin, ensuring stronger bonds between the plant-based aggregates, thus increasing the 85 aggregate fraction. In addition, because of its natural abundance and the facility of its extraction 86 87 at an industrial scale, gelatin is economically very interesting [32]. Different percentages of substitution were used for each binder in order to select the optimal value in terms of cost-88 89 performance.

90 2 Materials and methods

91 **2.1 Raw materials**

92 2.1.1 Binders

93 Three mineral binders were used in the present study to prepare the biocomposites:

- *Tradical PF70*: is a pre-formulated binder manufactured in accordance with the requirements of NF 459. It is based on aerial lime (75%), hydraulic binders (15%) and pozzolan (10%).
- *Tradical Thermo*: is also a pre-formulated binder manufactured in accordance with the
 requirements of NF 459. It is based on aerial lime (85%) and hydraulic binders (15%).

99 It is characterized by a shorter curing period than Tradical PF70 PF70 for the same100 properties.

A commercial plaster produced by Diall, wich is characterized by its quick setting time
 (10-15 minutes).

103 *2.1.2 Additives*

- *Hemoglobin*: this is a proteinaceous substance from pork blood obtained by
 fractionation and spray drying. Vepro 95 PHF is the commercial name of the product
 used in this study and is manufactured by the Vapran Group in powder form.
- *Casein*: this is a protein extracted from milk, produced by EPI Ingredients Group in the
 form of a fine white powder (<400µm). It is used as a natural fixative for lime coating.
- *Gelatin*: this is a technical gelatin 200 bloom produced by the Weishardt Group in
 powder form with a particle size less than 20 mesh (841 μm).

111 2.1.3 Wheat straw

The straw used in this study was harvested in the Region Centre Val de Loire in France in 2016. It was manually cut in the laboratory only in the longitudinal direction in order to maintain its natural tubular shape. Three different shapes were identified: flat, cylindrical, and elliptical (**Fig.1.a, b**). The observation of the straw by scanning electron microscopy (SEM) showed that the surface of the outer wall (**Fig.1.c**) was rough compared to that of the inner (**Fig1.d**), which promotes a good bond between the straw and the binder.

The particle size distribution of the straw was determined using the image analysis method according to the RILEM recommendation [33]. A sample of 100 g, containing more than 3000 particles, was spread on a black background and scanned. The acquired images were processed using the Matlab code. Firstly, the images were segmented, then each detected particle was adjusted to an ellipse (**Fig.2**). The length and width of each particle was defined respectively according to the large and small axis of the adjusted ellipse. The results obtained are shown in. Fig.3 The size obtained after cutting is the one that was intended for mixing with 90 % strawof 3.5 cm.



126

- 127 Fig. 1. General aspect of the wheat straws used (a) and (b) identified section shapes (c) outer
- 128 surface (d) inner surface.



129

Fig. 2. Image analysis steps to determine the particle size distribution.





Fig. 3. Particle size distribution of wheat straw

2.2 Optimization Methodology and Formulation of the Composites

Two formulations were selected from our previous work [27–29] for this investigation. The first is based on lime with a ratio of Water/Binder =1.1 and Straw/Binder = 0.2 and the second is based on plaster with a ratio of Water/Binder = 1.1 and Straw/Binder = 0.4. As noted above the objective of this work was to optimize these two formulations based on three procedures, the first and the second concern only the formulation based on lime and the third procedure concerns both formulations:

140 I^{st} procedure: consists in the first step in substituting 5% of lime dry mass by hemoglobin 141 keeping the same fractions of the reference formulation Water/Binder = 1.1 and Straw/Binder 142 = 0.2.

143 The manufacture of the composites was carried out in two steps:

144 *Preparation of binders*: the lime and additive were dry mixed for 1 min at a speed of 140 rpm 145 using an electric mixer, then water was added gradually for 1 min maintaining the same speed 146 (**Fig.4.a, b**). Finally, the whole was mixed at a speed of 285 rpm for 3min to promote air 147 entrainment.

148 Preparation of straw-binder mixture: after the preparation of binders, the aggregates of the 149 straw and the pre-wetting water were introduced into the mixer and mixed for 1 minute. Then, 150 the previously prepared binder was added and the whole was mixed for 5 min (Fig.4.c, d).

The resulting composite showed a very different appearance from that of the reference (**Fig5.a**, **b**). The aggregates were no longer coated by the binder but had become totally embedded in a very porous matrix. This cellular structure of the matrix is mainly due to the surfactant properties of hemoglobin that promote the formation of a stable foam when it is mixed with lime and water [34–36]. Then, the observed aspect which is characterized by an excess of binder made it possible to increase the Straw/Binder ratio to: S/B = 0.3 and 0.4.

 2^{nd} procedure: The purpose of this procedure is to substitute 10% of lime by 5% of hemoglobin 157 158 and 5% of casein. The Straw/Binder ratio was kept at 0.2 while the Water/Binder ratio was 159 reduced to 1 to avoid the segregation phenomenon in the composite that was observed for the ratio 1.1 (the composites were prepared according to the same steps as in the first procedure). 160 It was observed in the composite obtained that the intergranular porosity disappeared and that 161 the composite became denser and more compact, which will significantly influence its 162 properties (Fig.5.c). This can be explained by the fact that casein prevents the molecules of the 163 air entrainer from forming a foam when it is used in the same percentage as the latter. 164 Consequently, the percentage of hemoglobin was kept at 5% and the casein percentage was 165 decreased to 2.5% (Fig.5.d). Following the same reasoning as in the first procedure, the 166 Straw/Binder ratio was increased to 0.3 and 0.4. 167

 3^{rd} procedure: the aim here is to substitute a percentage of mineral binder (lime + water) with a 168 gelatin-based binder. The latter is prepared by dissolving powdered gelatin in water at 50 °C to 169 obtain a Water/Gelatin ratio of 3. This ratio was determined based on a preliminary study (four 170 171 ratios were tested: Water/Gelatine=1, Water/Gelatine=2, Water/Gelatine=3 and Water/Gelatine= 4. The fraction Water/Gelatine=3 selected is the one which ensures the bonds 172 between the aggregates with a minimal amount of gelatin). 173

For this last procedure, the binder (Lime-gelatin or plaster-gelatin) was prepared according to the following steps in order to introduce the gelatin: firstly, the lime (or plaster) was mixed with water for 2 min at a speed of 140 rpm. The water was heated to 50 °C (**Fig.6.a**), then the gelatin was added and was mixed 2 min at the same speed until disappearance of the grains. Finally the gelatin binder was added to the lime binder (or plaster binder) (**Fig.6.b**) and the whole was mixed 2 min at 285 rpm.

180 The mixing of the straw and binder prepared was carried out according to the same protocol181 described above.

With regard to the optimization of the PF70 lime formulation, three percentages of substitutions were chosen: 10%, 20% and 50%. This substitution was also accompanied by an increase in the Straw/Binder fraction from 0.2 to 0.4. In a second step, PF70 lime was completely replaced by thermo lime. This binder was also substituted by gelatin using the same percentages as above (10%, 20% and 50%) and likewise increasing the Straw/Binder from 0.2 to 0.4. For the plasterbased formulation, the binder was substituted by two percentages: 10% and 20% while maintaining the Straw/Binder ratio at 0.4.

The mixtures were poured into wooden moulds measuring $30 \times 30 \times 10$ cm³ without compaction and nor vibration. The lime-based composites were stored in the air-conditioned room at T = 20 °C and 65% RH for 28 days. The plaster-based composites were dried in a

- ventilated oven at 45 °C until mass stabilization to avoid the development of microorganisms
 and were then stored in the same air-conditioned room for 28 days.
- 194 After this curing period, the composites were cut in order to obtain samples with the 195 dimensions of $20 \times 20 \times 10$ cm³ for thermal conductivity and mechanical tests.
- 196 The samples were named according to their compositions, as indicated in Tab.1.

(a)

(c)

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- 206
- Fig. 4: Manufacturing process: (a) and (b) Binder preparation with hemoglobin and casein, (c)
 and (d) Mixing of the components

(b)

(d)





Fig. 5: The aspect of the composites of Lime_PF70+Straw (a) Reference (b) +5%

Hemoglobin (c) +5% Hemoglobine+5% Casein (d) +5% Hemoglobin+2.5% casein.

Fig. 6: Binder preparation for third procedure (a) Gelatin binder (b) Mixing of gelatin binder and mineral binder

Mixture-ID			Ν	lass ratio	
Short Ref	Long Ref	S/B	H/B	C/B	GB/B
PF0	PF70_Reference_S/B=0,2	0.2	-	-	-
PF1	PF70 +5% H_S/B=0,2	0.2	0.05	-	-
PF2	PF70+5% H_S/B=0,3	0.3	0.05	-	-
PF3	PF70+5% H_S/B=0,4	0.4	0.05	-	-
PF4	PF70+5% H+5% C_S/B=0,2	0.2	0.05	0.05	-
PF5	PF70+5% H+2,5% C_S/B=0,3	0.3	0.05	0.025	-
PF6	PF70+5% H+2,5% C_S/B=0,4	0.4	0.05	0.025	-
PF10	PF70+10%GB_S/B=0,4	0.4	-	-	0.1
PF20	PF70+20%GB_S/B=0,4	0.4	-	-	0.2
PF50	PF70+50%GB_S/B=0,4	0.4	-	-	0.5
TH0	Thermo_Reference_S/B=0,2	0.2	-	-	-
TH10	Thermo+10%GB_S/B=0,4	0.4	-	-	0.1
TH20	Thermo+20%GB_S/B=0,4	0.4	-	-	0.2
TH50	Thermo+50%GB_S/B=0,4	0.4	-	-	0.5
G0	Gypsum_Reference_S/B=0,4	0.4	-	-	-
G10	Gypsum+10%GB_S/B=0,4	0.4	-	-	0.1
G20	Gypsum+20%GB_S/B=0,4	0.4	-	-	0.2

- 224 S/B : Straw/Binder H/B : Hemoglobine/Binder C/B : Caseine/Binder
- 225 GB/B : Gelatin Binder/Binder

 Tab. 1. Composite designation and detailed mixture proportions (by mass)

2.3 Laboratory characterization 230

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2.3.1 Thermal conductivity and mechanical test

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Thermal conductivity was measured using a NeoTIM conductivity meter based on the hot wire 233 technique. The measurements were made on samples with the dimensions $20 \text{ cm} \times 10 \text{ cm} \times 10$ 234 cm, along the perpendicular to the preferred fibre direction (Fig.7). The probe was placed in 235 five different positions and the test was repeated three times in each position. The test was 236 carried out in a wet state (immediately after curing the composites in an air-conditioned room 237 238 at 65% RH) and in a dry state (the composites were dried in a ventilated oven at 60 °C until mass stabilization). 239

The mechanical behavior of the composites was evaluated in the preferred fibre direction which 240 is the loading direction of the block in the wall. Uniaxial compression tests were carried out on 241 samples measuring $20 \text{ cm} \times 10 \text{ cm} \times 10 \text{ cm}$, using a compression testing machine (IGM250), 242 243 equipped with a load cell of 250 kN at a displacement rate of 0.5 mm/min.

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249





(a)







(b)

255 2.3.2 Microstructural analysis

In order to establish the effect of the additives on the composition and the microstructure of thebinders, following analyses were carried out:

258 - Thermogravimetric analyses were performed using a LINSEIS STA PT-1000 apparatus under 259 inert atmosphere. Powder samples weighing approximately 60 mg were placed in an alumina 260 crucible and heated from ambient temperature (20°C) to 1000 °C at a heating rate of 5°C/min. 261 - X-ray diffraction (XRD) analyses by a Philips PW-1830 diffractometer, were performed to 262 investigate the mineralogical composition of specimens. The analyses were performed under 263 these conditions: radiation Cu K α 1 (λ = 1.78897 Å), 20 explored range 2–60°, 40 kV voltage, 264 15 mA current intensity.

- Scanning electron microscopy (SEM) has been used to observe the surface morphology and
the microstructure of different specimens.

267 **3 Results and Discussion**

268 **3.1 Thermal conductivity**

Fig.8 reports the results of thermal conductivity in the wet and dry state. As expected the wet thermal conductivity values are higher than dried ones for all composites, with differences between values obtained on the same composite in two states (dry and wet) varying in range 11% to 25% respectively. This is due to the fact that in biosourced composites, as in other porous materials, water vapor that fills the pores supplies an extra conductivity to that of matrix. Similar results have been reported by other workers [37,38].

From the Fig.8.a, it appears clearly that the substitution of 5% of the binder by hemoglobin
(according to the first procedure) leads to a significant decrease of thermal conductivity thanks
to the porosity created in the matrix. It can also be seen that despite the increase in the straw
fraction Straw/Binder from 0.2 to 0.3 and to 0.4, the thermal conductivity remains practically

the same. This can be explained by the fact that the conductivity of the porous matrix in thatcase is equivalent to that of straw.

In the case of the second procedure (Fig.8.b), as expected for the first formulation (PF4) when 281 10% of the lime was replaced by 5% of hemoglobin and 5% of casein, the thermal conductivity 282 increased and exceeded that of the reference formulation. This could be explained by the 283 decrease of both porosity of the matrix and the intergranular porosity. It is however possible to 284 obtain, lower condutivity values, close to those obtained when use the first procedure, by 285 286 reducing the percentage of casein to 2.5% and increasing the Straw/Binder ratio to 0.3 and 0.4. When the third procedure is used, the substitution of mineral binder by gelatin binder and 287 288 increase of mass fraction of fibers (Straw/Binder) from 0.2 to 0.4, led to a significant decrease of thermal conductivity in wet and dry state. When, 50% of mineral binder is substituted, the 289 mean value of dried thermal conductivity has decreased by 21% as compared with the reference 290 291 composites, similarly for both types of lime (PF70 and Thermo-lime) (Fig8.b, c).

In the case of plaster-based composites (Fig.8.d), the thermal conductivity decreased from 0.064
W/m.°C to 0.058 W/m.°C and 0.057 W/m.°C for a substitution percentage of 10% and 20%,
respectively.

In general, the thermal conductivity values obtained for the studied biocomposites are situated in lowest range of thermal conductivities compared to literature results (Tab.2) and fall into the class of thermal insulation materials according to the French standard NFP 75-101.

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- 300



Fig. 8. Thermal conductivity of the composites in dry and wet state (a) PF70 lime with
 hemoglobin and casein (b) PF70 lime and gelatin binder (c) Thermo lime and gelatin binder
 (d) plaster and gelatin binder.

Composites	λ (W/m.°C)	References
Lime (PF70) +Hemoglobin+Straw	0.054-0.057	Present study
Lime (PF70) +Hemoglobin+Casein+Straw	0.065	Present study
Lime (PF70) +Gelatin+Straw	0.059-0.069	Present study
Lime (Thermo)+Gelatin+Straw	0.057-0.065	Present study
Plaster +Gelatin+Straw	0.057-0.058	Present study
Lime+Hemp Shiv	0.09-0.16	Collet et al. [38]
Lime+Hemp Shiv	0.138	Walker et al [16]
Pozzolanic +Sunflower	0.132	Magniont [6]
Chitosan+Sunflower Stalks	0.056	Mati-Baouche et al [24]
Starch + Hemp Shiv	0.049	Umurigirwa-Vasseur [39]
Proteinic Binder +Flax Shives	0.1-0.14	EL Hajj et al [25]
Binder extracted from wheat +Hemp Shiv	0.071-0.076	Collet et al [26]
Corn Stalk+Magnesium Phosphate Cement	0.051-0.643	Ahmad et al [40]
Cement+Wood aggregate	0.24-0.54	Akkaoui [41]
Cement+Straw	0.75-1.32	Bederina et al [42]
Starch based or silica based matrix+Hemp Shive	0,051-0,058	Hussain et al [23]
Lime+maize/sunflower barkchips	0,112-0,127	Lagouin et al [43]
Cement+Sand+Gravel+prickly pear	1,02-1,59	Kamoun et al [44]

Tab. 2 : Comparison of thermal conductivity of the present study with previous studies in theliterature

310

311 3.2 Mechanical behavior and compressive strength

312 The nonlinear compressive stress-strain curves of different mixtures are presented in Fig.9.

313 They were used to calculate the Young modulus as the slope of the elastic zone as well as the

314 compressive strength of various formulations (**Tab.3**).

As expected, the compressive strength of the reference formulations (with the exception of PF4

and the plaster-based composites) is higher than that of the optimized formulations, since a

317 larger amount of binder was used on the reference samples. Composites obtained using first

- 318 procedure, manfiste a massively reduced compressive strength. In fact, the use of hemoglobin,
- as already indicated certainly decreases the thermal conductivity, but it promoted in the same
- time the embrittlement of the binder matrix because of the porous structure created (Fig10.a)
- 321 [45]. The increase in the Straw/Binder ratio further decreased the strength of the composites,
- 322 since the intergranular porosity was increased, and the amount of binder was reduced. The

addition of casein in the second procedure improved the strength compared to the first 323 324 procedure. We also note that in the case of the third procedure, the reference composite strength based on Thermo lime (TH0) was twice as high as that of the same composite based on lime 325 326 PF70 (PF0). This is due to the fact that the setting time of Thermo lime to obtain its full strength is shorter than that of PF70. Moreover, it is observed that the strength of the composites 327 containing gelatin varies proportionally with the replacement percentage. The more this 328 percentage increases, the more the strength increases for both limes PF70 or Thermo. This is 329 mainly due to the adhesive properties of the binder formed (lime + gelatin binder) which creates 330 good adhesion between the aggregates when the percentage of gelatin binder is high (Fig 10.b). 331 332 The tendency is not the same for plaster binder with a higher strength for 10 % than 20 % of replacement. The microscope images (Fig10.c and Fig 10.d) show that mixing gelatin binder 333 with the plaster leads to a matrix with a cellular structure that seems to be responsible for this 334 335 difference. As a result, the binder becomes more vulnerable.

The Young modulus variation followed the same tendency as compressive strength with measured values in range from 1.22 MPa to 11.82 MPa. Most of these values are greater than 3MPa, consigned value according to French professional regulations for hemp concrete (roof application) [46].

The low compressive strength values of the studied bio-composites do not qualify them for use as structural materials. However, the materials respect the condition of supporting the stresses due to their self-weight according to standard NF EN 1992-1-1. The ability of each composite to support its self-weight for a wall of 3 m in height $\sigma_{sw(h=3m)}$ is checked (the mean height between slabs in the building). **Tab.3** indicates that this condition was well verified for all studied composites with the exception of PF3. Moreover, the deformations ε_{sw} (h=3m) induced by the self-weight range between 1.4.10⁻³ and 9.7.10⁻³, which is admissible. Even with worstcase loading, the deformation remains lower than the breaking strain.



Fig. 9. Typical mechanical behavior of composites (a) PF70 lime with hemoglobin and casein
(b) PF70 lime and gelatin binder (c) Thermo lime and gelatin binder (d) plaster and gelatin
binder.

Composites	σ _{rupture} (Mpa)	E(Mpa)	$\sigma_{sw(h=3m)}$	$\varepsilon_{sw(h=3m)}$
PF0	0.064	8.02	0.018	0.0023
PF1	0.021	2.52	0.012	0.0047
PF2	0.013	1.22	0.012	0.0097
PF3	0.009	1.41	0.011	0.0078
PF4	0.184	9.44	0.022	0.0024
PF5	0.058	6.70	0.013	0.0019
PF6	0.033	2.82	0.012	0.0041
PF10	0.036	7.54	0.012	0.0016
PF20	0.045	7.39	0.011	0.0015
PF50	0.058	7.29	0.011	0.0016
TH0	0.118	11.82	0.020	0.0017
TH10	0.033	1.70	0.012	0.0069
TH20	0.037	5.25	0.012	0.0022
TH50	0.057	5.80	0.011	0.0019
G0	0.031	6.88	0.010	0.0014
G10	0.089	5.38	0.011	0.0021
G20	0.06	4.05	0.010	0.0025

Tab. 3. Mechanical properties of the composites



Fig. 10. Microscope visualization of (a) PF1 (b) PF20 (c) matrix of G10 composite and (d)

361 matrix of G20 composite.

363 3.3 Optimal formulations

In order to select optimal formulations in terms of thermal and mechanical performance, the various composites were classified according to their thermal conductivity and their mechanical compressive strength. The best composites are those with both good thermal conductivity and good mechanical strength. The results obtained are illustrated in Tab.4. The best compromises are obtained in the case of the G10, PF50, TH50, and PF5

Formulation	λ (W/m.°C)	σ max (Mpa)
PF0	+	+++
PF1	++++	+
PF2	++++	+
PF3	++++	+
PF4	+	+++++
PF5	+++	+++
PF6	++++	+
PF10	++	+
PF20	++++	++
PF50	++++	+++
TH0	+	+++++
TH10	++++	+
TH20	++++	+
TH50	++++	+++
G0	++++	+
G10	++++	++++
G20	++++	+++

369

370 +++++ : High performance + : Low performance

371 **Tab. 4.** Classification of composites according to thermal conductivity and mechanical

372 resistance

373 **3.4 Thermogravimetric analysis**

- In order to evaluate the effect of the additives on microstructural mechanisms such as the carbonation of lime and the hydration of plaster, one formulation was chosen for each procedure.
- 377 Fig.11. a and b show the mass loss and DTG curves obtained for lime binders. Four phases
- were observed [47]:

- T_{ambient}-200°C: evaporation of free water
- 200 °C-380 °C: decomposition of additives (hemoglobin, casein and gelatin).
- 400 °C-500 °C: dehydroxylation of portlandite according to the following chemical
 reaction: Ca(OH)₂ (s) → CaO(s) + H₂O(g)
- 500 °C-850 °C: decarbonation of calcite according to the following chemical reaction:
 CaCO₃(s) → CaO(s) + CO₂(g)
- The amounts of $Ca(OH)_2$ and $CaCO_3$ were calculated from the mass loss (ML) curves using relations (1) and (2). The carbonation rate was deduced according to equations (3) [47].
- 387 $(Ca(OH)_2)\% = (ML_{200-380^{\circ}C}) \times k_1$ (1)
- $388 \quad (CaCO_3)\% = (ML_{500-850^{\circ}C}) \times k_2 \tag{2}$
- 389 With: $k_1=Mw(Ca(OH)_2)/Mw(H_2O)$ and $k_2=Mw(CaCO_3)/Mw(CO_2)$; Mw : Molar mass
- $390 \quad \text{ROC} = \text{CH}_{\text{carb}}/\text{CH}_{\text{carb}} + \text{CH}_{\text{binder}}; \text{ Rate of Carbonation}$ (3)

391 $CH_{carb} = CC_{binder} \times k3$: portlandite consumed in carbonation reaction; $CC_{binder} = ((ML_{500-580^{\circ}C}))$

- 392 ×k₂))-(CC_{RL}×(%lime)) : calcite content of the binder; CC_{RL} : calcite content of the raw lime; 393 $k_3 = Mw(Ca(OH)_2)/Mw(CaCO_3)$; CH_{free} = (ML₂₀₀₋₃₈₀)×k₁ : free portlandite content of the
- 394 binder; $CH_{binder} = CH_{carb} + CH_{free}$: total portlandite content of the binder.

The results obtained are shown in **Tab.5**. For the PF70 lime, the carbonation rate reached 76.56% in the case of reference sample (PF0). It increased to 90.74% and 88.18% respectively for PF1 and PF5. It seems that the porosity created by the hemoglobin promotes the diffusion of CO_2 into the material in the cured state and therefore a higher degree of carbonation is accessed. The addition of the gelatin binder reduced the carbonation rate to 55.94% (PF20), similarly for Thermo lime (TH20). This can be explained by the fact that the gelatin polymerizes and forms a thin film which slows down or prevents the diffusion of CO_2 into the material.

- 402 **Fig.11.c** shows the results obtained for gypsum binders. Two steps of mass loss were detected
- 403 in the case of the reference sample: the first, between 80 °C and 200 °C due to dehydration of

the plaster according to the chemical reactions (4) and (5) according to literature [48]. The 404 second between 500 ° C and 700 ° C attributed to the decarbonation of calcite according to the 405 chemical reaction (6). For the G10 sample, a third step appears between 200 $^\circ$ and 380 $^\circ$ C 406 corresponding to the decomposition of gelatin. The mass loss due to dehydration of the plaster 407 in the G10 sample was estimated at 7 %. It is larger than that of the reference sample, indicating 408 a greater degree of hydration .Wu et al [49] studied the effect of a polyacrylic ester emulsion 409 on gypsum plaster. They noticed from thermogravimetric analyses that the presence of this 410 additive decreased the mass loss due to dehydration of the plaster and therefore a low degree of 411 hydration 412

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 $Ca_2SO_4 \cdot 2 H_2O(s) \rightarrow Ca_2SO_4 \cdot 0.5 H_2O(s) + H_2O(g)$ (4)

414 $Ca2SO4 \cdot 0.5 H2O(s) \rightarrow Ca2SO4 (s) + 0.5 H2O(g)$

	$CaCO3 \rightarrow CaO+CO2(g)$		(6)		
Samples	Ca(OH)2 (%)	CaCO3 (%)	Carbonatation ra	te (%)	
PF70 lime (raw)	40.29	20.3		416	
PF0 (Reference)	10.29	65.96	76.56	447	
PF2 (PF70+5%H)	4.11	75.06	90.74	417	
PF5 (PF70+5%H+2.5%C)	4.52	66.18	88.18	110	
PF20 (PF70+20 GB)	14.81	41.85	55.94	418	
Thermo lime (raw)	40.21	8.84		419	
TH0 (reference)	9.36	64.41	81.04	415	
TH20 (Thermo+20%GB)	19.67	32.68	47.33	420	

421 **Tab 5.** Results from TGA to characterize the effects of additives on carbonation

(5)



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Fig. 11. TG-DTG curves (a) PF70 lime-based binders (b) Thermo lime-based binders (c) plaster-based binders

425 **3.5 Morphology and Mineralogy analysis**

The effect of the studied additives on the microscopic structure of the binders is shown in Fig.12. We can see that the various lime-based binders contain needle-like calcite crystals with the exception of the PF5 sample, when casein was introduced. In this case, the crystals became smaller and have a rounded shape (Fig.12.c) itwhich leads to a good mechanical performance. Similar results were found by Ventolà et al.[50] and Liu et al.[51], with the change in the morphology of the calcite crystals by casein additive. In the case of gypsum binders (Fig.12.g and Fig.12.h) the calcium sulfate dihydrate crystals
(CaSO₄H₂O) formed in G0 and G10 are not similar. In the case of the reference sample, large
rod-like crystals were observed, while in the case when gelatin was added, the crystals present
an irregular shape and a small size which improves the mechanical strength.

The DRX results obtained for the different binders illustrated in Fig.13, show that the three 436 additives (hemoglobin, casein, gelatin) do not modify the mineralogical composition of the 437 materials (no new chemical elements) : the same phases were observed in binders without and 438 439 with additives. Portlandite (Ca(OH)₂) and calcite (CaCO3) are the main minerals detected in the case of lime binders. Fig.13.a shows that the peak intensity corresponding to portlandite (at 440 18°) is greater in the case of PF20 while the minimum value is observed in the case of PF1. The 441 same trend was observed for thermo lime Fig.13. b. This confirms the results of carbonation 442 obtained from the TG analyses. 443

444 As regards the gypsum binders, the mineral phases were dihydrate (CaSO₄.2H₂O), hemihydrate 445 (CaSO₄0.5H₂O) and anhydrite (CaSO4). It is clear in Fig.13.c that the peak intensity 446 corresponding to CaSO₄ 0.5H₂O (at 14.7°) is greater in the case of G10, confirming that the 447 degree of hydration is greater by adding gelatin.

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Fig. 12. Scanning electron microscope images of the binder specimens (a) PF0; (b) PF1; (c)
PF5; (d) PF20; (e) TH0; (f) TH20; (g) G0; (h) G10.



462 Fig. 13. X-ray diffraction patterns (a) PF70 lime-based binders (b) Thermo lime-based
463 binders (c) plaster-based binders

464 **4** Conclusions

The objective of the present study was to reduce the thermal conductivity of a bio-based composite based on cereal straw while keeping sufficient mechanical properties for it to support its self-weight. The optimization approach was based on three different procedures using three additives obtained from a renewable and biodegradable source. The following conclusions can be drawn from this investigation : The addition of 5% of hemoglobin to the lime reduced the thermal conductivity but induced
a drastic decrease in the mechanical strength. The combination of 5% of hemoglobin and
5% of casein resulted in a denser composite with a mechanical strength three times greater
than that of the reference sample but with a very high conductivity. A compromise was
achieved between thermal conductivity and mechanical strength using 5% of hemoglobin
and 2.5% of casein.

The mixture of gelatin binder with lime and plaster increased the volume fraction of the
vegetable fibers in the composites thanks to its adhesive properties. Consequently, the
thermal conductivity was decreased for the different composites studied. It diminished with
increasing gelatin binder content.

The carbonation rate of lime was improved when hemoglobin was used thanks to the porosity created which promotes the diffusion of carbon dioxide into the material.
 Moreover, although the gelatin reduced the carbonation rate of two types of lime, the mechanical strengths obtained for the composites were acceptable thanks to its adhesive properties. The hydration degree of the plaster was slightly improved in the presence of the gelatin binder as was shown by the TG and XRD analyses.

SEM images showed that the addition of casein led to the formation of calcite crystals in
 rounded shapes, which improves the mechanical strength of the composites. Similarly,
 gelatin causes a change in the plaster microstructure which also leads to an improvement in
 the mechanical properties of the composites.

490 The bio-based composites developed in this study have an interesting thermal conductivity with491 sufficient mechanical properties for thermal insulation use and building energy performances.

492 **5** Acknowledgements

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