CHARACTERISATION OF VEGETAL COMPOUNDS RESPONSIBLE FOR THE SETTING DELAYS IN HYDRAULIC BINDERS

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Abstract

Biobased materials, integrating vegetal compounds in their composition, are used for various civil engineering applications. However, mechanisms underlying the association between plants and mineral binders are not well known. Issues have been raised concerning the durability or strength performance, attributed as a consequence of the manufacturing process. Especially, during the setting phase of hydraulic binders. Indeed, some studies showed the implication of vegetal molecules acting as hydration retarders.These molecules come from the leaching of plants by water during mixing, which are also known as extractives. The main molecules identified to have a role are sugars and a few organic acids. However, several studies suggest that other molecules derived from plant material, such as polyphenols, have an influence on the setting of the hydraulic binder as well. Moreover, the chemical composition of plants is subject to great variability, as well as many other characteristics, depending on variety, growth conditions and seasons…

Here, we compare two types of raw material used in the fabrication of biobased materials. These materials have significative differences in strength performance correlated with a difference of hydration time found with calorimetric assays. The difference between the raw materials is also found in the chemical investigation, indeed the HPLC analysis on sugars showed a significative difference on certain molecules, especially on glucose, which is a well-known sugar acting as hydration retarders. Moreover, a focus on other compounds type was achieved, especially on polyphenols. By observation and UV-Vis analysis on crudes water extracts, quantitative and qualitative differences were found between raw materials. Roughly, polyphenols, particularly flavonoid-type molecules seem to be present in extracts, a consistent element correlated with calorimetric assays and literature. This is a relevant clue suggesting that a deeper analysis of these molecules could therefore shed some light on this topic.

Keywords:

Biobased material, chemical characterization, hydraulic binder, plants, biochemistry, calorimeter

1 INTRODUCTION

Biobased materials are increasingly used for building, especially for insulation by mixing vegetal aggregates with a mineral binder, like hemp concrete already used in environmentally friendly building projects. Vegetal aggregate's (called shiv for the hemp) insulation performances come, on one hand, from their porosity, derived from the role of the plant stem, which is the part of the plant utilised. The stem is mainly composed of vascular tissues in order to ensure the sap flow between roots and leaves. On the other hand, their insulation performances come from their hydrophilic behaviour that is due to the molecular composition of the cell wall. Indeed, cellulose, hemicellulose and pectin, which are the main component of the plant stem [Magniont 2017], are hydrophilic macromolecules.

However, this kind of material has hard time making their way. Indeed, some studies on hemp concrete showed a lack of hydration of the mineral binder giving rise to a decrease of its mechanical performance [Delannoy 2018; Diquélou 2015]. This lack of hydration is attributed to the absorption of water by the shiv [Arnaud 2012; Nguyen 2010], and the presence of some molecules from the plant, called extractives, that have an influence on the hydration time. [Bilba 2003; Sedan 2008; Wei 2002].

Influence of extractives on the hydration delay is mainly due to two different mechanisms. The first one is an adsorption of organic molecules on anhydrous grains. Leading to a thin layer formation surrounding anhydrous grains resulting in a lack or a total inhibition of the hydration of these grains [Na 2014]. Or, with same consequences, a water-impermeable hydrate layer in presence of sugars has been reported [Bishop 2006; Doudart de la Grée 2017]. The second well-known mechanism is the capacity of some organic compounds to chelate Ca^{2+} ions [Milestone 1979]. This results in the formation of molecules – Ca^{2+} complex which block the nucleation sites and prevent the hydrates growth [Kochova 2017; Thomas 1983]. Among extractives from

plants, some molecules are already known as hydration retardants.

Sugars are well known for delaying the setting delay. Indeed, some studies showed hydration delays when they are mixed with a mineral binder or cement [Thomas 1983]. Thomas and Birchall have identified glucose, maltose, cellobiose, raffinose and sucrose as good hydration retarders. Setting delay effect have been also studied for sugars which are transformed into their acids forms (saccharinic acids) [Fisher 1974]. Sugars affect hydration by the first mechanisms mentioned above while their acids forms act by both mechanisms.

As saccharinic acids, some organics acids have been reported to have an impact on hydration time such as malic acid [Rai 2004], citric acid [Möschner 2009], tartaric acid [Wilding 1984] and glycolic acid [Ramachandran 1992].

Other organic molecules act only by means of the second mechanisms, Ca^{2+} ions chelation. This is the case for plant specific compounds from the polyphenols family. Indeed, few molecules have been reported to have an effect on hydration time such as quercetin [Miller 2007], teracacidin, sequirin-C [Tachi 1989] and tannins [Semple 2002], which all belong to the flavonoids family.

Sugars, organic acids and polyphenols are naturally present in plant. Accurately they are free in cells or in vascular tissues. A relative important part of sugars among extractives can be derived from the degradation of the cell wall as well. Indeed, the cell wall is mainly made of sugars units.

Plants chemical composition is subject to an important variability between species and individuals. Consequently, intensity of mechanisms cited above depends on the variability of this chemical composition. This is why hydration time can be different from a species or a plant to another, from a batch of shiv to another.

To overcome these problems, solutions on the vegetal has been studied; like lixiviation of the vegetal material with water, thermic treatment or plants aggregates coating [Bilba 1996; Nozahic 2012]. Although these solutions reduce the time of hydration, they are not reliable considering their cost. Moreover, the effectiveness of these solutions depends on the chemical composition variability. Thereby solutions must be adapted for each batch of vegetal aggregates.

In this study, extractives composition of two hemp shiv were compared, they are materials for hemp concretes used in mechanical study frame of G. Delannoy thesis [Delannoy 2018]. Comparing extractives from shiv used in hemp concrete, presenting different mechanical behaviours, may highlight molecules responsible for the setting delay effect. We firstly focus on sugars then on other families of compounds, especially polyphenols.

2 MATERIALS AND METHODS

2.1 Material

1. Type of shiv

Two types of shiv previously studied were selected for this study [Delannoy 2018; Marceau 2017]. Hemp shiv, HS1 showed mechanical strength lower than HS2. HS1 and HS2 are reduced to powder, in order to increase and homogenize the amount of extractive during the extraction, using a bladed crusher, sieved to 500µm particle size, dried at 105°C for 48 hours. Shiv reduced to powder are called HP1 and HP2 corresponding to HS1 and HS2 respectively. Shiv main components characterisation (Table 1) was carried out by the Van Soest method and French standard NF-18-122.

Table 13. Chemical composition of hemp shiv determined by Van Soest method

Proportion (%)	Hemp shiv 1 (HS1)	Hemp shiv 2 (HS2)
Cellulose	53.0 ±0.9	54.9 ± 0.5
Hemicellulose	12.1 ± 0.9	12.0 ± 0.4
Lignin	15.0 ± 0.2	15.5 ± 0.3
Others	19.9 ± 2.0	17.6 ± 1.2

2. Standard sugars

Standard sample of glucose (N° CAS 50-99-7), sucrose (N° CAS 57-50-1), xylose (N° CAS 58-86-6), mannose (N° CAS 3458-28-4), arabinose (N° CAS 5328-37-0), galactose (N° CAS 59-23-4) are supplied by Sigma Aldrich.

3. Cement

A Portland cement CEMI, whose chemical composition given by the manufacturer is shown in Table 14, is used.

Table 14. Mineral phases of cement

Mineral phases	C_3S	C_2S	C_3A	C_4AF	gypsum
(%)	60	13	2	13	4

2.2 Methods

1. Calorimetry

Binder hydration was measured on a TA instrument, TAM AIR 8, Fontainebleau sand as reference sample. Measurement is carried out at 25°C. The heat flux released over time in relation to a sample of sand used as a reference. The quantity of sand is adapted to the size of the sample being analysed, so that the specific heat capacities are the same in both test tubes.

The measurements are made on pure cement paste and on cement paste containing shiv powder. The composition of the different types of samples and the masses analysed are set out in Table 3. A different water to cement ratio is selected for the cement paste mixed with hemp powder. In order to offset the absorption of water by the shiv.

Table 3. Formulations of cement pastes and hemp concrete

Sample	Pure cement paste	Cement paste + hemp powder
Water to cement mass ration	0.5	1
Cement to vegetal mass ratio	0	50

2. Extraction

One gram of shiv is added to 100mL of ultrapure water (N° CAS 7732-18-5) and agitated for one hour at ambient temperature. Then the mixture is filtered using an 8-12µm pores cellulose filter (185 mm diameter, supplied by Verfilco) to remove the solid part of shiv. Volumes of filtrate are measured. Filtrate are filtered again through 0.20µm membranes (Acrodisc, CR GHP 0.20µm) in order to prevent bacteria or fungi growth and conserved in fridge at 4°C.

3. HPLC analysis

Standard sugars and shiv extract are analysed using a Waters HPLC system (Waters 600 controller, a Waters 2707 Autosampler, Waters 2414 Refractive Index Detector, Waters In-Line Degasser AF). Column temperature is ensured by a Varian ProStar column oven model 510. Separation is performed with the use of a ligand exchange column Hi-Plex Pb, (300 x 7.7 mm, 8 µm) (p/n PL1170-6820) and a Hi-Plex Pb (50 x 7.7mm, 8µm) Guard column supplied by Agilent.
Samples are eluted at 80°C with ultrapure water (impurities ≤ 1 EU/mL, N° CAS 7732-18-5) supplied by Sigma Aldrich, with a 0.5 mL/min flow rate. Injection volume is set at 20µL. Detection with refractive index detector is performed at 55°C. Before analysis, standard sugars and shiv extracts were filtered through 0.20µm membranes (Acrodisc, CR GHP 0.20µm) and the mobile phases solvents were degassed. Shiv extract analysis is performed in 4 replicates stemmed from the same extraction. Chromatogram are recorded and integrated on Empower 3 software provided by Waters. Retention time (RT) of standard sugars are reported in Table 2.

Table 2. Retention time of standard sugar, determined by HPLC.

Standard sugar	Retention time (min)
Sucrose	17.4
Glucose	20.2
Xylose	21.6
Arabinose	23.8
Mannose	27.8

4. UV analysis

UV spectra are recorded on a Jasco V-630 spectrophotometer and analysed through Spectra Manager software provided by Jasco. One millilitre of filtered shiv extracts are half diluted in pure water before analysis. Samples were analysed in 10mm quartz cell supplied by Hellma Analytics. Absorbance measurement is recorded between 190 and 600nm using a bandwidth of 2nm and a 400nm/min recording speed. Ultrapure water is used as reference sample.

3 RESULTS AND DISCUSSION

1. Effect of type of shiv on hydration delay

To study the influence of the nature of the shiv used on the hydration of CEMI cement, isothermal calorimetry measurements were taken on cement pastes with a C/HP of 50 with the two types of shiv. This quantity of hemp powder does not correspond to that of hemp concretes and the particle size is smaller, but these conditions facilitate the homogenisation of the cement pastes necessary for calorimetry measurements and the comparison of the different types of shiv.

The results obtained are presented in Figure 1. The curves illustrating the heat flow over time recorded, for all samples, show the peak corresponding to the hydration of C3S, where the maximum is situated at 22 hours and 16.5 hours, for cement pastes containing HP1 and HP2 respectively, whereas it is at 9 hours for cement on its own.

Isothermal calorimetry confirms that HS1 causes a greater modification in the binder hydration than do HS2. This is in agreement with the previous studies conducted with the two types of shiv [Delannoy 2018; Marceau 2017], in which the mechanical strengths of the hemp concretes were found to be very different depending on the type of shiv used.

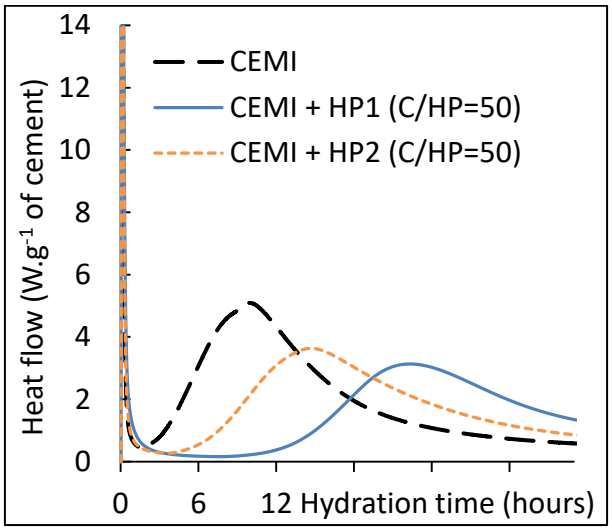

Figure 1. Heat flow for pastes of CEMI, CEMI with HP1 and HP2 (C/HP=50)

2. Sugars composition

To highlight the sugars composition, an HPLC analysis was performed on shiv water extracts. Chromatograms obtained from water extracts solutions of HP1 and HP2 are represented in Figure 2 and 3. Same peaks are present in both chromatograms with different intensities of refractive index (RI). Peaks of HP2 extract have lower intensities except for the peak with the retention time (RT) of 25.2min (Figure 2). This suggest that sugars composition of both extracts are the same but present different quantities for some compounds. Standard sugars analysis allowed to identify sucrose (RT: 17.2min) and glucose (RT: 20.2min).

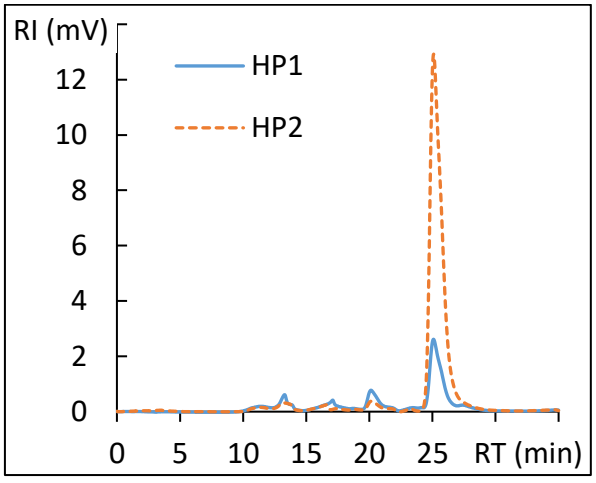

Figure 2: Chromatograms of HP1 and HP2 water extract

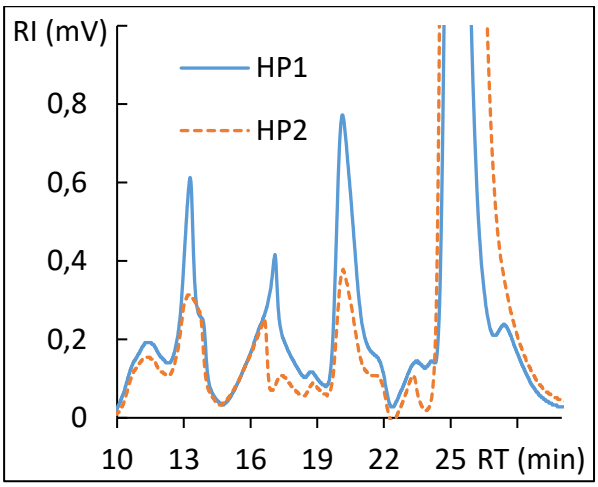

Figure 3: Chromatograms of HP1 and HP2 water extract zoomed on minor peaks

The percentage of the area of each integrated peak is summed up in Table 4. Only the major peak (RT: 25.2min) is more abundant in the HP2 extract solution. Since calorimetry result showed a greater setting delay for HP1 than HP2, we can confirm that the latter is not implicated in hydration time delay. While the others compounds, which have upper intensity in HP1 (Figure 3), may have leading implication on hydration delay. That is consistent with the identification of sucrose and glucose, both known to have effect on binder setting delay [Thomas 1983].

Table 4. Summary of peaks with retention time, percentage of peak area and intensity of HS1 and HS2 shiv extract.

Retention time (min)	Peaks area (%)	
	HP1	HP2
11.1	4.3 (± 1.1)	1.2 (± 0.5)
13.2	6.2 (± 1.6)	2.2 (± 0.7)
16.6	NF	1.8 (± 0.7)
17.2	7.9 (± 1.1)	0.8 (± 0.2)
18.7	1.1 (± 0.3)	0.5 (± 0.2)
20.1	14.2 (± 2.5)	2.6 (± 0.9)
21.2	1.0	0.1
23.3	0.9	0.3 (± 0.2)
25.2	65.0 (±4.4)	91.2 (± 3.4)
27.5	0.9	NF

5. Polyphenols investigation

A yellow coloration is observed on HP1 and HP2 water extracts. Intensity of coloration is higher for HP1 than HP2 (Figure 4). In plants, yellow coloration is often associated with the presence of flavonoids, which are polyphenols compounds including the tannins family as well. As mentioned in introduction, flavonoids are implicated in setting delays effects [Miller 2007; Semple 2002; Tachi 1989]. Thus, according to the calorimetry results, we can correlate the stronger yellow coloration with the higher hydration time delays in HP1.

Figure 4: Crude extracts from HS1 and HS2, corresponding to HP1 and HP2 respectively

The UV-Vis spectra of water extract (Figure 5) highlight the difference in intensity coloration in the corresponding absorbance zone (between 430 and 480nm) (Figure 5). Where HP1 is 1.34 times higher than HP2 at 440nm for instance. Alongside that an important UV absorption (between 200 and 400nm) is reported for both extract. Although we first notice a higher absorbance in HP1 extract than in HP2, qualitative difference are found between both extracts. A maximum absorbance at 279 and 274nm for HP1 and HP2 respectively and a shoulder at 310nm in both spectra is reported (Figure 5).

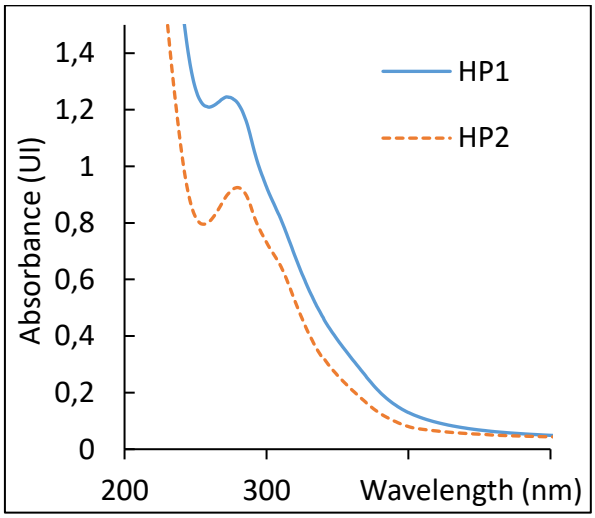

Figure 5: UV-Vis spectra of HP1 and HP2 water extracts solutions

These values can be attributed to a flavonoid structure [Stefova 2003]. UV spectra of flavonoids are influenced by substitutions on their cycle A and B, represented in Figure 6a. All flavonoids spectra are characterised by two absorbance bands, except for isoflavones, flavanones and dihydroflavanones where the two absorbance bands are superposed, as in Figure 5 [Kumar 2013]. Indeed, isoflavones (Figure 6b) are characterised by a band of absorbance between 245 and 275nm followed by a shoulder between 310 and 330nm. And flavonones and dihydroflavonols (Figure 6c) are characterised by a band of absorbance between 275 and 295nm also followed by a shoulder between 300 and 330nm [Markham 1975]. Therefore, our values can be attributed to one of the three latter structure.

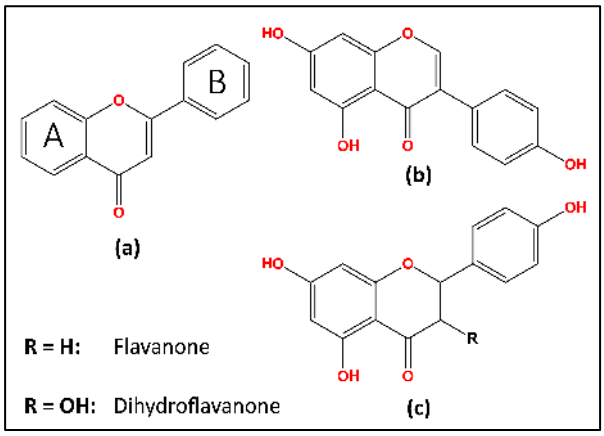

Figure 6: Structure of flanonoids with A and B cycle (a), isoflavone (b), flavonone and dihydroflavonones (c)

4 CONCLUSION

Two shiv which induce different mechanical strength when they are used in hemp concrete were compared. A significative difference on their hydration time was found by calorimetry assays, where HP1 induced a longer hydration time than HP2.

Then these two shivs were compared in terms of chemical composition. Qualitatively, water extract from HP1 and HP2 were almost the same in terms of sugars content. While several differences were found on quantitative results, especially for sucrose and glucose, well-known to be implicated in setting delay. HP1 was found to have greater quantities of sucrose and glucose. These two sugars were not major compounds in extract, but a slight difference of their intensity was enough to induce a significative hydration time delay.

However, this affirmation must be correlated with the results of the polyphenols investigation. Difference between both extracts has been observed by eye. This observation coupled with the UV-Vis analysis allowed to confirm the presence of different type of flavonoids compounds in both extracts in various quantities. A greater quantity of supposed flavonoids was found in HP1 than in HP2. Which was consistent with calorimetry results, as flavonoids are known to increase the hydration time.

Although these results are consistent with the literature, identifications of flavonoids are infirmed by means of a UV-Vis analysis performed on crudes extracts. Meaning that these identifications are not hundred percent reliable and need a deeper investigation to accurately highlight which flavonoids are present in extract solutions. In addition, all the results rely on solely one extraction and the experimentations was performed on only four replicate. To consolidate these results others iteration of experiences mentioned in this paper must be done. Despite this, these results are relevant clues on the mechanism of hydration in presence of extractives.

Moreover, we did not evaluate the effect of sugars and polyphenols separately on hydration time to identify compounds most implicated in setting delay.

This study is included in a larger study concerning the interaction between vegetal material and mineral binders, in the frame of bio-based materials. As mentioned above, the goal is to highlight molecules implicated in the binder setting delay. And this study suggests that the accurate identification of sugars and polyphenols in shiv water extracts are necessary to go further in this study.

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