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Properties of cellulosic fibre reinforced plaster: influence of hemp or flax fibres on the properties of set gypsum

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Abstract In the last few years, eco friendly materials have become an important part of the building materials market. Natural fibres are already used in various types of materials, like plastics, concrete and lime-based products. They demonstrate different attributes like the combination of good mechanical, thermal and acoustic properties that allow these types of materials to be used for different applications. The main drawback associated with plaster is its brittleness, especially under tensile stress. Therefore, it is interesting to investigate different methods that could potentially enhance the mechanical properties of plaster. Adding fibres to gypsum to obtain a composite material is one way to improve the behaviour of the product, especially after the failure of the matrix. The aim of this work was to the study the effects of adding natural fibres, namely hemp and flax fibres, on the setting time of plaster and the mechanical properties of the composite matrix. It was shown that hemp delayed the setting of plaster, unlike flax. The initial and final setting times almost doubled when hemp was added in a plaster matrix, whereas flax fibres did not drastically change them. Different chemical treatments of hemp were tested and the impact on the setting time was measured. The setting times of both composites made with hemp and flax were reduced once the fibres were treated (25–40% reduction), compared to the setting time of the calcium sulphate hemihydrate alone. The mechanical properties of the composite materials are also discussed. The behaviour of plaster was modified from brittle to a non-linear one when fibres were added, and even at small levels of addition, flax fibres allowed slightly higher values of flexural strength to be reached.

Introduction

Plaster is a very cheap building material, which has been used since ancient times. It has a lot of applications such as plasterboard for interior building system, fireproofing and decoration. The fast setting and the lightweight characteristics are the two main advantages of this material, compared to cement products. The main drawbacks associated with plaster are its brittleness and weakness in tension. Therefore, it is potentially interesting to reinforce plaster with fibres to enhance the mechanical properties.

In the last few years, eco friendly materials have become an important part of the building materials market. Natural fibres are already used in various types of materials, like plastics, concrete and lime-based products. They demonstrate different attributes like the combination of good mechanical, thermal and acoustic properties allowing its use for different applications [1].

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Natural vegetal fibres are made of crystalline cellulosic chains embedded in a matrix of semi crystalline products like hemicellulose, pectin and lignin [2]. These substances are mainly composed of sugars (e.g., glucose, rhamnose, galacturonic acid). Natural fibres are characterised by variations in their properties mainly due to the fact that they are a natural product. Therefore, the composition of the fibres can slightly change depending on the location, the growing conditions and the age of the plant. Their high tensile strength is a major advantage in increasing the fracture toughness and improving the behaviour of gypsum-based products, especially in reducing the catastrophic failure of gypsum.

In the early 1970s, attempts to add fibres to plaster were done but mainly with synthetic fibres like glass [3, 4]. In the past, several studies tried to evaluate the relevance of adding natural fibres in gypsum matrices mostly in terms of mechanical characteristics of the composite material [5–9]. However, these studies did not really focus on what the chemical interactions at the interfaces with the gypsum matrix were. Various attempts were reported in the literature such as adding natural fibres to plaster together with additives like cement, wood or sand. Generally, the percentages of addition were quite low (less than 10 wt%) compared to cement-based materials, which could reach up to 40 wt%. The addition level was also strongly related to the process [10, 11]. A pressing process allowed the addition of a greater amount of fibres compared to a casting process. In fact, casting needed sufficient fluidity to obtain a homogeneous material; the ability of the slurry to be cast was strongly reduced as the amount of fibre increased.

This article examines the effect of the addition of either hemp or flax fibres, also chemically treated, to plaster on the setting time and on the mechanical properties of the composites.

Methods and materials

Methods

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) observations were done on a Cambridge Stereoscan S260 equiped with energy dispersive spectroscopy (EDS) microanalysis. Characterisation was done on untreated and treated fibres. After drying at 40 °C for 24 h, fibres were glued on carbon adhesive films and coated with platinum using a vacuum sputtering coater. The fracture surfaces of broken prisms were also observed. A platinum coating was used to prevent sample charging under the electron beam at high magnification.

Gas chromatography

Gas chromatography analysis was conducted with a Perichrom gas chromatograph (Saulx le Chartreux, France) fitted with a flame-ionisation detector. A capillary column (CPSIL-5CB, Chrompack, 0.32 mm; 50 m, Palo Alto, United States) was used. The temperature of the column was gradually increased from 130 to 260 °C. Nitrogen was the carrier gas.

Setting time monitoring techniques: Vicat test and temperature rise set (TRS)

Two methods were used to monitor the setting of the paste. The hardening of the paste is a good indicator of the degree of conversion of the hydration reaction. Vicat test, consisting of following the evolution of the slurry's consistency, defines an initial and a final setting time. The initial setting time is determined by the 3-cm penetration of a standardised needle. The end of the setting corresponds to a 0.5-mm penetration of a needle equipped with a ring. However, for composite materials containing fibres, the initial setting time was subject to variations due to the fact that bundles of fibres can block the needle penetration. The final setting time was a more reliable parameter for such materials. Moreover, the percentages of fibres was low enough (lower than 10 wt%) to obtain consistent information with this technique.

To confirm the Vicat test results, temperature measurements of the paste during the setting reaction were carried out. The exothermicity of the transformation of hemihydrate into dihydrate enabled the characterisation of the behaviour of the paste during the setting by temperature measurements. The mixture was poured into a standardised polystyrene cup (75 mm diameter at the top, 58 mm at the base and a height of 45 mm) and closed in an adiabatic container. A temperature probe was introduced in the paste to follow the temperature change during setting.

Three point bending test

Tests were conducted on a Zwick Z010 testing machine. Tests were done on $20 \times 20 \times 100$ mm^3 prisms.

Samples were put in a 40 °C oven for 24 h and then stored in a climatic chamber at 20 °C and 50% relative humidity for 48 h. For each composition, 10 prisms were tested.

A span of 80 mm and a deflection rate of 25 mm min^{-1} (according to ASTM C473 standard) were used. Modulus of rupture, MOR, noted σ_r (MPa) was deduced from the load/displacement curves.

The value used in the formula for the stress calculus is the maximum applied load which can be either F^*, beyond

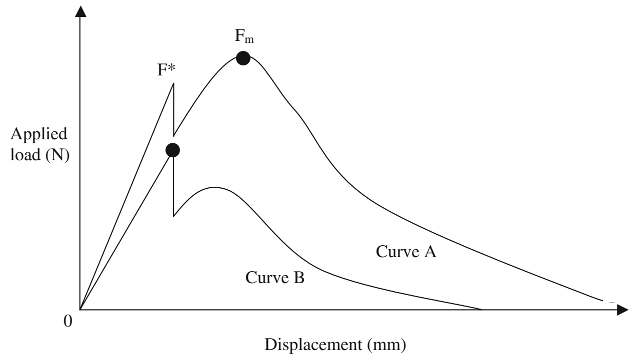

Fig. 1 Definition of F^* (load corresponding to the breakage of the matrix) and F_m (the maximum load of the post crack part of the curve). The *dot* shows the load taken into account to obtain the MOR in two cases: $F^* > F_m$ and $F^* < F_m$

which a fall of load occurs due to the first macroscopic damage, or F_m, which corresponds to the gain of load due to the load transfer from the matrix to the fibres (Fig. 1). Equation 1 was used to determine the MOR as the material is assumed to be homogeneous:

$$\sigma_r = \frac{3 \times \mathrm{Max}(F^*, F_m) \times L}{2wh^2}, \qquad (1)$$

where L is the length of the beam between the supports and w, h the width and height, respectively.

Elastic properties

An ultrasonic method was used to determine the E modulus. It is a non-destructive method based on the propagation of ultrasonic waves in the material (Fig. 2). Ultrasonic pulses are sent through the sample through a transducer (Panametric Sofranel) and collected via another transducer. Transmission pulse echo technique was chosen in order to avoid problems due to the absorbent properties of the composite. The central frequency of the transducers was 500 kHz. The ultrasonic waves first propagate into an alumina buffer layer acting as a delay line. The time of flight τ was measured and was related to V and e, respectively, the wave velocity and the thickness of the sample by Eq. 2:

$$V = \frac{e}{\tau}. \qquad (2)$$

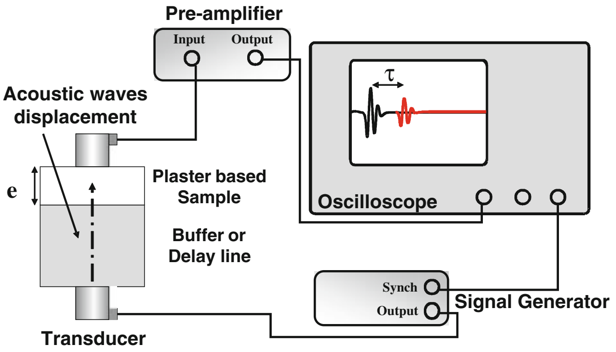

Fig. 2 Experimental setup for ultrasonic measurements

The experimental error on V is approximatively 2%. Then, E and G, respectively, Young's modulus and shear modulus were calculated following Eqs. 3 and 4:

$$E = \rho \frac{3V_L^2 - 4V_T^2}{\frac{V_L^2}{V_T^2} - 1}, \qquad (3)$$

$$G = \rho V_T^2, \qquad (4)$$

where ρ is the sample density, V_L and V_T are, respectively, the longitudinal and transversal wave velocity (m s^{-1}). Finally, the Poisson ratio, Nu (ν), was determined using Eq. 5:

$$\nu = \frac{E}{2G} - 1. \qquad (5)$$

Raw materials

Calcium sulphate hemihydrate

The material used as a matrix is a high purity natural gypsum. Calcium sulphate hemihydrate was obtained by calcination of gypsum (calcium sulphate dihydrate) at about 130 °C. The main problem of calcium sulphate hemihydrate conservation is the rehydration into dihydrate (gypsum) when it is exposed to ambient air. This can occur during ageing. In order to limit rehydration, the hemihydrate was stored in hermetically sealed plastic bags.

BET measurements were done after degassing samples overnight at 45 °C. The specific surface area was 3.7 ± 0.1 m^2 g^{-1}. XRD measurements were chosen to control the quantity of gypsum, which was the parameter selected to track the ageing. The composition of the hemihydrate was measured on each batch. The analysis showed that all the batches were made of 95% of hemihydrate ($CaSO_4$, ½H_2O), about 4% of insoluble anhydrite ($CaSO_4$) and 0.5% of free water. Neither gypsum nor soluble anhydrite ($CaSO_4$, εH_2O) were detected.

An important parameter is the water demand of the plaster. This is defined as the ratio of water and dry material necessary to reach a standard viscosity of the paste. This parameter varies for each type of calcium sulphate hemihydrate depending on the chemical composition, the location of manufacture and the age of the hemihydrate. The one used for this study had a water demand of 0.85. The water/plaster ratio used was equal to 1 as it was easier to use more water to cast prisms. Indeed, the elimination of flaws was eased and it also enabled use of a higher percentage of fibres for further casting.

The matrix of the composites is then made of rehydrated gypsum ($CaSO_4$, $2H_2O$) when the hemihydrate and the water are mixed together following the hydration reaction noted Eq. 6:

$$CaSO_4,\ {}^1\!/\!_2H_2O\ +\ 1.5\ H_2O \rightarrow CaSO_4,\ 2H_2O. \qquad (6)$$

Cellulosic fibres

Cortical hemp fibres (*Cannabis sativa*) were supplied by Agrofibra (Barcelona, Spain). Their density, measured with a pycnometer (Accupic helium pycnometer, Creil, France), was equal to 1.58 g cm^{-3}. The basic unit consists of cellulose polymeric chains, aligned and gathered in microfibrils. They are linked to each other by lignin, pectin and hemicellulose. Table 1 presents the composition of the fibres, which were obtained following a procedure described in the literature [2]. They contained 58.7 wt% of cellulose, 14.2 wt% of pectin, 16.8 wt% of hemicellulose and 6 wt% of lignin [12]. These values were in accordance with the literature [13].

Flax fibres (*Linum usitassimum*) were supplied by Lin 2000 (Normandie, France). Their density was equal to 1.59 g cm^{-3}. They contained 63.6 wt% of cellulose, 2.3 wt% of pectin, 3.0 wt% of hemicellulose and 29.9 wt% of lignin.

The two fibres have similar microstructures [14]. The main aspects that differ from one type of cellulosic fibre to another is the ratio of cellulose and semi crystalline products and the microfibrillar angle, defined as the angle that the microfibrils form with the longitudinal axis of the cell. These two parameters explain partially the difference of mechanical properties between different types of cortical fibres [15]. Values found in the literature showed a big spread. The tensile strength of flax fibres was between 600 and 2000 MPa [16–20] and the one of hemp fibres around 400 MPa [21].

For hemp and flax, the diameter of the fibres was, respectively, measured at 30 ± 30 and 16 ± 6 µm. These measurements were done on fibres cut with a waring blender for 1 min as they were used to make the composite. This type of high energy mixing induced a splitting of the fibre bundles making the fibres thinner than the original ones. Consequently, the measurements were done on fibres that were cut with the same protocol to ensure the reliability of the results. Diameter measurements were conducted using an optical microscope at 252× magnification. The diameter of each fibre was measured using an eyepiece graticule, which was calibrated against a 50 µm × 2 µm micrometre. A hundred fibres were measured for each sample and the average value as well as the standard deviation were calculated. The diameter of hemp fibres was twice as big as the one of flax fibres. The dispersion of the results was larger for hemp. This was probably due to the fact that hemp fibres were received in a less refined state than flax. There were still some wood pieces remaining from the stem that were attached to the surface of the hemp fibres. On the contrary, flax was combed, which gave long and regular fibres. These results enabled the evaluation of the aspect ratio of the fibres, defined by the ratio of the length to the diameter of the fibre. For a given length, the aspect ratio is twice as large for flax as for hemp.

Then, the fibres were either used with no further treatment or chemically treated. The treatments used were sodium hydroxide (NaOH at 1.6 mol/L; pH = 14), ethylene diamine tetraacetic acid (EDTA at 13.5×10^{-3} mol/L; pH = 11) or calcium chloride ($CaCl_2$ at 34×10^{-3} mol/L; pH = 7). A concentration of 30 g of fibres/litre was used for all treatments. The residence time of fibres in solution was 48 h at 20 °C except for EDTA (2 h). The fibres were washed with deionised water and dried at 40 °C for 24 h. For the NaOH treatment, an extra washing with acetic acid was done to neutralise the alkalinity of the treated fibres.

Soda treatment is well known to bleach and/or to clean the surface of the fibres [22, 23]. This treatment was chosen to see if the modification of the surface morphology of the fibres would affect the properties of the composite material. It was also reported that soda treatment increased the rigidity of the fibres by removing amorphous compounds [24]. EDTA was used as a chelating agent, which could potentially react with calcium ions and therefore prevent the grafting of calcium ions on the fibres' surface through the reaction with pectins [25]. Calcium chloride was tested with the idea of saturating the fibres' surface with calcium ions prior to mixing with calcium sulphate hemihydrate.

Table 1 Chemical composition of hemp and flax fibres (in wt%) [10]

	Cellulose	Hemicellulose	Pectins	Lignins	Others (waxes, proteins,…)
Hemp fibres	58.7	16.8	14.2	6.0	4.3
Flax fibres	63.6	3.0	2.3	29.9	1.2

Composite materials

First, the fibres are cut and separated in a laboratory blender (Waring Laboratory, Torrington, USA). The fibres length roughly ranged between 1 mm and 1 cm. The dry compounds (fibres and calcium sulphate hemihydrate) were first mixed by hand until the fibres were coated with calcium sulphate hemihydrate. Then, the dry mix was slowly added to water and mixed for 10 s in a blender (Waring blender, Torrington, USA). The water/dry compound ratio used was equal to 1 to ensure a sufficient fluidity even for the highest percentages of fibres. The mix is then poured into moulds and vibrated for 30 s.

Results and discussion

The impact of the type of fibres and the different treatments on the setting of the plaster and the mechanical behaviour of the composites are analysed in the next two sections.

Effect on setting

Calcium sulphate hemihydrate

As the calcium sulphate hemihydrate is made of a natural mineral, it is subjected to some inherent variation due to batch effects and ageing of the hemihydrate. Depending on the raw materials, the calcium sulphate hemihydrate properties can change slightly. The main characteristic that was affected was the setting time of the material. Extreme values for final setting times of 11 ± 3 min for the shortest and 25 ± 3 min for the longest were found. Therefore, all experiments were preceded by a control batch (setting time and MOR) to evaluate the starting material. Indeed, large differences in setting time values can lead to a different microstructure of the set material, which would affect the mechanical properties.

Figure 3 illustrates the variation of the hydration curves for four runs using the same batch of hemihydrate. If the variation could be explained by the fact that calcium sulphate hemihydrate is made from natural gypsum, it is also necessary to keep in mind that it can also be due to some inherent variation during the calcination process. Figure 3 also shows the three main steps of the hydration of hemihydrate into gypsum. The first is known as an induction period where the temperature remains unchanged. This step corresponds to the formation of gypsum nuclei [26]. Then, the hemihydrate/dihydrate conversion rate increases and the crystals grow. This is characterised by an increase of temperature until the reaction slows down and stops.

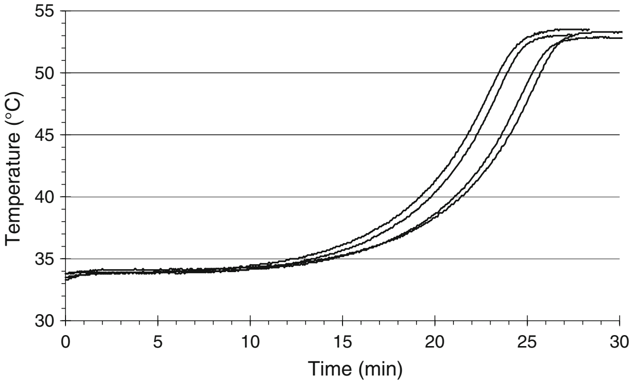

Fig. 3 Temperature versus time curves showing the variations of the hydration duration for a same batch of hemihydrate

Fibre reinforced plaster

Untreated fibres Table 2 presents the effect of adding untreated fibres on the initial and final setting time of the calcium sulphate hemihydrate. The water/dry materials ratio was equal to 1.

If flax did not modify notably the setting time of the paste, hemp almost doubled it. Looking at the composition (Table 1), the biggest difference between hemp and flax seemed to be the amount of lignin and pectin. Hemp was particularly rich in pectins (about 14 wt%). Pectin is known as a chelating agent. It was shown [27, 2] that pectin can trap calcium ions. Some studies [28] showed that calcium ions can be trapped in an ‘egg box’ like structure. However, the hypothesis is still discussed today [29]. The ions are trapped in a calcium pectate gel under acidic conditions. During the calcium sulphate hemihydrate dissolution stage (corresponding to the induction period), some of the calcium ions might react with pectin. The combination of this phenomenon and the fact that extractable materials contained in the fibres dissolve when immersed in water could explain the delay in setting [30].

Figure 4 shows the effect of untreated fibres on the temperature evolution during the setting of the paste. The difference of the maximum reached temperature between paste without and with fibres could be explained by the fact that the thermal conductivity of the fibres is about 10 times smaller than that of plaster ($\lambda_{\text{plaster}} \sim 0.5\ \text{W}\ \text{m}^{-1}\ \text{K}^{-1}$) [31]. So, the fibres could limit the amount of heat emitted

Table 2 Influence of untreated hemp and flax fibres on setting times

	Initial setting time (min)	Final setting time (min)
Control (gypsum plaster)	22	25
Untreated hemp/plaster composite	40.75	44.5
Untreated flax/plaster composite	19.75	26.5

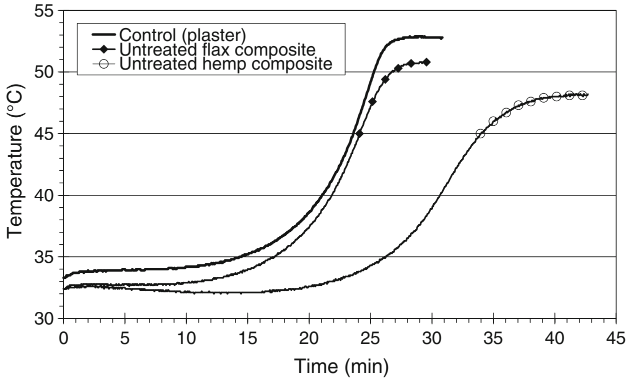

Fig. 4 Temperature versus time curves showing the effect of adding untreated hemp and flax fibres on the hydration process

during the setting of the plaster. Another explanation might be a stochastic behaviour of the hemihydrate/gypsum conversion reaction. Reactions that occur violently after an induction period are very sensitive to any small variation [32] of the initial conditions, like in this case modification of the initial temperature of the system by a few degrees.

The induction period, which is the time before the temperature starts to increase, is lengthened especially for hemp (Fig. 4). To decide if the delay of the setting time, particularly true for hemp, was an effect of either chemical compounds contained in the fibres or the fibres themselves acting as heterogeneities, fibres were washed with deionised water for 48 h at ambient temperature. The colour change of the solutions suggested that some of the compounds were washed from the fibres and dissolved in solution. The residual water was then mixed with calcium sulphate hemihydrate and the heat evolution of the paste during its setting was measured. The hydration curves of hemihydrate mixed with the washing liquors showed the same type of profile as those obtained with slurries containing untreated fibres (Fig. 5). The water used to wash flax did not modify the setting time compared to the control. However, the water used to wash hemp increased the setting time by about 50% (Table 3) by lengthening the induction time of the material. It seemed that the soluble compounds were responsible for the delay of the set. Moreover, it was noticed that when fibres were washed with water and used to cast composites, no delay on setting compared to the control batch was measured. In fact, an acceleration effect compared to the control value was noticed for both hemp and flax. So, the fibres themselves did not delay the set but the compounds that were washed from the fibres did, especially for hemp (Table 4).

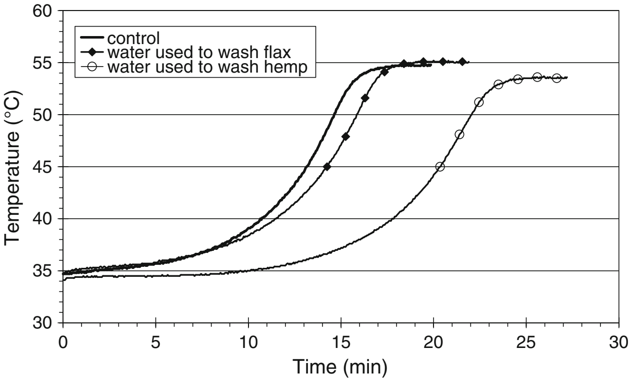

Fig. 5 Temperature versus time curves showing the effect of the fibres soluble compounds on the hydration of calcium sulphate hemihydrate

Table 3 Effect of washing liquors on the setting times of gypsum

	Initial setting time (min)	Final setting time (min)
Control (plaster)	12	14
Calcium sulphate hemihydrate + hemp washing liquor	19	21
Calcium sulphate hemihydrate + flax washing liquor	12	14

Table 4 Effect of water washed fibres on the setting time of gypsum

	Initial setting time (min)	Final setting time (min)
Control (plaster)	9	11
Water washed hemp/plaster composite	8	10.75
Water washed flax/plaster composite	6.5	9.25

The liquors resulting from the 48 h wash in deionized water were kept frozen before being neutralised for characterisation by gas chromatography [33]. The results (Table 5) show that the liquors obtained after soaking hemp and flax fibres in water contained mainly galactose and galacturonic acid. These two sugars are characteristic of pectins as well as arabinose and rhamnose. Therefore, soaking in deionised water was efficient enough to remove some pectins. These were probably weakly linked pectins, characterised by a high methylesterification coefficient [28], which are known to be soluble in water. These results gave qualitative results of the composition of the liquors. Finally, the fact that hemp is seven times richer in pectin than flax could explain why hemp delayed the setting so much compared to flax.

Effect of the treatments on the gypsum matrix and the fibres Various chemical treatments were tested to evaluate their cleaning effect or the possibility to improve the chemical compatibility between the fibre and the plaster and possibly to enhance the strength at the interfaces between the different components.

Table 5 Gas chromatography analysis of liquors obtained after hemp or flax fibre treatments (in mol.%)

Samples	Arabinose	Rhamnose	Fucose	Xylose	Mannose	Galactose	Galacturonic acid	Glucose	Glucuronic acid
Water-treated hemp liquor	16.5	15.9	1.1	3.8	4.5	21.5	19.8	13.3	3.7
NaOH-treated hemp liquor	11.2	7.6	1.1	21.7	18.7	12.3	7.6	18.3	1.5
$CaCl_2$-treated hemp liquor	17.5	15 .4	1.1	3	9	21.8	18	10.2	4
EDTA-treated hemp liquor	11.4	8.5	1	4.6	3.9	17.1	40.1	8.1	5.4
Water-treated flax liquor	8.7	13.2	1.7	6.9	5.7	19.6	31.2	8.9	4.1
NaOH-treated flax liquor	6.8	9.4	0.9	18.9	21.8	16.6	5.2	18.9	1.4
$CaCl_2$-treated flax liquor	9.6	15	2.4	3.7	9.9	25.4	17.2	12.6	4.4
EDTA-treated flax liquor	7.5	9	1.3	2.9	5.5	15.7	46.6	9.6	1.9

Table 5 shows the results of gas chromatography on liquors obtained after the treatments of hemp and flax, respectively. All treatments showed a high content of sugars that are characteristic of pectin, which is logical as they had a similar effect as water on high methylesterified pectin extraction. For the low methylesterified pectins, a more adapted treatment is required. During the plant growth, these pectins (low methylesterified) are strongly linked in the plant cell wall due to calcium ions that stabilise them. For these pectins to be extracted, it is necessary to remove calcium ions from the structure. EDTA, as a strong chelating agent, can trap calcium in both high and low methylesterified pectins. Potentially, EDTA can solubilise more pectins than the other treatments, which was the case. These samples contained a high percentage of galacturonic acid. Nevertheless, the highly linked pectins, which are insoluble in water, should not play a role in the retardation of gypsum setting.

Sodium hydroxide is well known to be able to extract hemicellulose [34], which was confirmed by the gas chromatography results. The corresponding liquors contain mainly xylose and mannose, which are related to hemicelluloses. This treatment produced more aggressive conditions. So, more than extracting pectins, sodium hydroxide actually decomposed these molecules. It explains the low level of galacturonic acid for NaOH-treated fibres. However, these conditions were still sufficiently mild not to destroy the cellulose structure [14–35]. The liquors resulting from the immersion of fibres into a $CaCl_2$ solution had sensibly the same composition as those obtained from a deionised water washing.

Table 6 Setting times of the calcium sulphate hemihydrate

	Initial setting time (min)	Final setting time (min)
Control	9	11
NaOH	9	11
EDTA	5	6
$CaCl_2$	11	13

The chemicals chosen as treatments for the fibres were also used as additives to examine their effect on the hydration of calcium sulphate hemihydrate. The additives were dissolved in the water, and then the calcium sulphate hemihydrate was added. A water/hemihydrate ratio of 1 was used for these experiments and a 0.1 wt% addition level was selected for the additives. Table 6 presents the setting times for the different additives. It is important to notice that for this part of the study, the setting time of the control batch of calcium sulphate hemihydrate was greatly reduced. By comparing the setting times, only the EDTA treatment seemed to accelerate the setting of the plaster. The complexation of calcium ions by EDTA favoured the hemihydrate dissolution. The necessary conditions for gypsum to precipitate are thus obtained sooner, which is characterised by an accelerated setting time.

The other treatments did not affect significantly the setting time of calcium sulphate hemihydrate. For instance, NaOH treatment did not reduce the final setting time of the plaster (compared to the control). However, when the fibres were treated with the same solution, the final setting time was reduced by 45% for flax and 58% for hemp (compared to untreated fibres). Therefore, the accelerating effect was obvious when NaOH was used for treating the fibres (Table 7). $CaCl_2$ actually slightly retarded the set for about 2 min when added to plaster. However, when the fibres were treated with $CaCl_2$, the initial setting time was reduced from 45 to 18 min for hemp and from 27 to 17 min for flax (compared to untreated fibres). Knowing NaOH and $CaCl_2$ have different effects on the setting times when they were used as treatments or additives, it showed that the most important effect of the treatments was to modify the surface of the fibres, mainly by cleaning the soluble compounds from their surface.

Table 7 Setting times of the treated fibre reinforced plasters

	Initial setting time (min)	Final setting time (min)
Plaster	22	25
Untreated hemp composite	41	45
Untreated flax composite	20	27
NaOH-treated hemp composite	13	19
NaOH-treated flax composite	10	15
EDTA-treated hemp composite	13	17
EDTA-treated flax composite	12	17
$CaCl_2$-treated hemp composite	13	18
$CaCl_2$-treated flax composite	12	17

Mechanical behaviour

General behaviour

The mechanical behaviour of plaster-based composite was tested in flexion with a three-point bending test and *E* modulus ultrasonic measurements.

Figure 6 shows the behaviour of three different materials: plaster (gypsum matrix), plaster containing hemp and plaster containing flax fibres. Plaster alone presents a linear behaviour with a catastrophic failure, characteristic of a brittle behaviour. Plaster failed catastrophically for a displacement of 0.2 mm (about 1% of displacement regarding the thickness of the prism). The MOR is 3.2 ± 0.4 MPa for the gypsum matrix alone (Table 8). The values of the MOR depend on the starting material and the fact that the failure is governed by the critical defect. The process of casting a paste to form prisms could also generate flaws that were difficult to eliminate. Even if a vibrating plate and a high water gauge were used, the paste was rather thick. This was also the case when high percentages of fibres were added.

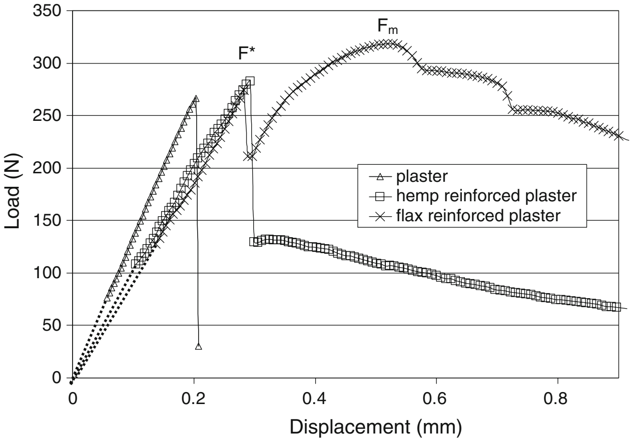

Fig. 6 Typical load/displacement curves of gypsum-based materials

When fibres were added, even in a small quantity, the behaviour of plaster changed. For the two composite materials, the failure happened in a more controlled way. The propagation of microcracks was delayed by the fibres that bridged the cracks and supported a part of the load. For the composites, a lower rigidity was noticed compared to the plaster alone. The incorporation of the fibres could create defects, mainly flaws, in the materials. However, this reduction in the rigidity was followed by an increase of the sustained displacement (about 0.3 mm in the case of hemp, 0.5 mm in the case of flax, Fig. 6) before the macrocrack propagation.

The fall of load noticed for the hemp/plaster composite tended to be catastrophic in the first place but then a transfer of load from the matrix to the fibres happened. After this point, the fall of load became smooth and regular. During the whole experiment, even after several millimetres of displacement, the prisms were still in one part. However, hemp is rather detrimental for the mechanical properties of plaster. Even at low levels, the MOR was reduced to 2.8 ± 0.3 MPa (Table 8).

For flax/plaster composites, the post linear behaviour was slightly different. Indeed, the load transfer from the matrix to the fibres occured after a smaller fall of load than for hemp. This improvement of the load transfer could be a combined effect of a stronger plaster/fibre interface and a more favourable aspect ratio of the fibres. As it can be seen in Fig. 6, the load transfer for flax is more efficient than the

Table 8 Modulus of rupture of hemp or flax fibre gypsum-based composite

	Average MOR (MPa)	Standard deviation (MPa)	Density (kg/m^3)
Plaster	3.2	±0.4	834
Untreated hemp composite	2.8	±0.3	827
Untreated flax composite	3.6	±0.4	824
NaOH-treated hemp composite	3.4	±0.3	827
NaOH-treated flax composite	3.7	±0.5	825
EDTA-treated hemp composite	3.5	±0.2	827
EDTA-treated flax composite	3.7	±0.4	827
$CaCl_2$-treated hemp composite	3.8	±0.3	836
$CaCl_2$-treated flax composite	3.9	±0.3	832

one for hemp. After the macrocrack propagation (F^*), the load was increasing again to reach values equal or even higher than the one of the matrix. This maximum load (F_m) was noticed for a displacement of about 0.5 mm and the deduced MOR was 3.6 ± 0.4 MPa (Table 8).

Figure 7 illustrates the separation at the gypsum/fibre interface after a mechanical test where the prism was put in flexion. First, the fibre bridged the crack and as the crack propagated, the load was transferred to the fibre until the interface broke. Then, the fibre started to be pulled out of the matrix and the load started to decrease.

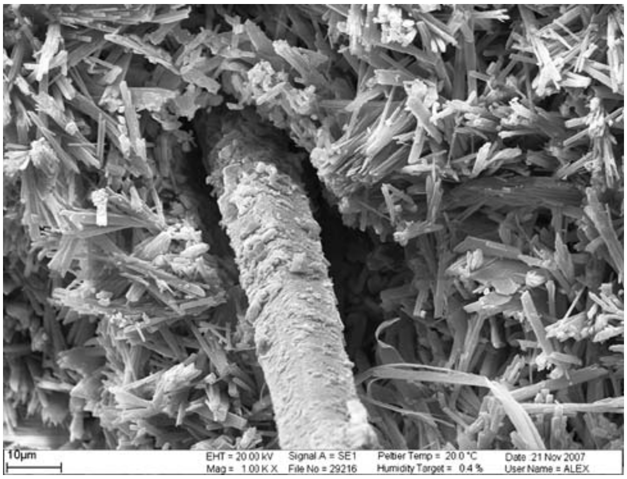

Fig. 7 SEM micrograph of the debonding of a flax fibre and the gypsum matrix after a three-point bending test

Effect of chemical treatments of the fibres on the mechanical strength of plaster

The effects of the treatments on Young's modulus and on the flexural properties were investigated. Some treatments, like NaOH, are known to wash out the amorphous compounds from the fibres, leaving the surface of the fibres roughened (Fig. 8). This was expected to increase the strength of the fibre/matrix interface by strengthening the adhesion between the crystals and the fibres.

Table 8 presents also the results obtained for composites reinforced with treated hemp or treated flax fibres. The MOR and its standard deviation is presented. For each material, 10 prisms were tested.

Adding untreated hemp fibres to plaster was clearly detrimental to the material considering that the composite had a smaller MOR than the gypsum matrix alone. Treating the fibres had a positive effect on the mechanical strength of the material, allowing attainment of values close to or slightly higher than those obtained for the gypsum matrix. However, no difference between the treatments was clear. The deviation of the results was quite noticeable due to the inherent variations because both gypsum and fibres are natural materials. The density of the composite was also slightly lowered compared to a pure gypsum matrix. Considering that the density of the fibres is 1.5 kg/m^3 (both for hemp and flax fibres, which is a value smaller than that calcium sulphate hemihydrate powder used), the trend of a decrease of the density is logical regarding the starting materials.

Fig. 8 SEM micrographs of an untreated (**a**) and NaOH-treated (**b**) hemp fibre

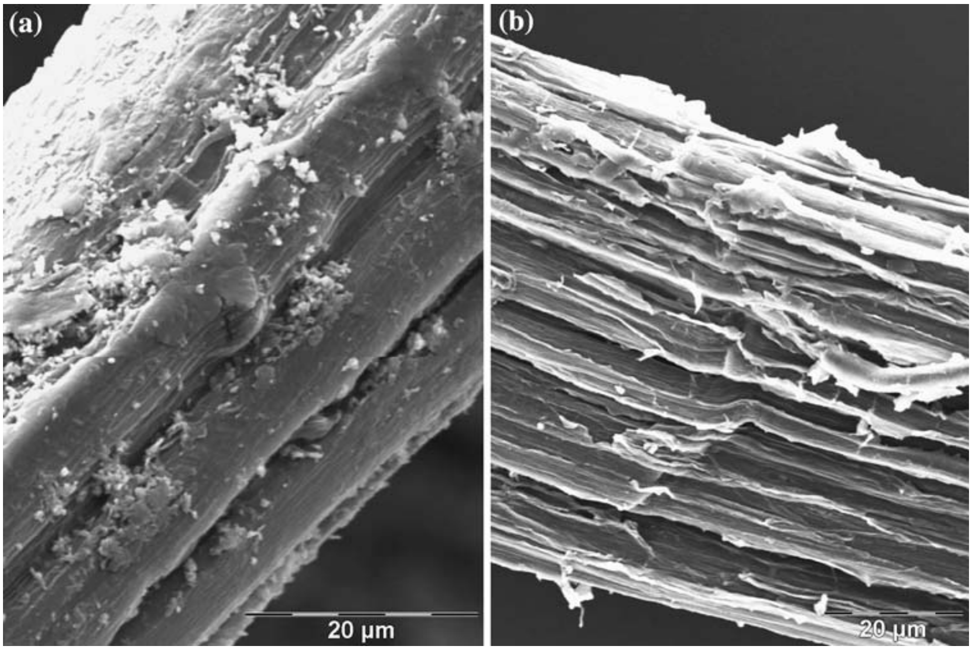

Table 9 Elastic properties of natural fibre/gypsum-based composite

	E (GPa)	*G* (GPa)	*ν*
Plaster	3.2 ± 0.2	1.3 ± 0.1	0.23 ± 0.05
Untreated hemp composite	2.4 ± 0.1	1.0 ± 0.1	0.18 ± 0.01
Untreated flax composite	2.8 ± 0.2	1.1 ± 0.1	0.25 ± 0.03
NaOH-treated hemp composite	2.8 ± 0.1	1.1 ± 0.1	0.25 ± 0.02
NaOH-treated flax composite	3.1 ± 0.1	1.3 ± 0.1	0.23 ± 0.01

The same experiment was conducted with flax fibres (Table 8). Compared to hemp fibres, the untreated flax fibres did not reduce the MOR of the gypsum matrix, and actually increased the MOR slightly from 3.2 to 3.6 MPa. Treatment with NaOH, EDTA and $CaCl_2$, however, did not noticeably improve the MOR of the composites.

The elastic properties were measured for both flax and hemp fibres. It was decided to study the NaOH treatment because it is reported to increase the rigidity [24, 14]. Untreated and NaOH-treated fibres results are reported in Table 9. The addition of fibres, either treated or not, generally decreased Young's modulus of the composite compared to the value of the gypsum material. Untreated hemp fibres especially lowered the elastic properties. Even if the elastic properties of hemp fibres are evaluated at 38 GPa for hemp [36] and 58 GPa for flax [37], their addition reduced the *E* values. The introduction of fibres created defects by trapping air, which decreased both density and elastic properties [38]. However, the NaOH treatment gave higher values of *E* moduli compared to untreated fibres. The same effect was noticed for flax fibres and with values that were slightly higher compared to hemp fibres.

The same tendency was noticed for both elastic and flexural properties. Flax fibres were stronger than the hemp ones. Especially, the untreated hemp lowered the mechanical properties. This may be due to the chemical composition of the fibres. As seen in 'Untreated fibres' section, pectins were identified as a retarder. This can modify the setting of gypsum crystals, especially at the fibre/matrix interface, which could involve a modification of the mechanical properties of the material.

The treatments listed consisted of washing out the free sugars and soluble components first from the fibres, before mixing them with the hemihydrate. The retardation effect of the fibres was, therefore, diminished and the mechanical properties tended to those of a gypsum matrix. The drop of the MOR due to hemp fibres was also reduced when the fibres were treated. For flax fibres which contained less pectins, the mechanical properties were not deteriorated by untreated fibres and therefore the effect of the treatments was less noticeable.

Conclusion

The effect of two natural fibres, hemp and flax, on the setting time and the mechanical properties of gypsum were investigated in this article.

Plaster is a hydraulic setting material with a dissolution/precipitation mechanism. The kinetics of setting as well as the shape and size of the crystals depend on the admixtures.

Fibres were found to delay the setting of plaster when they were untreated. This effect was greater for hemp than for flax. The treatments reduced this retardation effect, by removing some soluble compounds that were in the fibres.

The behaviour of plaster was also modified from brittle to a non-linear one when fibres were added. Even at small levels of addition, fibres, especially flax, lowered the crack propagation and bridged them. The load transfer from the matrix to the fibres allowed slightly higher values of flexural strength to be reached.

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