

USE OF SISAL MICROFIBRES AND BLEACHED EUCALYPTUS PULP AS REINFORCEMENT OF MgO-SiO₂ FIBRE CEMENT

Christian Gauss, University of Waikato, New Zealand / University of São Paulo, Brazil
cgauss@waikato.ac.nz

Gonzalo Mármol, Construction Science Institute Eduardo Torroja, Spain, gonmrde@gmail.com

Carlos Fioroni, University of São Paulo, Brazil, carlosfioroni@usp.br

Holmer Savastano Jr., University of São Paulo, Brazil, holmersj@usp.br

ABSTRACT

In this work, minimally processed sisal microfibres along with commercial eucalyptus pulp were used as reinforcement of composites based on magnesium oxide and silica cement (60/40 ratio by weight of MgO/SiO₂) with high filler content. The fibre cement composites were submitted to a fast carbonation process, resulting in the formation of hydrated magnesium carbonate, which contributed to improved physical and mechanical properties. All composites presented a strain-hardening behaviour and high specific energy under flexural loading, in special the composites with 10% of fibres. We demonstrated that the sisal microfibres produced by a chemical/mechanical process can be used as an efficient reinforcing material in combination with commercial cellulose pulp for MgO-SiO₂ composites.

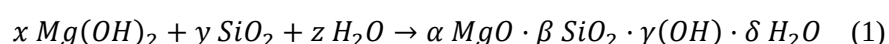
KEYWORDS

Clinker-free; Lignocellulosic fibres; Sustainability; Magnesium oxide; Silica fume.

INTRODUCTION

The building and construction sector has a big challenge in the next decades to decrease carbon emissions in a world with increasing demand for building materials and resources. Approximately one-third of worldwide greenhouse gas (GHG) emissions are related to the building industry (Bui et al., 2021; Nations, 2009; Pearce & Ahn, 2017). Ordinary Portland cement (OPC) production alone contributes more than 7% of worldwide anthropogenic GHG, with an annual production of over 4 billion metric tons (Miller et al., 2021). In this scenario, alternative clinker-free binders and carbon-rich natural materials can be used to mitigate the carbon emissions attributed to materials in the built environment (Fonseca et al., 2019; Santos et al., 2015).

Magnesium oxide-based cements have been used as inorganic binders for a long time. However, there has been a recent interest in their use as a sustainable alternative for ordinary Portland cement (OPC) as MgO requires lower temperatures of calcination and it has been demonstrated that it can be obtained from natural silicates without releasing chemical CO₂ during the process (Scott, Oze, et al., 2021; Scott, Shah, et al., 2021). Low-pH cement systems based on MgO and SiO₂ (MSH cement), for example, have been developed and comprehensively studied in the last decade (Jin & Al-Tabbaa, 2014; Szczerb et al., 2013; Zhang et al., 2011). In this system, the binder is obtained by combining reactive MgO and highly amorphous SiO₂ to produce magnesium silicate hydrates (M-S-H), according to the reaction (1):



The promising mechanical properties and lower alkalinity of MSH cements (pH <11) in comparison to OPC is a key benefit for the production of fibre cement using natural fibres, that work as reinforcement and additional carbon storage. Their lower pH prevents the chemical degradation

phenomena of lignocellulosic fibres common in conventional cement composites (Gonzalo Mármol, Ribes, et al., 2020; Gonzalo Mármol & Savastano, 2017).

Many commercial cellulose fibres can be used as reinforcement in fibre-cement composites. Eucalyptus and pine fibres, for example, have appropriate length (between 1-2 mm), adequate aspect ratio and a large number of reinforcing elements per unit of mass (Tonoli et al., 2010). These fibres are produced on large scales using traditional pulping methods through the Kraft and bleaching processes. However, other lignocellulose fibres, such as sisal, are also suitable as reinforcing elements for both inorganic and polymeric matrices (Gonzalo Mármol, Ribes, et al., 2020; Savastano et al., 2000; Wu & Hao, 2019). Sisal fibres have excellent mechanical properties, high cellulose content, and low microfibrillar angle, which are all beneficial for the reinforcement of fibre-cement (Savastano et al., 2000). In addition, sisal fibres can be obtained in different fibre lengths depending on the process, and generally requires simple manufacturing methods with low energy requirements. It has been shown that the degradation of sisal fibres is avoided in MSH cements in comparison with conventional Portland cement, which is highly beneficial for a long-term stability of the composite (Gonzalo Mármol, Ribes, et al., 2020). Despite this advantage, there has not been studies focused on the mechanical performance of MSH composites reinforced with sisal fibres.

During the curing of MSH binders, the main binding component is M-S-H phase; however, depending on the ratio of MgO and SiO₂, free Mg²⁺ ions can also be available to react with aqueous CO₂ and form stable hydrated carbonates such as nesquehonite and hydromagnesite, which can also be facilitated by the capillary voids associated to lignocellulosic fibres (Gonzalo Mármol, Mattoso, et al., 2020). Therefore, accelerated carbonation processes can be used to enhance the stability of MgO-SiO₂ fibre cement in the early stages and improve physical and mechanical properties of the composites.

Considering the technical and environmental advantages of sisal and clinker-free cements, we developed novel MSH fibre-cement composites using sisal microfibres and commercial bleached eucalyptus pulp. The main objective of this study was to evaluate the reinforcing potential of minimally processed sisal fibres and their combination with commercial cellulose for MSH fibre-cement produced by the water/dewatering method. The sisal microfibres were obtained only by a mild alkaline pre-treatment followed by mechanical refinement and characterised through optical microscopy and infrared spectroscopy. The composites were also submitted to a carbonation process using pure CO₂ under pressure, a process known to improve the physical properties of fibre-cement and improve long-term stability of vegetable fibres. The effect of carbonation was studied by X-ray diffraction and thermogravimetric analysis and the performance of the composites was assessed by physical, mechanical, and microstructural characterisation.

MATERIALS AND METHODS

Materials

The sisal fibres (*Agave sisalana*) used in this study were obtained from Pocinhos region (Paraíba state, Brazil). The fibres were washed at 90-95 °C for 30 min by the producer. The chemical composition of these fibres was obtained through the Laboratory Analytical Procedure NREL/TP-510-42618: 66% wt% cellulose, 18% wt% hemicellulose, 13 wt% of lignin and 2% wt of pectin. Bleached eucalyptus pulp was provided by Fibria, Jacareí, Brazil. The eucalyptus microfibres were refined before being used in the composites, as described in (Gonzalo Mármol & Savastano, 2017). The reactive MgO was provided by RHI, Magnesita (Brumado, Bahia state, Brazil) and it has a specific gravity of 3.5 g/cm³, surface area of 22.7 m²/g, and MgO content of 97.4 wt%. The silica fume supplied by Elkem Materials South America has a specific gravity of 2.3 g/cm³, average particle size of 19.02 µm, surface area of 16.1 m²/g, and SiO₂ content > 95.1 wt%. Commercial limestone, produced by Votorantim Cimentos (Santa Helena, SP, Brazil), was used as a filler in all the fibre-cement compositions. Sepiolite (Si₆Mg₄O₁₅(OH)₂·6H₂O) with high anionic charge provided by Tolsa Group was also added to the formulations to enhance the hydration of MgO-SiO₂ cement and facilitate the formation of M-S-H, as described in (Gonzalo Mármol et al., 2019).

Sisal fibre processing

Before processing, approximately 200 g of the as-received sisal fibres were chopped into 3-5mm fibres. These fibres were then boiled in water for 30 min, drained, and pre-treated in an aqueous solution of NaOH (2% m/V) at room temperature for 24 h. After these treatments, the fibres were drained and washed with water until a pH=7 was achieved. The alkaline pretreatment was necessary to facilitate the separation of the microfibrils from the fibre bundles during refining. The treated fibres were then dispersed in water (approximately 0.5% m/V) and refined in a mechanical defibrillator, SuperMasscolloider grinder, Massuko-Sangyo®, model MKCA6-2. The fibres were passed through the defibrillator 15 times at 1000 rpm with a gap of 100 μm between the rotating and fixed silicon carbide grindstones. The fibres after each step are shown in Figure 1. After this process, the excess water was drained using a centrifuge and the fibres were stored in a laboratory fridge at 4 °C until further use.



Figure 1 – From left to right: as-received fibres, chopped fibres before treatment and optical microscopy image of microfibrils after defibrillation.

Fibre characterisation

The as-received and processed sisal fibres were analysed in a stereoscope to measure the fibre length and in an optical microscope (Axio Lab. A1, Zeiss®) to measure the fibre diameter. Before the microscopy analyses, the fibres were stained with safranin and dispersed in a droplet of glycerol between two microscopy slides. The fibres were also analysed by Fourier transform infrared (FTIR) spectroscopy. Samples were dried at 60 °C until a constant weight was achieved and analysed in a PerkinElmer Spectrum One FTIR equipped with ATR (Attenuated Total Reflectance). For each analysis, 32 scans were used in the spectral region of 4000-600 cm^{-1} with a resolution of 4 cm^{-1} .

Composites formulation and production

Fibre-cement composites were produced using the formulations shown in Table 1. Fibre-cement boards of 200 x 200 mm and thickness of approximately 6 mm were produced using a slurry-dewatering process followed by pressing, as described in (Gonzalo Mármol & Savastano, 2017; Savastano et al., 2000). This process uses a similar concept applied in industrial production of fibre-cement. First, the micro silica and sepiolite were dispersed in 2L of water and mixed at 3600 rpm for 15 min in a high-speed mixer (MA758 model, Marconi). Then the fibres (processed sisal and/or bleached eucalyptus pulp) were added and mixed for 5 min at 3600 rpm and the mixture was kept in the mixing container overnight. Before adding the fibres, their moisture content was determined using an infrared moisture balance and the weight was corrected according to the dry weight content necessary for each formulation. Finally, MgO and limestone were added and mixed for 15 min at 3600 rpm. The obtained slurry was then poured into a casting box where vacuum is used to filter the excess water. The obtained pad was then pre-pressed (still inside the moulding chamber) using 3 tons for 3 min to further remove excess water. After this step, the pads were demoulded and pressed with 25 ton for 5 min. Subsequently, the fibre-cement boards were cured in a steam-curing chamber at 60 °C for 5 days to speed up the hydration process of MgO. Each board was then cut wet into four 165 x 40 mm flexural test specimens using a diamond blade saw cooled with water and conditioned in a climatic chamber at 30 °C with 70% RH for 24 h before the carbonation process. Samples of each

formulation were extracted at this stage for X-ray diffraction analyses (named “before carbonation”). These samples were ground and immersed in isopropyl alcohol for 24h to stop the hydration reaction.

Table 1 – Composition of composites. Each flat board was produced with a total of 210g of dry material. The proportion of MgO/SiO₂ was kept the same for all the conditions (60/40). Two boards were produced for each composition.

Sample ID	Composition wt% (of total weight)					
	MgO	SiO ₂	Filler	Sisal microfibre*	Bleached eucalyptus pulp*	Sepiolite
E5	36.3	24.2	32.5	-	5.0	2.0
E10	34.3	22.9	30.8	-	10.0	2.0
S5	36.3	24.2	32.5	5.0	-	2.0
S10	34.3	22.9	30.8	10.0	-	2.0
E5S5	34.3	22.9	30.8	5.0	5.0	2.0

*As dry fibres.



Figure 2 – Processes used to produce the fibre-cement boards. a) Sisal microfibres; b) Slurry mixing process; c) compression of composite after moulding.

Carbonation process

After conditioning the samples in the climatic chamber, the samples were submitted to accelerated carbonation in a pressure reactor (Figure3) at 45 °C. A vacuum of approximately 550 mmHg was first applied for 30 min to remove the excess water in the open pores and then pure CO₂ was injected at a pressure of 100 psi. The samples were kept inside the reactor for 24 h. After carbonation, the samples were removed from the reactor, weighed and placed in water for at least 24h. These samples were used for all the subsequent analyses.

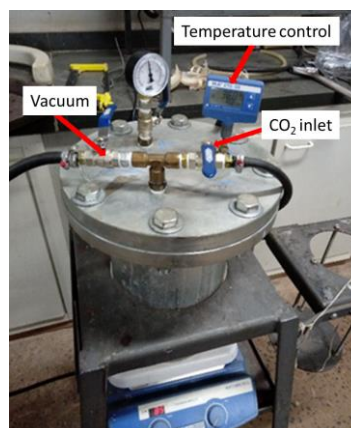


Figure 3 – Pressure vessel used for the carbonation process.

Characterisation of composites

The physical properties, bulk density (BD), water absorption (WA), and apparent porosity (AP) of each formulation were determined according to ASTM C 948-81 Standard (American Society for Testing and Materials. ASTM C948-81.; 2016). Four-point bending was conducted in a EMIC DL30000 universal mechanical testing machine equipped with 1 kN loadcell and a deflectionometer to measure the displacement in the middle of the specimen. The major span was set to 135 mm (lower part) and the minor span to 45 mm (upper part). The modulus of rupture (MOR), limit of proportionality (LOP), modulus of elasticity (MOE), and specific energy (SE) were determined according to Equations 1-4 (Fioroni et al., 2020; G. Mármol et al., 2013). The SE was calculated as the area under the stress-strain curve up to the MOR. Eight samples were tested for each condition. The four-point bending results were analysed in the statistical software Minitab® 18 using one-way analysis of variance (ANOVA) test. The significant differences among averages were calculated using Tukey's method with a 95% of confidence.

$$MOR = \frac{[3P_{max}(L_{inf}-L_{sup})]}{2wh^2} \quad \text{Eq. 1}$$

$$MOE = \left[\frac{(276L_{inf}^3)}{(1296wh^3)} \right] \left(\frac{P}{\delta} \right) \quad \text{Eq. 2}$$

$$LOP = \frac{[3P_{lop}(L_{inf}-L_{sup})]}{2wh^2} \quad \text{Eq. 3}$$

$$SE = \left[\frac{1}{(hw)} \right] \int P(\delta)d\delta \quad \text{Eq.4}$$

Where P_{max} is the maximum load, L_{inf} is the major span, L_{sup} is the minor span, w and h are the sample width and depth, respectively, δ is the deformation and P is the load. P_{lop} is the maximum load of the linear region.

Samples extracted before and after carbonation were analysed by X-ray diffraction (XRD) and Thermogravimetric analysis (TGA) to identify the phase evolution in each formulation. Before the analyses, the samples were immersed in isopropanol to interrupt the cement hydration process, oven-dried at 60 °C, and then ground and sieved below 600 µm. The XRD analysis was conducted in a Horiba LA-60 diffractometer with CuK α radiation generated with a voltage of 40 kV and a current of 30 mA between 2 θ angles of 5-75 °C. The phase identification and Rietveld analysis was performed using the software HighScore Plus Version 4.9.0. The following phases were used for the refinement: Calcite-CaCO₃ (ICDD 96-900-0966); Periclase MgO (ICDD 96-900-6751); Brucite Mg(OH)₂ (ICDD 96-100-0055); Quartz SiO₂ (ICDD: 96-900-9667); Dolomite MgCO₃·CaCO₃ (ICDD 96-900-3509); Nesquehonite MgCO₃·3H₂O – Crystal Information File obtained from (Yamamoto et al., 2021). The TGA analysis was conducted in a Netzsch STA 440 F3 Jupiter analyser under nitrogen flow of 50 mL/min from 25-1100 °C at a heating rate of 10 °C/min.

For microstructural characterisation, samples extracted from the four-point bending specimens were embedded in epoxy resin and sanded for 5 min on three different silicon carbide sandpaper (grit 600, 1200 and 2000, in this order), lubricated with isopropanol and then polished with diamond suspensions with the particle sizes of 6 µm (10 min), 3 µm (20 min) and 1 µm (30 min). The samples were cleaned in an ultrasonic bath with isopropanol for 10 min between each polishing step and analysed in a low vacuum electronic microscope Hitachi TM 3000 using backscattered electron detector mode (BSE) and acceleration voltage of 15 kV. Fracture surfaces of the samples were also analysed without embedding in resin or sanding in low-vacuum mode as well.

RESULTS AND DISCUSSION

Sisal fibre characterisation

Microscopy images of the fibres before processing and after pre-treatment and fibrillation are shown in Figure 4. After processing, it was possible to separate most of the microfibrils from the bundles (Figure 4a), which resulted in microfibrils with an average length and width of 2.17 mm (COV=0.31) and 19.4 μm (COV=0.25), respectively (Figure 4b). It is worth mentioning that without pre-treatment with NaOH, the sisal fibres could not be successfully fibrillated using the mechanical process, resulting in a high content of fibre bundles and fines.

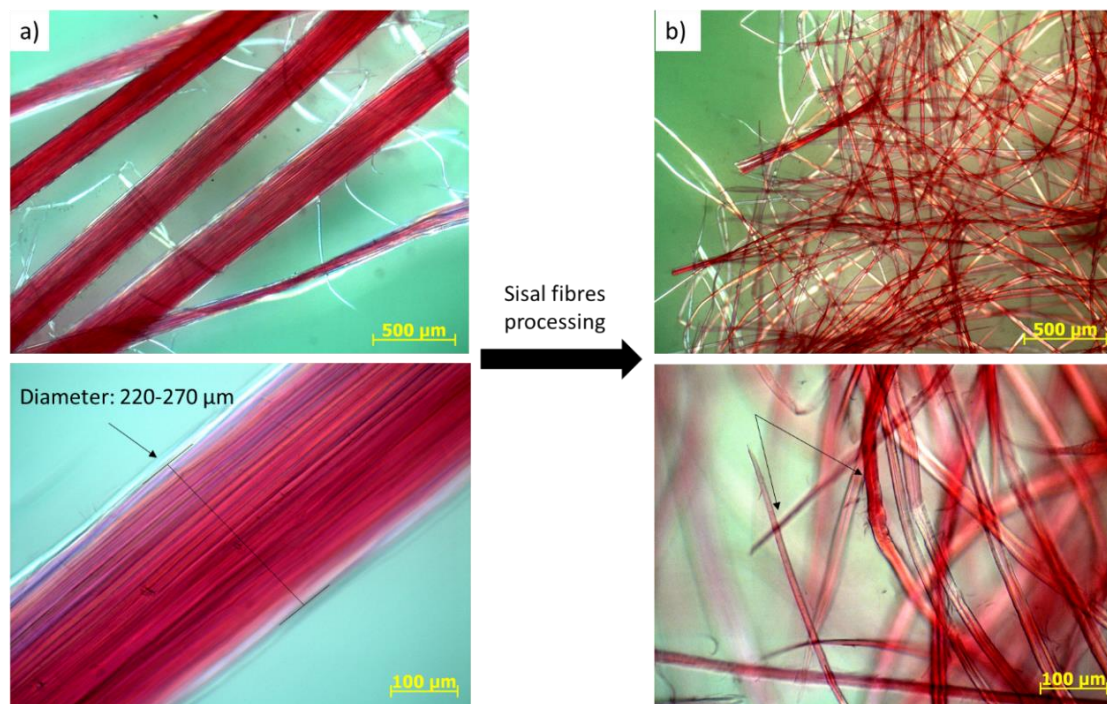


Figure 4 – Representation of the sisal fibres in different stages of the process: a) after alkaline pre-treatment; b) after mechanical refining.

The FTIR spectra of the as-received and processed fibres are shown in Figure 5. The free-carbonyl groups associated with hemicellulose generate a peak at a wavelength of 1737 cm^{-1} . The absence of this peak in the processed fibre indicates that most of the hemicellulose was removed during the process. Similarly, the decrease in the intensity of the peaks at 1239 cm^{-1} (CO-stretching in lignin and hemicellulose) and 1396 cm^{-1} (C-H deformation in hemicellulose and cellulose) indicate that although some lignin is still present, most of it (and hemicellulose) were removed using the pre-alkaline treatment and mechanical refinement (Meng et al., 2016; Xu et al., 2013). Therefore, the alkaline pre-treatment was advantageous for two main reasons; 1- to facilitate the separation of the microfibrils from the fibre bundles and 2- prevent possible alkaline hydrolysis of the fibres in the composites by removing lignin and hemicellulose (de Klerk et al., 2020).

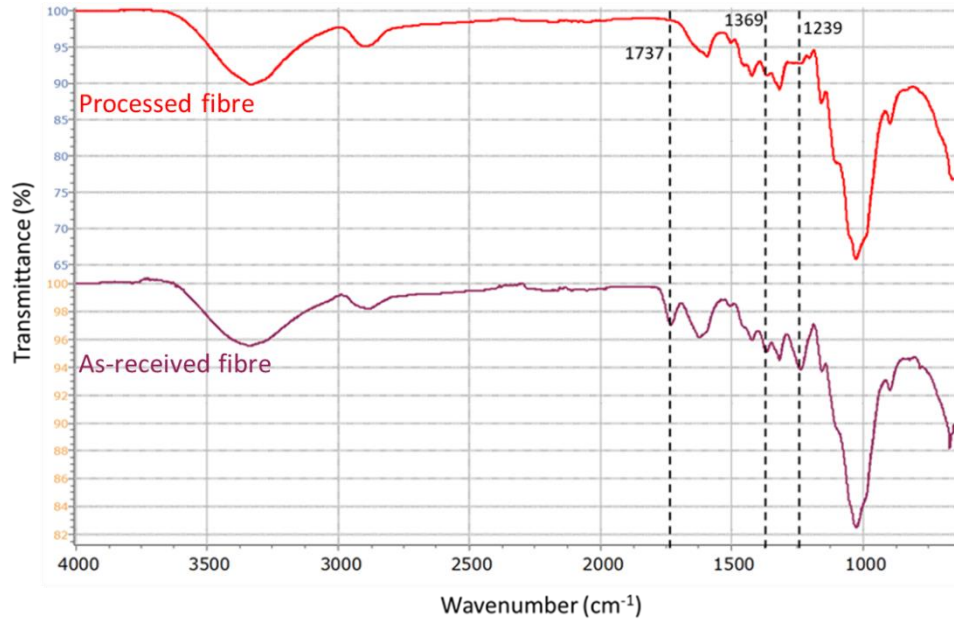


Figure 5 – FTIR spectra of the sisal fibres before and after processing.

Effect of carbonation on the composites

The effect of carbonation process using CO₂ under pressure can be visualised in the XRD patterns of the S5 formulation presented in Figure 6. Before carbonation, the typical phases in MSH cements can be observed: brucite (Mg(OH)₂), periclase, and the M-S-H gel (shown in the grey areas of the insert). Magnesium silicate hydrated formed by the hydration of MgO and reactive silica (see reaction (1)) is poorly crystalline (highly disordered), which is reflected in the broad peaks in different 2θ regions of the diffraction pattern (Zhang et al., 2011, 2014). Because of the high content of filler, dolomite, quartz, and calcite phases are also clearly seen in the XRD patterns. The low intensities of brucite and periclase mean that most of the Mg(OH)₂ reacted to form M-S-H.

With the carbonation process, there is a reduction in the peak intensities of brucite and periclase, and a new phase appears; nesquehonite. Nesquehonite is a hydrated form of magnesium carbonate (HMC) with a monoclinic structure formed according to the reaction (2) (Gonzalo Mármol, Mattoso, et al., 2020). The corresponding peaks of nesquehonite are marked by the dotted red line in Figure 5. Therefore, the main effect of carbonation is the consumption of brucite to form nesquehonite, which was completely absent in the non-carbonated samples.

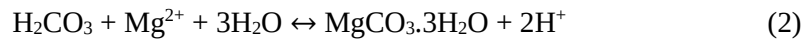


Figure 7 presents the XRD patterns of all samples in the 2θ range of 10-30° before and after carbonation, showing that this process happened in all formulations. Some minor differences are observed in the 17-25° range, which are attributed to the presence of unreacted silica and the potential contribution of the cellulose fibres that could have passed through the sieve during samples preparation. None of the samples had any signs of nesquehonite before the carbonation process. It is worth mentioning that one of the main advantages related to the formation of nesquehonite is that it is considered an acid carbonate since its reaction in water reduces the pH of the water in the pores (H⁺ from reaction (2)) and therefore contributes to preserve the cellulose fibres from alkaline hydrolysis (Gonzalo Mármol, Mattoso, et al., 2020). Another noteworthy advantage in cellulose-cement composites is the large volume of hydrated phases formed. This is especially important in Mg-based cements since CaCO₃, formed in OPC-based fibre-cement, does not include bonded water.

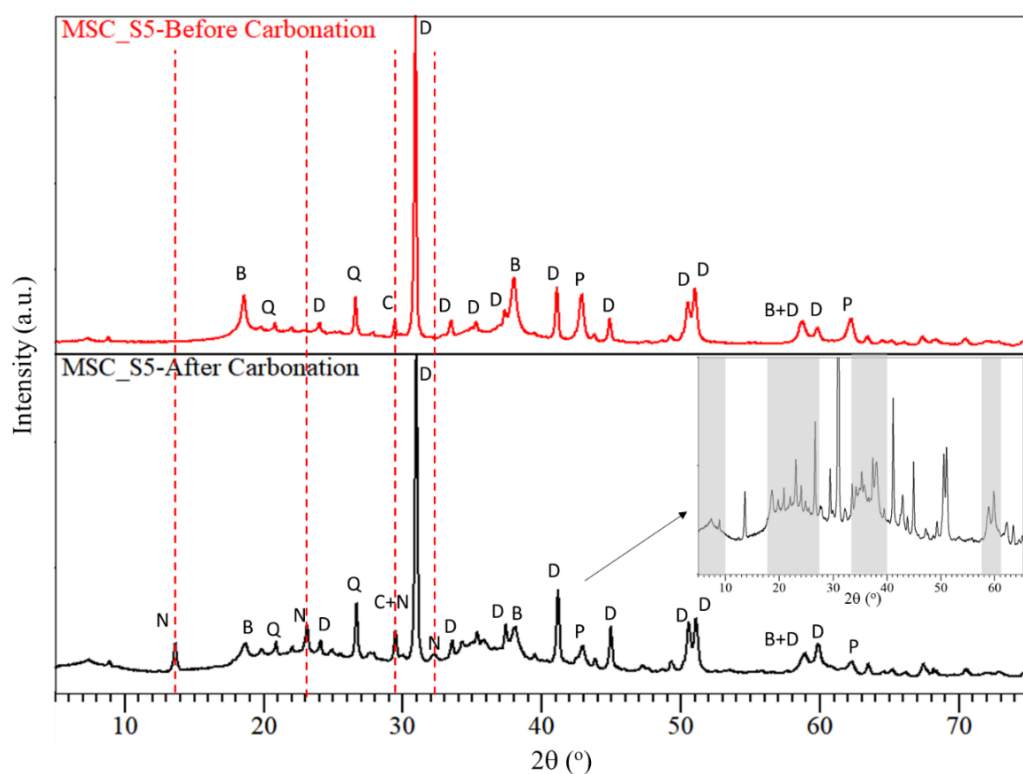


Figure 6 – XRD patterns of formulation S5 before (in red) and after carbonation (in black). The red dotted lines show the 2θ angles related to nesquehonite. Regions corresponding to M-S-H are shown in light grey in the insert plot. B=Brucite; Q=Quartz; D=Dolomite; P=Periclase; N=Nesquehonite

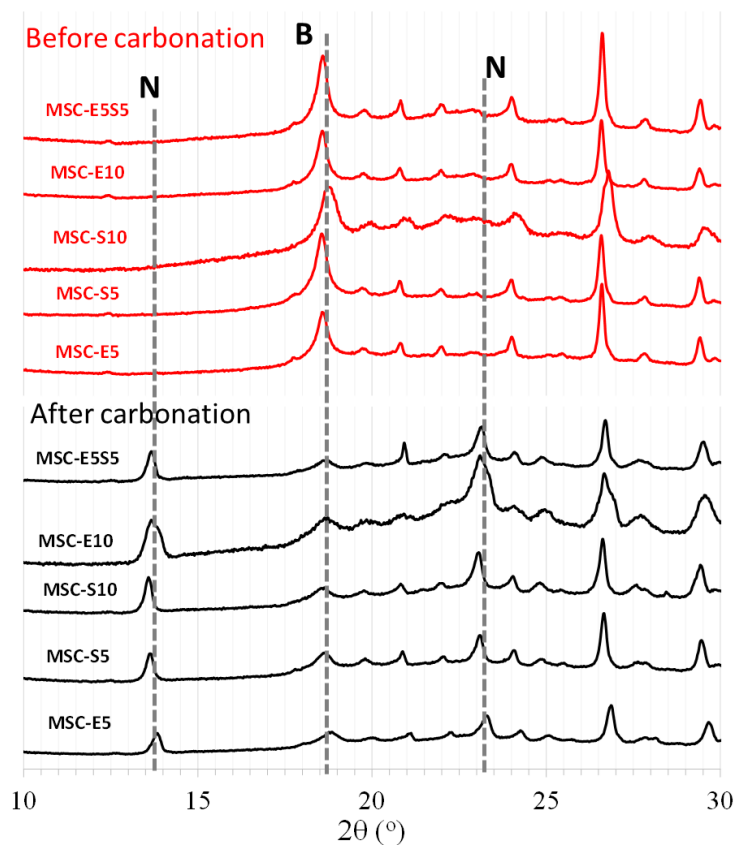


Figure 7 – XRD patterns of all the formulations before and after accelerated carbonation in the 2θ range of 10-30°.

Rietveld refinement was also conducted in all the samples to estimate the amount of nesquehonite formed after carbonation. Figure 8 shows the experimental and calculated XRD pattern of the S5 condition before and after carbonation. For this analysis, the crystal structure of talc (magnesium silicate) was modified increasing the full-width-half-maximum (FWHM) of the peaks to simulate the contribution of M-S-H gel in the XRD pattern. It is worth mentioning that there could be a minor contribution of the unreacted amorphous silica in the 2θ range of $18-30^\circ$. However, in most cases the addition of the modified M-S-H in the refinement (considered an amorphous phase) was sufficient to have a proper refinement. Minor peaks that were not used in the refinement may be attributed to the sepiolite (also a magnesium silicate) added to the formulation.

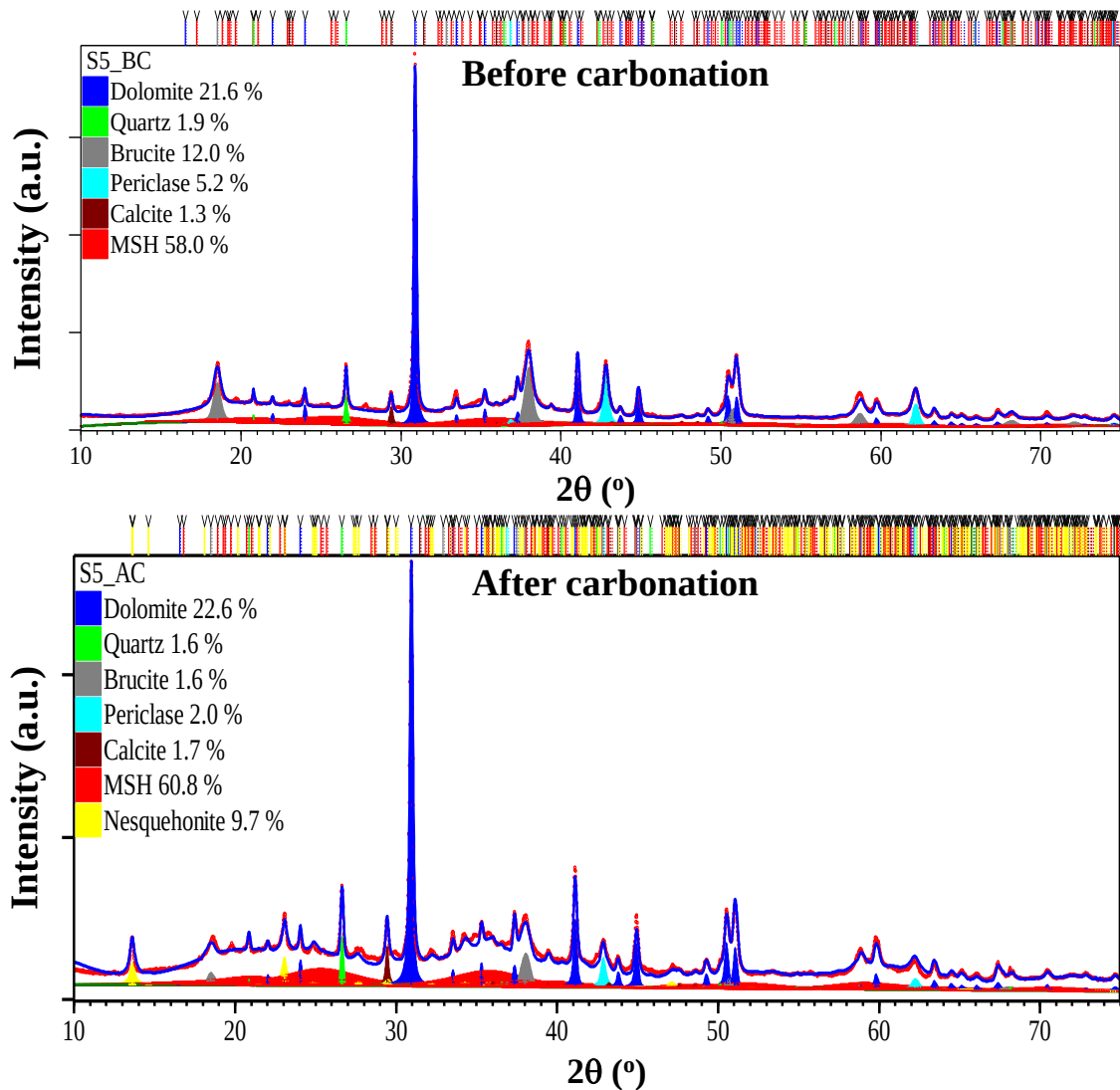


Figure 8 – Rietveld analysis of carbonated and non-carbonated samples (E5) showing the percentage of each phase. The blue line corresponds to the calculated profile and the red line corresponds to the experimental profile. The individual peaks of each phase are represented by different colours according to the legend.

A summary with the approximate wt% of each phase for all formulations before and after carbonation is given in Table 2. Considering the high content of M-S-H gel and possibly unreacted amorphous SiO_2 , the quality of Rietveld analysis is affected, especially due to the absence of an internal standard. Therefore, this is regarded as a semi-quantitative characterisation that was used for a relative phase analysis (the refinement of all the samples was conducted the same way).

One of the first things to notice is the low values of periclase, especially in the carbonated samples, indicating the composites almost achieved full hydration of MgO . Brucite is first consumed

to form M-S-H and then it drastically decreases after carbonation to form stable nesquehonite. Another important aspect is that the M-S-H content in all the samples is similar, with minor variation after the carbonation process. It is also possible to observe that the increase in the fibre content facilitates the carbonation process, resulting in higher content of nesquehonite in the samples E10, S10, and E5S10. In a study about the carbonation process of pure MgO binder with cellulose fibres, Mármol et al. (2020) reported that higher content of cellulose promotes higher carbonation degree, which is explained by higher CO₂ diffusion in the material due to higher porosity introduced by the fibres (Gonzalo Mármol, Mattoso, et al., 2020). The high volume associated with the nesquehonite phase reduces the porosity of the composites while the consumption of brucite protects the cellulose fibres against exposure to alkaline environment.

Table 2 – Phases content of each formulation obtained by Rietveld analysis before and after carbonation.

Sample	Condition	Phase content (wt%)				
		Filler (D+Q+C)	B	P	M-S-H*	N
S5	Before Carbonation	24.8	12.0	5.2	58.0	-
	After Carbonation	25.9	1.6	2.0	60.8	9.7
S10	Before Carbonation	28.3	9.4	2.2	60.1	-
	After Carbonation	25.2	1.0	1.3	62.7	9.8
E5	Before Carbonation	29.0	9.6	2.4	59.0	-
	After Carbonation	26.8	1.3	1.8	61.3	8.8
E10	Before Carbonation	24.3	9.0	2.7	64.1	-
	After Carbonation	19.9	0.9	2.8	61.3	15.2
E5S5	Before Carbonation	26.3	9.6	1.4	62.7	-
	After Carbonation	24.4	3.3	1.4	59.1	12.5

D=Dolomite; Q=Quartz; C=Calcite; B=Brucite; P=Periclase; N=Nesquehonite

**M-S-H + unreacted SiO₂*

Complementing the XRD results, TGA analysis was also conducted in one of the formulations (E5S5) to evaluate the thermal decomposition of the main constituents present in the composites. Figure 9 shows the TG and DTG curves of E5S5 before and after carbonation. By comparing both curves in the range of 50-200 °C, the carbonated samples had 4.54% extra weight loss. In this temperature range, dehydration of M-S-H and nesquehonite occur (Gonzalo Mármol et al., 2019; Gonzalo Mármol, Mattoso, et al., 2020) and since both conditions have similar content of M-S-H, the extra weight loss is associated with the release of water by nesquehonite. In the region between 450-470 °C decarbonation of nesquehonite occurs (Lanas & Alvarez, 2004; Morgan et al., 2015), and it is possible to observe a small peak in this temperature range in the carbonated sample.

It is worth mentioning that the peak observed at around 350 °C, more pronounced in the carbonated sample, is related to the decomposition of cellulose (Gauss et al., 2021). During the preparation of the samples for TGA analysis, some fibres could have passed through the sieve and unintentionally measured with the inorganic matrix. Although the peak is pronounced in the DTG curve due to the fast degradation reaction of cellulose, the resulting mass loss attributed to the fibres in the TG curve is minimal. In the region between 350-600 °C dehydroxylation of M-S-H, nesquehonite, and brucite occurs and between 700-820 °C dolomite goes through a decarbonation process (Gunasekaran & Anbalagan, 2007; Gonzalo Mármol et al., 2019). The final residual weight percentages of un-carbonated and carbonated samples at 1100 °C are 65.7% and 57.6%, respectively. In summary, this difference is attributed to the additional weight losses from dehydration, dihydroxylation, and decarbonation of nesquehonite formed with the carbonation process.

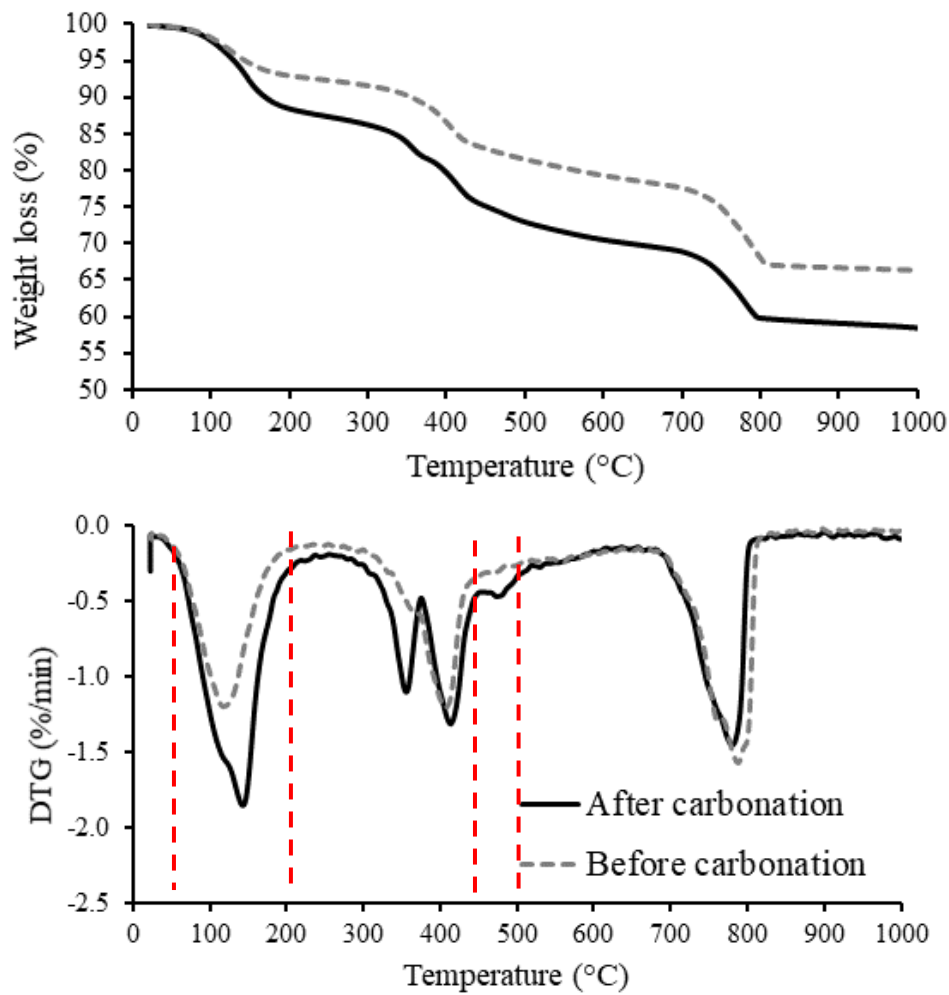


Figure 9 – TG (top) and DTG (bottom) curves of the formulation E5S5 before and after carbonation. The red dotted lines represent the regions related to dehydration (70-200 °C) and decarbonation (450-470 °C) of nesquehonite.

Mechanical and physical properties

All the formulations were tested in four-point bending after carbonation. Even with the addition of 35 wt% of filler, very interesting mechanical behaviour was observed in the composites reinforced with both types of fibres. Figure 10 shows a typical flexural stress/strain curve of all the formulations. All the samples presented a pronounced strain-hardening behaviour after the limit of proportionality. The serrated type of curve of the formulations with 5 wt% of fibres indicates that the fibres have good bonding with the matrix and prevent crack growth with the increase in stress. In this case, the fibres get “stretched” which requires higher forces to proceed with displacement. In the samples with 10 wt% of fibres, all the curves show a smooth behaviour due to the higher amount of reinforcing elements that prevent crack growth. The resulting effect is a remarkable plastic region with a modulus of rupture similar to the composites with low fibre content. It is also hypothesised that the high content of filler also contributes to this plastic behaviour. The fracture surface obtained by SEM of the E5S5 sample (Figure 11), demonstrates that the failure occurred by the combination of pull-out and breakage of the fibres, which is desirable for composites with high toughness/specific energy.

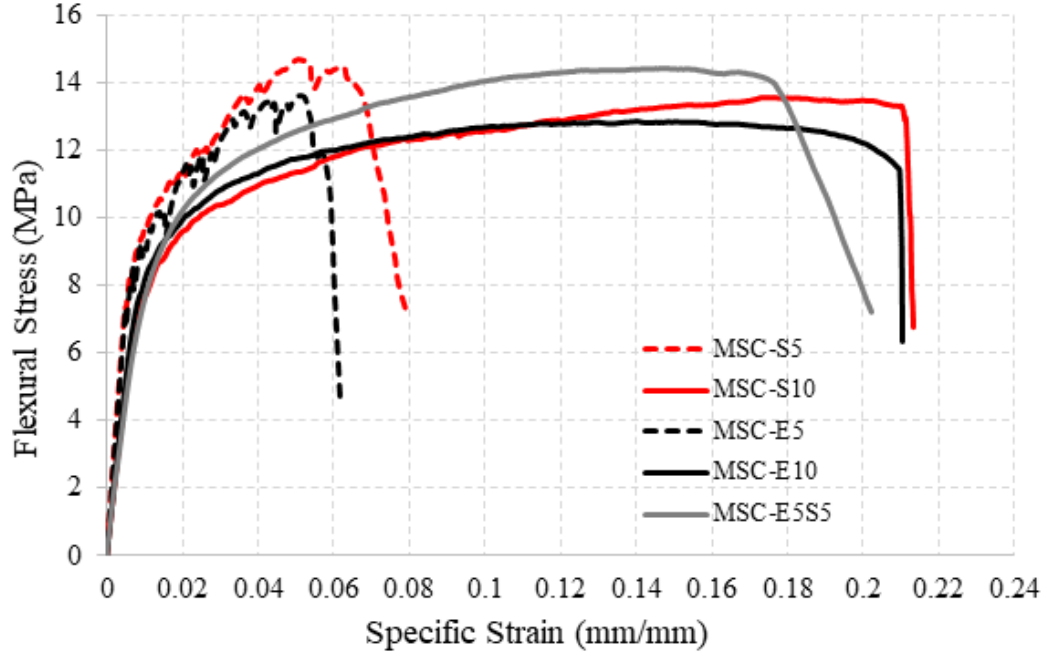


Figure 10 – Four-point bending stress-strain curves of all the formulations.

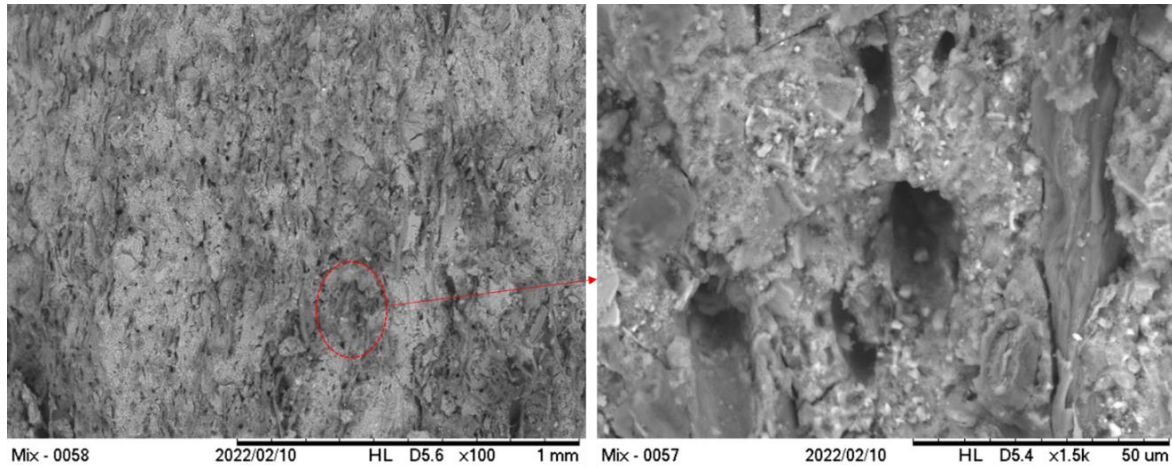


Figure 11- Fracture surface of E5S5 formulation after four-point bending test. The magnified image shows the effect of fibre pull-outs.

Table 3 summarises the four-point bending tests results of all formulations. Interestingly, independently of the type of fibre or fibre content, all the conditions presented very good results for MOR, with no relevant statistical differences among them. Nevertheless, the hybrid condition, using both types of fibres presented the highest average, 13.95 MPa. For comparison reasons, conventional fibre-cement (with OPC) reinforced with cellulose fibres or with synthetic fibres (PP or PVA) produced by the same method have a MOR between 8-15.8 MPa (Ballesteros et al., 2019; Fioroni et al., 2020; Gonzalo Mármol & Savastano, 2017; Santos et al., 2015). In addition, in most cases, filler content ≤ 25 wt% is used.

In terms of the different types of fibre, it is possible to observe that the composites with bleached eucalyptus pulp had higher MOE than those produced with sisal fibres. However, the LOP and especially the specific energy of the composites with sisal microfibres were higher than the ones with eucalyptus. This effect is explained by the different surface morphology and dimensions of the fibres. The bleached eucalyptus fibres are considerably shorter than the sisal fibres (Sisal ≈ 2.2 mm; Eucalyptus ≈ 1 mm) which results in a higher number of reinforcing elements per unit of mass, and generally bleached fibres have a rougher surface. These two characteristics contribute to better load

transfer between fibre and matrix in the early stages of deformation, which reflects in better MOE. On the other hand, the long sisal fibres have higher aspect ratio and better capacity to prevent crack growth, which is reflected in better LOP and energy required to fracture the composite. This effect can also be seen in the specific deflection at MOR, in which higher values were observed for all the samples reinforced with sisal fibres. Other intrinsic properties of each type of fibre, such as Young's modulus and tensile strength, may also contribute to the overall performance of the composites. The combination of both fibres (E5S5) is demonstrated to result in lower values of LOP and MOE (statistically irrelevant though), but the highest value of MOR and high specific energy at MOR of 8.45 kJ/m² was achieved by this formulation. The higher mechanical properties obtained in this study compared to other publications using the same binder system (MSH) are attributed to the additional carbonation process used in our composites (Gonzalo Mármol et al., 2019, 2018; Gonzalo Mármol & Savastano, 2017)

Table 3 – Summary of mechanical properties of all formulations obtained through four-point bending test. Eight samples were tested per condition. Same letters (a-c) indicate that there is no statistical difference.

Condition		MOR (MPa)	LOP (MPa)	MOE (MPa)	Specific Energy at MOR (kJ/m ²)	Specific deflection at MOR (mm/mm)
S5	Avg.	13.21^a	7.22^a	9298^b	2.66^c	0.061^c
	Stdev	1.70	0.73	1429.36	0.63	0.01
	COV	0.13	0.10	0.15	0.24	0.17
E5	Avg.	13.65^a	7.30^a	10801^a	2.05^c	0.047^c
	Stdev	0.92	0.53	606.43	0.23	0.00
	COV	0.07	0.07	0.06	0.11	0.07
S10	Avg.	13.31^a	5.52^b	6183^c	6.84^{a,b}	0.133^{a,b}
	Stdev	1.27	0.53	790.33	1.55	0.02
	COV	0.10	0.10	0.13	0.23	0.19
E10	Avg.	13.17^a	4.92^b	6420^c	6.43^b	0.123^b
	Stdev	2.37	0.67	643.05	2.15	0.03
	COV	0.18	0.14	0.10	0.33	0.24
E5S5	Avg.	13.95^a	4.80^b	6046^c	8.45^a	0.153^a
	Stdev	0.98	0.53	581.11	1.10	0.02
	COV	0.07	0.11	0.10	0.13	0.12

Table 4 gives the overall physical properties (bulk density, apparent porosity, and water absorption) of all the formulations. The first thing to notice is that even though the S10, E10, and E5S5 conditions have twice the amount of fibres as the other formulations, the water absorption and apparent porosity had only a small increase. As shown in the XRD results, the composites with more fibre content had a higher degree of carbonation (higher content of nesquehonite), which reduced the content of pores in the composite (compared to a non-carbonated sample). We hypothesise that the carbonation process can be used to produce composites with high-fibre content without compromising the physical properties, often negatively affected by the increase in fibre loading. In fact, the physical properties of the E10, S10, and E5S5 composites shown in Table 4 have higher values of bulk density and lower values of apparent porosity and water absorption than non-carbonated composites produced by the same methodology using 8 wt% of fibres and 25 wt% of filler (Gonzalo Mármol et al., 2019).

Table 4 – Summary of the physical properties of MgO-SiO₂ composites. Eight samples were tested per condition.

Condition		Weight gain after carbonation (%)	Bulk density (g/cm ³)	Apparent porosity (%)	Water absorption (%)
S5	Avg.	4.61	1.62	29.43	18.16
	Stdev	0.26	0.03	1.04	0.93
	COV	0.06	0.02	0.04	0.05
E5	Avg.	4.70	1.66	26.95	16.07
	Stdev	0.44	0.05	0.69	0.59
	COV	0.09	0.03	0.03	0.04
S10	Avg.	4.15	1.48	32.45	21.88
	Stdev	0.55	0.02	0.98	0.88
	COV	0.13	0.01	0.03	0.04
E10	Avg.	5.77	1.51	31.84	21.09
	Stdev	1.28	0.04	1.75	1.59
	COV	0.22	0.02	0.06	0.08
E5S5	Avg.	4.22	1.49	31.87	21.35
	Stdev	0.71	0.02	0.82	0.74
	COV	0.17	0.01	0.03	0.03

Microstructural characterisation

Figure 12 presents the microstructures obtained by SEM of composites with 10 wt% of sisal fibres and 10 wt% eucalyptus fibres. Since a backscattered electrons detector was used, it is possible to infer the identity of the microstructure constituents according to the brightness related to each phase. Having a higher concentration of calcium (which has the highest atomic weight), dolomite particles (from the filler) appear as the brightest components in the microstructure and are indicated as the green arrow. The M-S-H and nesquehonite matrix (and the residual brucite and periclase), being mainly composed of Si, Mg, C, O, and H, has lower brightness and is indicated with the blue arrow. The fibres are mainly composed of C, O, and H (lower atomic weight compared to the other elements) and appear as the component with the lowest brightness (indicated by the red arrow). As expected, the sisal fibres look longer than the eucalyptus fibres and appear to be better distributed in the MSH matrix. However, it is possible to observe minor gaps between the sisal fibres and the matrix (bottom images of Figure 10), which may explain the higher apparent porosity of the sisal reinforced composites and the lower MOE in comparison with the composites reinforced with eucalyptus fibres.

Figure 13 shows the microstructures of the transverse (thickness x width) and longitudinal (length x width) sections of the E5S5 fibre-cement board. It is difficult to differentiate both fibre types, but they are homogeneously distributed in the matrix. The transverse cross-section of this composite show that the fibres are mainly parallel to the surface of the board, which is related to the dewatering process used to produce the composites. It is also noteworthy that the process used to obtain the sisal fibres was successful in separating microfibrils from the original fibre bundles, which is clearly seen by the cross-section of the single fibres in the bottom micrographs of Figure 11.

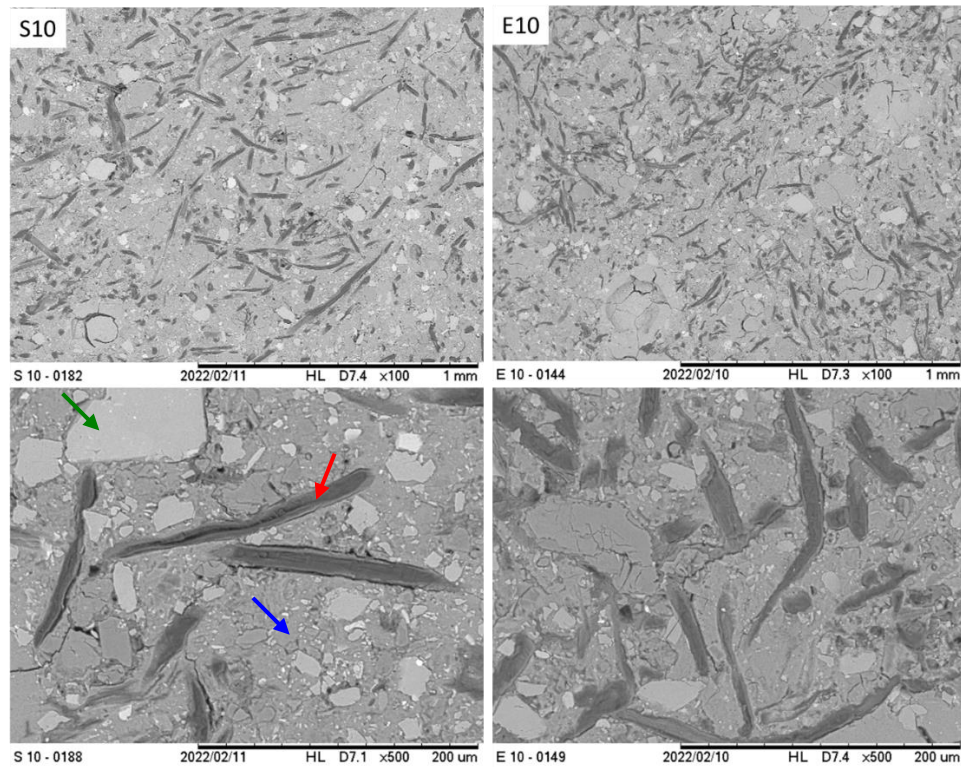


Figure 12 – Polished surface of MgO-SiO₂ composites with 10% of sisal (S10) and eucalyptus fibres (E10). The green arrow indicates filler particles (dolomite), the red arrow indicates the fibres, and the blue one shows the MSH matrix.

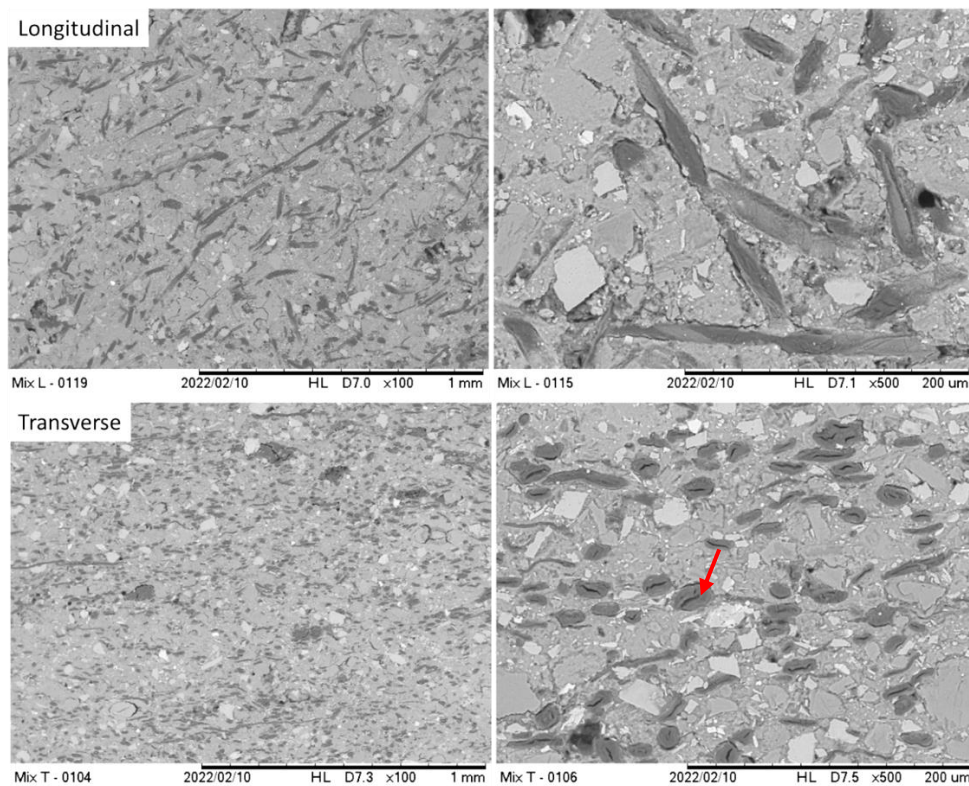


Figure 13 – Polished surface of hybrid formulation with 5% of sisal and 5% of eucalyptus fibres (E5S5) in the longitudinal and transverse sections. The fibre cross-section is indicated by the red arrow.

CONCLUSIONS

In this work, minimally processed sisal microfibres were used as reinforcement of low alkaline composites based on magnesium oxide and silica (MgO-SiO₂) cement with high filler content. The simple process to produce sisal microfibres resulted in partially delignified microfibres with high aspect-ratio and average fibre length above 2 mm. All the formulations presented similar weight percentage gain and porosity after the carbonation process that resulted in the formation of up to 15 wt% of a hydrated form of magnesium carbonate (nesquehonite), consuming hydrated MgO (brucite) and consequently improving the physical-mechanical properties of the composites and stability of the fibres.

All composites had a stress x strain curve in the four-point bending test with strain-hardening behaviour, in special the composites with 10 wt% of fibres, which had an average increase of 200% in the specific energy in comparison with the composites with 5 wt% of fibres. The hybrid formulation with 5 wt% of sisal microfibres and 5 wt% of eucalyptus pulp resulted in the best overall mechanical properties, with an average modulus of rupture (MOR) of 13.95 MPa, modulus of elasticity (MOE) of 6.05 GPa, and specific energy at MOR of 8.45 kJ/m². This work demonstrates the high potential of alternative lignocellulose microfibres as reinforcement of clinker-free fibre cement composites. The fibres and processes used in this work are seen as methods to decrease carbon emissions associated with building materials through three main approaches: incorporation of high-content of carbon-rich materials, such as vegetable fibres; use of clinker-free binders (therefore reducing CO₂ emissions related to clinker production); carbon storage in the form of stable carbonates.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest associated with the work presented in this paper.

DATA AVAILABILITY

Data on which this paper is based is available from the authors upon reasonable request.

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