

# Surface Esterification of Sisal Fibres for use as Reinforcement in Cementitious Matrix

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Received: August 24, 2018; Revised: March 22, 2019; Accepted: May 19, 2019

Vegetable fibres have been shown to be promising as reinforcement in composites because they are abundant, renewable, and low cost. However, the fibre–matrix interaction can be damaged by dimensional variation of vegetable fibres, due to moisture variations. The alkaline medium of cementitious matrix is aggressive to natural fibres, compromising their durability. The aim of this study was to modify sisal fibres (*Agave sisalana*) by esterification with acyl chlorides to improve their stability and compatibility with the cementitious matrix in order to optimize the performance and durability of composites. The esterified fibres were characterized by moisture absorption, tensile tests, Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM) and the composites by bending tests and SEM. The results showed that esterification changed both the morphology and physical properties of sisal fibres. The composite produced using esterified fibres with octanoyl chloride maintained the properties of 28 to 90 days of age, which represented an improvement in the fibre stability compared to natural fibre composite.

**Keywords:** *Vegetable fibres, sisal, esterification, composites, durability.*

## 1. Introduction

Recent research has sought the use of more durable, profitable, and, particularly, sustainable materials. Cement-based matrices reinforced with lignocellulosic fibres have been shown to be promising when the goal is to obtain a low-cost material that allows energy savings and environmental preservation. Fragile matrices, such as cement-based matrices reinforced with fibres, have gained importance as a building material worldwide, mainly due to the possibility of producing thin elements in various shapes and with a high toughness<sup>1,2</sup>.

Research about the use of vegetable fibres as reinforcement of cementitious matrices is carried out in this context. In Brazil, coconut and sisal fibres are the most researched, as they can be easily obtained and extracted. Sisal fibres are an interesting option for reinforcement due to their high elasticity modulus, tensile strength, and availability<sup>3,4</sup>. Vegetable fibres have a low cost compared to synthetic fibres, and they are considered as unlimited resources<sup>5,6</sup>. However, vegetable fibres present disadvantages, including their durability in the cementitious matrix and maintenance of the integrity of the fibre–matrix interface<sup>7,8</sup>. Lignocellulosic fibres are deteriorated by the high alkalinity of the cementitious matrix, resulting in a decrease in composite performance over time, especially the toughness<sup>7,8</sup>.

Furthermore, in natural weathering conditions, the composite absorbs water, resulting in different volume variations of the cement matrix and the fibres. A loss of adhesion between fibre and cementitious matrix has been observed as a result of these water-absorption cycles, resulting in deterioration of the composites' mechanical properties<sup>9,10</sup>.

Therefore, the great challenge of the research on vegetable fibres is to minimize these undesirable properties.

To improve the performance of vegetable fibres used as reinforcement in cement-based composites, several alternatives have been studied such as impregnation with blocking agents and water-repellents, the use of sealing agents in matrix pores, reducing the matrix alkalinity, and combinations of impregnation and matrix modification<sup>11-13</sup>.

Lima and Tolêdo Filho<sup>14</sup> concluded that the use of 30% by mass content of metakaolin to replace the cement produced a calcium-hydroxide-free matrix that was less aggressive to the fibres, improving the maintenance of toughness of composites over time.

Fibre expansibility due to increasing moisture in the composite can create tensile stresses and may produce cracking since cement is a fragile material. In addition, the fibres shrinkage by reducing the composite moisture content also causes detachment of the fibres in the matrix, damaging the composite performance<sup>15</sup>. Achieving better fibre–matrix adhesion and reducing the moisture absorption of vegetable fibres by applying chemical or physical treatments can improve the performance of composites with vegetable fibres<sup>9,16,17</sup>.

In order to overcome these drawbacks, it is necessary to undertake a structural modification of the fibre surface. The cellulose chemical moieties exploited for this purpose are its hydroxyl functions, which are the source of well-known reactions used to prepare a wide array of cellulose derivatives. In the present context, these modifications must be limited to the superficial OH groups in order to preserve the integrity of the fibres and thus their mechanical properties<sup>18</sup>.

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This chemical modification of different cellulose substrates by esterification was studied by Pasquini et al<sup>18</sup>; using small amounts of reagents, the authors observed the loss of the highly polar characteristic of pulp, resulting in a strongly hydrophobic material without degradation of other physical and mechanical properties of the fibre. Pasquini et al<sup>19</sup> observed that chemical modification by esterification resulted in improved dispersion and adherence between cellulosic fibres and low-density polyethylene matrix in addition to the increased hydrophobic nature of the composites.

In this sense, the goal of this study consisted in surface chemical modification of sisal fibres through esterification reactions with acyl chlorides. The proposed treatment aimed at hydrophobization of the fibres, since the lower moisture absorption results in minor dimensional variation of the fibres. The fibre modification will reduce water absorption from the matrix pore and may improve the performance and durability of vegetable fibres as reinforcement in the cement matrix.

## 2. Experimental

### 2.1 Chemical modification of sisal fibres

The chemical modifications of sisal fibres by esterification reactions with acyl chlorides were performed according to Pasquini et al<sup>18,19</sup>. The modifying agents were stearoyl chloride, lauroyl chloride, and octanoyl chloride. Six modifications were made using two different solvents, dimethylformamide (DMF) and toluene, for each modifying agents. Pyridine was used as the catalyst.

The different proposed modifications are based on the following: i) changing the solvent medium will result in the difference in the extent of modification in the fibre structure, and ii) using modifiers with different sizes of aliphatic chains results in different degrees of hydrophobization of the fibres.

In the first case, when using the solvent DMF, because it is a swelling solvent for cellulose, will promote the inner modification in the fibres, while using toluene, because it is a non-swelling solvent for cellulose, the modification will be more concentrated in the external surface of the fibres preserving the original internal structure. This preservation is important for maintaining the mechanical properties of the fibres.

Fibres of 5 cm length were esterified using 1 mL of modifier agent for each gram of fibre. The quantities of reagents used in the esterification reactions are presented in Table 1. After mixing the fibres with reagents, the material was left under reflux for 2 h. Lastly, the material was filtered, washed with ethanol and acetone, and then oven dried. The mass loss of the fibres was calculated by the ratio between the mass variation with treatment and initial dry mass of the fibres.

### 2.2 Thermogravimetric analysis (TGA) of the fibres

TGA curves were obtained in a DTG-60H (Shimadzu) using aluminium pans. The experiments were carried out under continuous nitrogen flow of 50 mL min<sup>-1</sup> and the temperature ramp was set at 10 °C min<sup>-1</sup>. The weight was recorded from 25 to 600 °C.

### 2.3 Moisture absorption of the fibres

The fibres were oven dried at 100 °C for 24 h and then placed in a desiccator with a saturated solution of potassium nitrate (KNO<sub>3</sub>) to create an atmosphere with 95% humidity. The fibres were analysed for 120 h, with mass measurements being performed after 1, 2, 24, 48, 72, and 120 h.

### 2.4 Tensile test of the fibres

In order to evaluate the influence of the esterification process on the mechanical properties of the fibres, tensile tests were carried out as described by Motta *et al.*<sup>4</sup> and ASTM D3822 / D3822M - 14<sup>20</sup>. The tensile tests were realized in an Instron universal machine (model 5982) with a load cell of 1 kN at a speed of 2 mm/min. Twenty specimens were tested for each treatment. The fibres were in equilibrium with the environment, with humidity of 7% on average during the direct tensile test.

The micrographs were obtained in an optical microscope (Olympus, model CX40). The images were obtained with a Zeiss AxioCam camera (model ICc5). The dimensions of the fibres were determined by image analysis using the ZEN lite application, version 2012. Each specimen was analyzed before test. From the average of the dimension measures of the fibre, the cross-sections of each specimen were determined for the tensile test.

**Table 1.** Reagents amounts used in esterification reactions.

Fibre mass (g)	Solvent volume (mL)		Modifier agent volume (mL)			Catalyst volume (mL)
	DMF	Toluene	Stearoyl chloride	Lauroyl chloride	Octanoyl chloride	Pyridine
45	800	—	45	—	—	45
45	800	—	—	45	—	45
45	800	—	—	—	45	45
45	—	800	45	—	—	45
45	—	800	—	45	—	45
45	—	800	—	—	45	45

## 2.5 X-ray Diffraction (XRD)

The X-ray diffractograms of modified and unmodified sisal fibres were obtained at room temperature within a  $2\theta$  ranging from  $5$  to  $35^\circ$  and a scan rate of  $2^\circ \text{ min}^{-1}$ . The equipment used was a Shimadzu LabX XRD-6000 diffractometer operating at  $40 \text{ kV}$  with a current of  $30 \text{ mA}$  and  $\text{Cu K}\alpha$  radiation ( $1.5406 \text{ \AA}$ ). Before performing the XRD, all samples were dried at  $50^\circ\text{C}$  for  $12 \text{ h}$  in an air-circulating oven. The crystallinity index (CrI) of the samples were determined by the Segal et al<sup>21</sup> method, as shown in Equation (1).

$$\text{CrI} = \left[ \frac{I_{200} - I_{\text{AM}}}{I_{200}} \right] \times 100 \quad (1)$$

In Equation (1), CrI expresses the relative degree of crystallinity,  $I_{200}$  is the maximum intensity of the 200 lattice diffraction at  $2\theta = 23^\circ$ , and  $I_{\text{AM}}$  is the intensity of diffraction at  $2\theta = 18^\circ$ .  $I_{200}$  represent both crystalline and amorphous regions, while  $I_{\text{AM}}$  represent only the amorphous portion.

## 2.6 Mixing, moulding, and curing of composites

The process of mixing and preparing the specimens was a simulation of the Hatschek process for moulding fibre cement. The fibres ( $5 \text{ cm}$  length) were mixed with cement and water with subsequent removal of excess water by vacuum. Initially all the water was added to the mixer, followed by cellulose pulp, which were dispersed for  $5 \text{ min}$ . Cement was then added and mixed for over  $5 \text{ min}$ . Then, the sisal fibres were added and mixed for another  $5 \text{ min}$ . The mixture was inserted into the mould, subjected to water drainage, and tamped with a socket. Finally, the composite was compressed with a pressure of approximately  $3.2 \text{ MPa}$ <sup>22</sup>. The compression was maintained for  $5 \text{ minutes}$ . The plates were square shaped with a width of  $200 \text{ mm}$  and average thickness of  $7.5 \text{ mm}$ . For each formulation, three mouldings were conducted. Figure 1 provides a sketch illustrating the sequence of preparation of the composites.

The chemical composition of the used cement is described in Table 2. The composites were produced with volume proportions of  $95\%$  cement CIII 40 RS (a cement with blast furnace slag as the ASTM Type IS),  $3\%$  sisal fibres (natural and modified), and  $2\%$  cellulose pulp (eucalyptus bleached Kraft pulp). The percentages were calculated by volume proportions of the total volume of the composite.

The cellulose pulp was ground in a blender before being added to the mixture. The use of cellulose pulp aims to retain cement in the composite during vacuum suction. Therefore, in this work, there was no concern with the characterization and dispersion of cellulose pulp. The cellulose pulp was used in the same way in all the composites so that its influence was homogeneous. This study did not aim to optimize the composites, but to compare the different treatments. Fiber content and fiber length were fixed based on previous studies, which facilitated both the treatment of fibers and the molding of composites. The initial mass proportion of solids in the mixture was  $45\%$ .

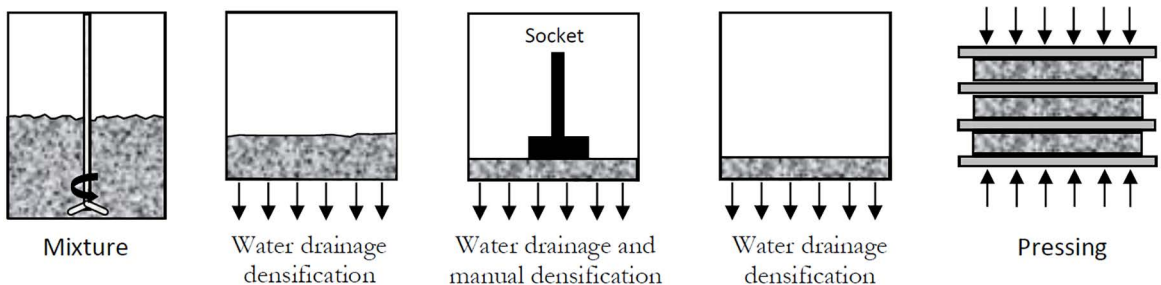
**Table 2.** Chemical composition of the cement.

Chemical composition	Percentage
$\text{SiO}_2$	24.98
$\text{Al}_2\text{O}_3$	7.61
$\text{Fe}_2\text{O}_3$	2.32
$\text{CaO}$	52.85
$\text{MgO}$	3.90
$\text{Na}_2\text{O}$	0.15
$\text{K}_2\text{O}$	0.28
$\text{SO}_3$	2.80
Loss on ignition	3.58

The curing of molded composite plates was carried out in the chamber with a relative humidity above  $95\%$  and temperature of  $(23 \pm 2)^\circ\text{C}$  during the first  $28$  days of ageing. After  $28$  days the specimens remained in an environment of  $50\%$  humidity and temperature of  $(23 \pm 2)^\circ\text{C}$ . The specimens for the bending test were obtained by cutting the plates in approximate dimensions of  $200 \text{ mm}$  length  $\times$   $40 \text{ mm}$  wide.

## 2.7 Composite bending test

The specimens were subjected to bending tests at ages of  $28$  and  $90$  days in order to determine the flexural strength, elasticity modulus, and toughness of composites. Four specimens were tested for each formulation at each age. The bending tests were carried out with parameters based on the recommendations of RILEM<sup>23</sup>, using an Instron universal machine (model 5982) with a  $5 \text{ kN}$  load cell.



**Figure 1.** Sketch showing the mixing and moulding of the specimens.

The applied method was four points and an automatic speed of 2 mm/min (Figure 2). The span was of 150 mm e the deflection in the center of the span was measured with an Instron LVDT with a 5 mm course. The samples were tested in natural air at equilibrium moisture content (about 8%).

The toughness of the composite was determined by fracture energy ( $\text{N.m/m}^2$ ) as proposed by Roma et al<sup>24</sup>. The specific energy was calculated from the area under the load-deflection curve divided by the cross-sectional area of the specimen.

### 2.8 Scanning Electron Microscopy (SEM)

To evaluate the modification of the morphology of the modified fibres, SEM analyses were carried out. The sisal fibres were oven dried at 100 °C and coated with gold. The composite samples were taken from the fracture section of the bending test specimens, oven dried at 100 °C, and coated with gold. The equipment used was a Hitachi TM 3000 scanning electron microscope at 15 kV, with backscattered electron detector.

The samples were previously coated with gold using a sputtering equipment (LEICA Metallizer EM SCD 050) under vacuum for 120s at 50mA.

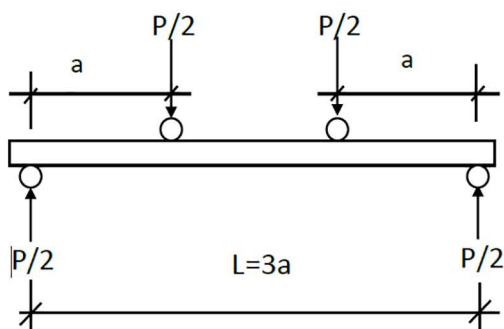
## 3. Results and Discussion

### 3.1 Chemical modification of sisal fibres

The treatment of fibres with dimethylformamide (DMF) solvent resulted in significant mass loss and reduction of cross section dimension. When toluene solvent was used, the mass loss and cross section shrinkage was smaller and the reaction was less intense and more superficial in the sisal fibres, as can be seen in Table 3. This is because DMF is a swelling solvent for fibres and changes occur more intensively within their structure. The esterification reaction with acyl chlorides generally degrades part of the fibre structure and this mass loss is due to the hydrolysis of cellulose (preferably the amorphous fraction) and hemicellulose that occurs during the reaction<sup>18,19</sup>.



a)



b)

**Figure 2.** Bending tests of composites: a) test in progress; b) method schema used.

**Table 3.** Mass loss and cross section reduction of the esterified fibres.

Solvent	Modifier Agents			Mass loss (%)	Cross section dimension reduction (%)
	Stearoyl	Lauroyl	Octanoyl		
DMF	X	—	—	25.76	50.57
DMF	—	X	—	31.25	40.49
DMF	—	—	X	35.63	43.00
Toluene	X	—	—	10.54	16.15
Toluene	—	X	—	11.07	31.42
Toluene	—	—	X	21.35	39.05

When the fibres are esterified with DMF, the modification occurs to a greater extent, and thus a greater mass loss was expected for this solvent.

### 3.2 Thermogravimetric Analysis (TGA) and crystallinity

Thermogravimetric analysis was performed for natural fibres and all the modified fibres, and the TG curves and degradation temperatures are presented in Figure 3 and Table 4, respectively. From the TG curves in Figure 3, a first mass loss event around 100 °C can be verified, this loss of mass can be attributed to the loss of water present in the fibres. It can be seen that the water losses for the modified samples are lower than for the untreated fibre, and this is a result of the modification that hydrophobised the fibres, and consequently reduced the moisture absorption thereof. The curves also show a second main degradation event of the fibres, between 200 °C and 400 °C. The fibres modified using DMF as a solvent had higher thermal stability compared to natural and modified fibres in toluene. The modifications using DMF as solvent, result in a modification inside the fibre, and the insertion of the modifier molecules result in a protection for the fibres. The removal of amorphous cellulose and hemicelluloses, which are compounds that have low degradation temperatures, leads to a greater concentration of crystalline cellulose and lignin in the resulting fibre, whose compounds have higher thermal stability. But, as can be seen from the crystallinity index (CrI) determined from XRD, presented in Table 4, independently of the modifier and solvent employed, the CrI of all modified fibres are very similar. As a consequence, the changes in the thermal stability cannot be attributed to the changes in the crystallinity of the fibres. When comparing the CrI of the unmodified sisal fibres with the modified fibres, it is possible to observe the increase of the CrI, that can be attributed to the removal of hemicellulose and some amorphous cellulose fractions, during the modifications. This confirms the data on the mass loss observed during the esterification process and discussed in the previous item.

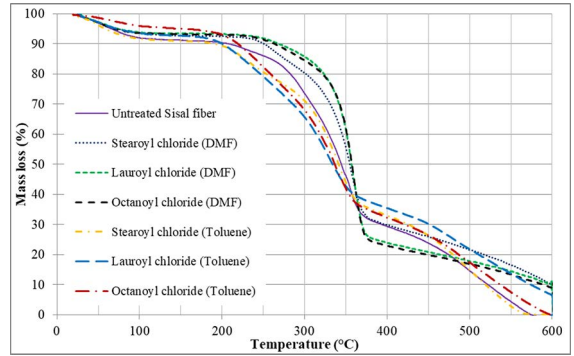


Figure 3. TGA curves of untreated sisal fibre and modified fibres.

### 3.3 Moisture absorption of the fibres

From the data of moisture absorption, it was possible to analyse which chemical modifications provided greater hydrophobization of fibres, which can reduce the dimensional instability of the fibres due to the moisture variation.

It can be observed in Figure 4 that there is a tendency of the fibres to reach maximum absorption by 120 h. The maximum moisture absorption of natural sisal fibres is approximately 9%. This absorption was in a medium with 95% humidity, the absorption would be greater for the fibres in contact with water, when they would have completely saturated pores.

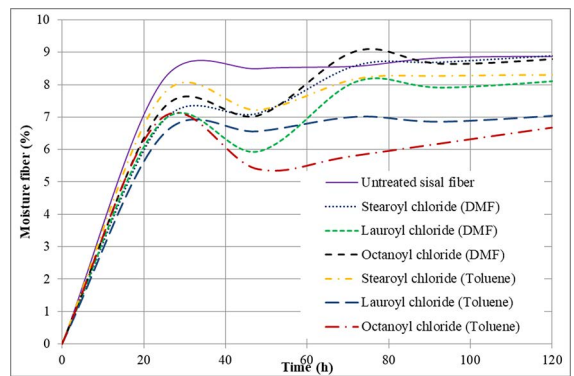


Figure 4. Isotherms of untreated sisal fibres and modified fibres.

Table 4. Degradation temperatures of the fibers, obtained from TGA ( $T_i$  = Initial degradation temperature) and DTG ( $T_{Max}$  = Maximum degradation temperature) results, and crystallinity index (CrI) determined from the XRD.

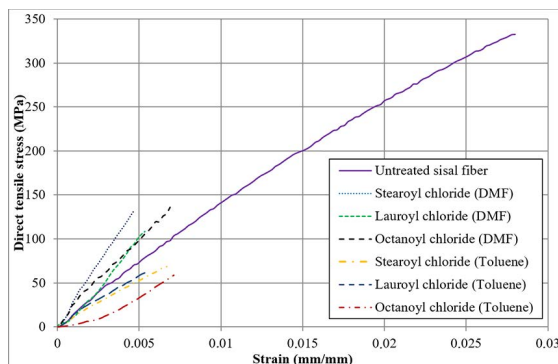
Sample	CrI (%)	$T_i$ (°C)	$T_{Max}$ (°C)
Sisal	74	208	353
Stearoyl Chloride (DMF)	79	224	356
Lauroyl Chloride (DMF)	79	228	357
Octanoyl Chloride (DMF)	80	222	357
Stearoyl Chloride (Toluene)	79	190	343
Lauroyl Chloride (Toluene)	80	182	337
Octanoyl Chloride (Toluene)	80	189	336

In the test, the absorption of the fibre walls with the different treatments was compared. The fibres that showed the highest reduction of moisture absorption (26%) were the sisal fibres modified with octanoyl chloride using toluene as solvent. Treatment with lauroyl chloride also presented a reduction in moisture absorption with both types of solvents. The esterified fibres with stearoyl chloride and octanoyl chloride in DMF showed no reduction in moisture absorption.

### 3.4 Tensile test of the fibres

It was found that despite the modifications, the use of DMF as solvent resulted in increased mass loss of the fibres and they presented the highest tensile strength compared to other modified fibres (Table 5). This may be associated with mass loss of the fractions of amorphous cellulose and hemicelluloses and consequently an increasing concentration of crystalline cellulose in the resulting fibre structure. The crystalline cellulose is stronger and more rigid. However, it should be noted that there was a reduction in tensile strength of all modified fibres, including when toluene was used as the solvent, compared to natural fibre, which was the expected behaviour given that degradation of part of the fibre structure occurs even in toluene. It is important highlight that the fibre structure degradation is related mainly to the cellulose chains degradation<sup>18,19</sup>.

However, the values of the elasticity modulus of the treated fibres improved, reaching an increase of almost three times (DMF and stearoyl chloride) or remained similar to that of the natural fibres. This fact is most evident in modifications using DMF solvent. This can also be explained by the higher degree of modification with DMF due to the insertion of the aliphatic chains of acyl chlorides in the fibre structure, as observed by Freire et al<sup>25,26</sup>. This behaviour can be clearly observed in Figure 5, with the fall of tensile strength and the elevation of the elasticity modulus of the fibres modified with respect to the natural fibres. This rise of the elasticity modulus combined with a reduction of moisture absorption can result in better performance as reinforcement in cementitious composite.



**Figure 5.** Typical stress-strain diagram obtained in tensile tests of the fibres.

It is known that chemical modifications of fibres are processes that even if they are well controlled, still lead to a certain degradation of the same, and that result in losses of mechanical properties. Research<sup>9,27</sup> showed that sisal fibres are completely deteriorated after ageing in cement matrix, so if the fibres modification ensure the maintenance of the properties in the composite over time, these initial losses would be compensated. The mechanical properties were affected by the esterification but still remain better than other natural vegetable fibres or other synthetic fibres used as reinforcement in composites. If the treatment results in better fibre performance, then they are still appropriate for composite reinforcement.

### 3.5 Composite bending test

The average results obtained in the bending tests of the composites at ages of 28 and 90 days can be seen in Table 6.

In general, all the esterification reactions reduce the mechanical properties of the fibres and thus the composite. Note that the initial toughness of composites with treated fibres was lower than that of the natural fibre composite. The elasticity modulus and tensile strength were also reduced with treatment, although less intensely, especially the composite produced using esterified fibres with octanoyl chloride and DMF solvent.

**Table 5.** Average results of tensile tests of the fibres.

Fibres	Tensile strength (MPa)	Standard deviation	Maximum strain ( $\mu\text{m}/\text{mm}$ )	Standard deviation	Elasticity modulus (GPa)	Standard deviation
Stearoyl chloride (DMF)	149.1	29.0	4.8	0.5	35.6	7.7
Lauroyl chloride (DMF)	113.7	18.8	4.7	0.9	28.5	5.6
Octanoyl chloride (DMF)	138.1	2.1	7.6	0.9	24.4	4.1
Stearoyl chloride (Toluene)	70.0	13.0	6.8	1.4	13.6	1.9
Lauroyl chloride (Toluene)	62.7	13.8	5.0	1.2	18.0	3.9
Octanoyl chloride (Toluene)	57.5	10.4	6.4	1.0	12.7	0.8
Untreated	322.3	69.2	29.19	3.9	13.8	2.7

**Table 6.** Results of bending tests of composites.

Modification	28 days			90 days		
	Tensile strength (MPa)	Elasticity modulus (GPa)	Toughness (N.m/m <sup>2</sup> )	Tensile strength (MPa)	Elasticity modulus (GPa)	Toughness (N.m/m <sup>2</sup> )
Stearoyl chloride (DMF)	1.89 (0.29)	10.29 (1.85)	102.1 (13.9)	2.36 (0.29)	10.72 (1.68)	16.60 (0.99)
Lauroyl chloride (DMF)	3.31 (0.69)	12.08 (2.12)	104.1 (9.2)	3.37 (0.74)	9.78 (1.57)	52.2 (5.1)
Octanoyl chloride (DMF)	4.86 (1.04)	14.49 (1.09)	84.2 (8.0)	5.79 (0.50)	11.27 (1.05)	138.0 (15.7)
Stearoyl chloride (Toluene)	3.06 (0.13)	9.63 (0.61)	85.3 (7.6)	1.47 (0.23)	10.08 (1.02)	24.3 (3.09)
Lauroyl chloride (Toluene)	5.34 (1.36)	11.30 (1.12)	242.6 (42.9)	1.91 (0.13)	7.61 (0.67)	64.0 (7.2)
Octanoyl chloride (Toluene)	0.61 (0.12)	8.43 (1.82)	3.4 (0.1)	1.08 (0.05)	8.58 (0.96)	3.8 (0.4)
Untreated	6.97 (1.41)	17.88 (2.15)	1636 (245)	6.42 (1.60)	13.53 (3.26)	802 (120)

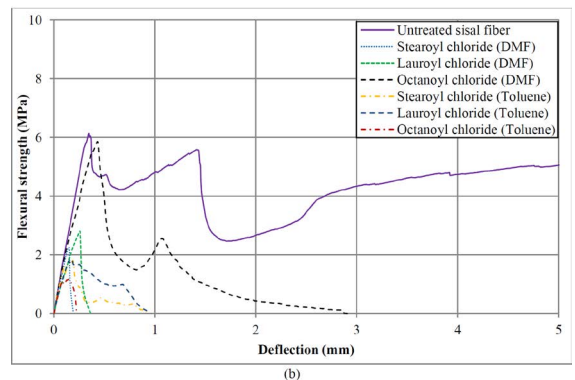
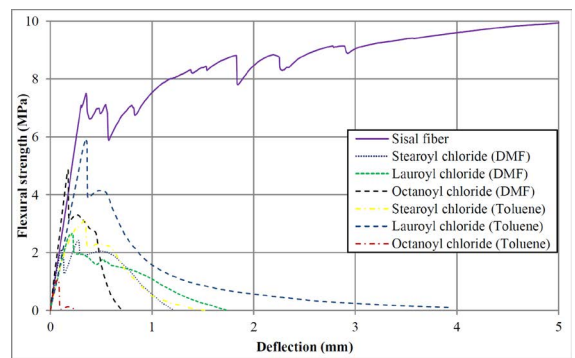
The natural fibre composite did not undergo a significant loss in its flexural strength between 28 and 90 days. In this case the matrix has determined the composite's strength before the first crack and remains with age, with the progression of the cement hydration. The increased adhesion between matrix and fibres could explain the reduction in the toughness, but the hardening of the matrix and the better adhesion with fibres should also increase the modulus of elasticity. However, the elasticity modulus was reduced and the toughness decreased by approximately 50%, indicating a possible deterioration of the sisal fibres in the cementitious matrix at 90 days.

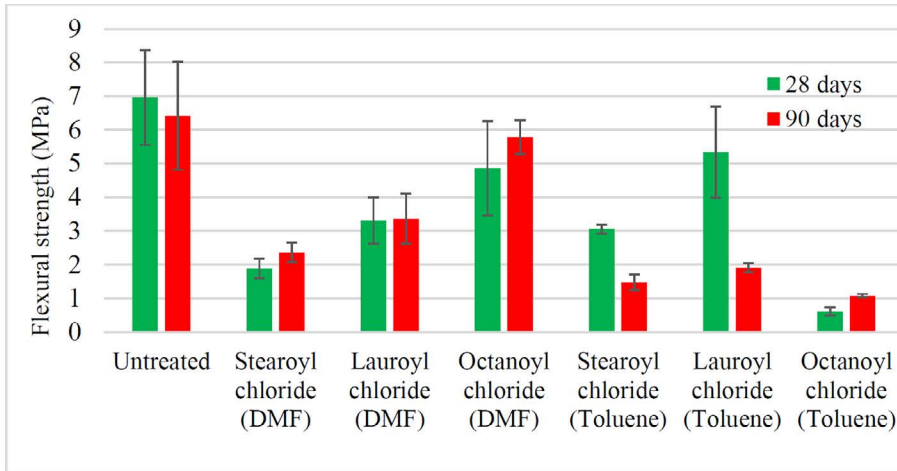
The octanoyl chloride and DMF modified fibre composite presented stability of flexural strength and toughness with ageing. This maintenance of toughness with age may be indicative of better fibre durability in the cement matrix.

The graphs presented in Figure 6 show variations of bending strength with deflections in the bending tests of the composites at ages of 28 and 90 days. It was observed at 28 days that after the stress peak, there was a decrease in stress for all treated fibre composites, which did not occur for the fibre without treatment composite. The fibre without treatment composite presented a growing stress in the post-peak zone, where the high strength of natural fibres kept or even increased the stress level. This behaviour explains the greater toughness value of natural composite fibres at 28 days compared to other treated fibres (Figure 7).

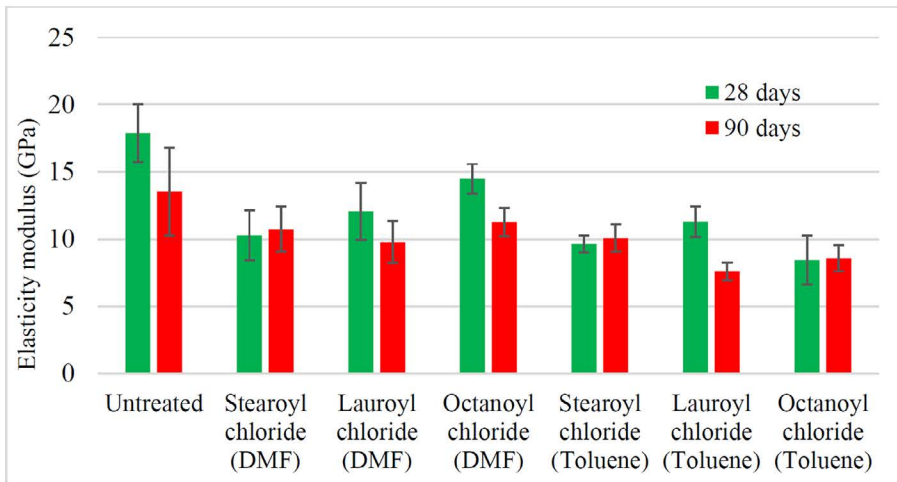
However, at the age of 90 days, it was observed that the natural fibre composite presented a fall in strength after the peak, resembling the behaviour of treated fibre composites. That is, natural fibres have undergone deterioration and a loss of their strengthening and reinforcement ability.

The stress-deflection curve of the octanoyl chloride and DMF modified fibre composite presented the same shape at ages of 28 and 90 days, indicating stability of the fibres and composite with ageing. Natural aging tests are in progress now, as a continuation of the present research program.

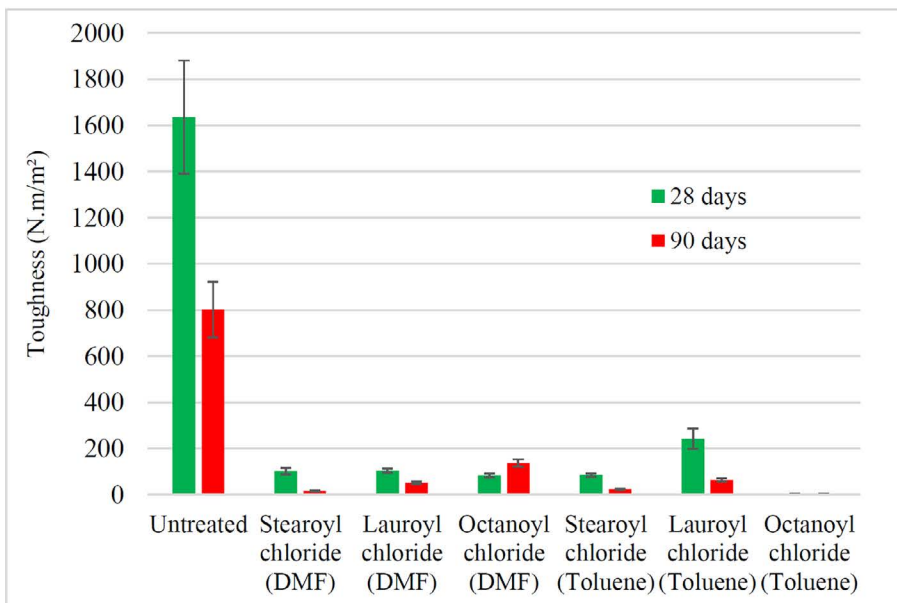
**Figure 6.** Typical behaviour of composites in the bending test: a) at the age of 28; b) at the age of 90 days.



(a)



(b)



(c)

**Figure 7.** Mechanical properties of composites in the bending test at the age of 28 and 90 days: a) Flexural strength; b) Elasticity modulus; c) Toughness.

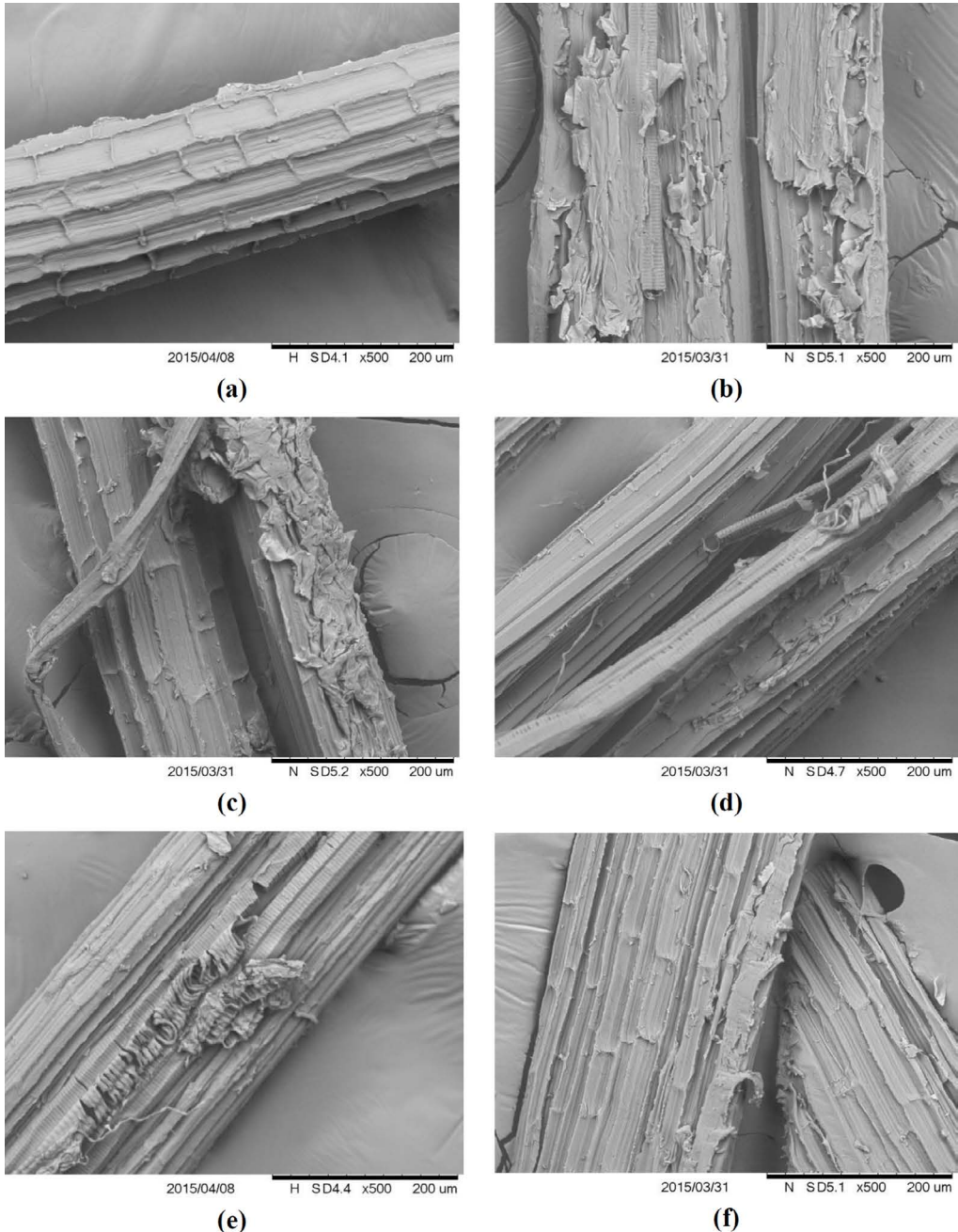


The toughness of composites with treated fibres is much lower than natural fibres composites in the early ages (10 times smaller) as showed at Figure 7, but is of the order of magnitude of toughness obtained in other works with vegetable fibres like Savastano et al<sup>28</sup> that considered the viable composite application as a component for the building industry. In addition, untreated fibres undergo mineralization and deterioration over time, losing completely the integrity and capacity of reinforcement, as well shown by Gram<sup>27</sup> and Wei and Meyer<sup>9</sup>.

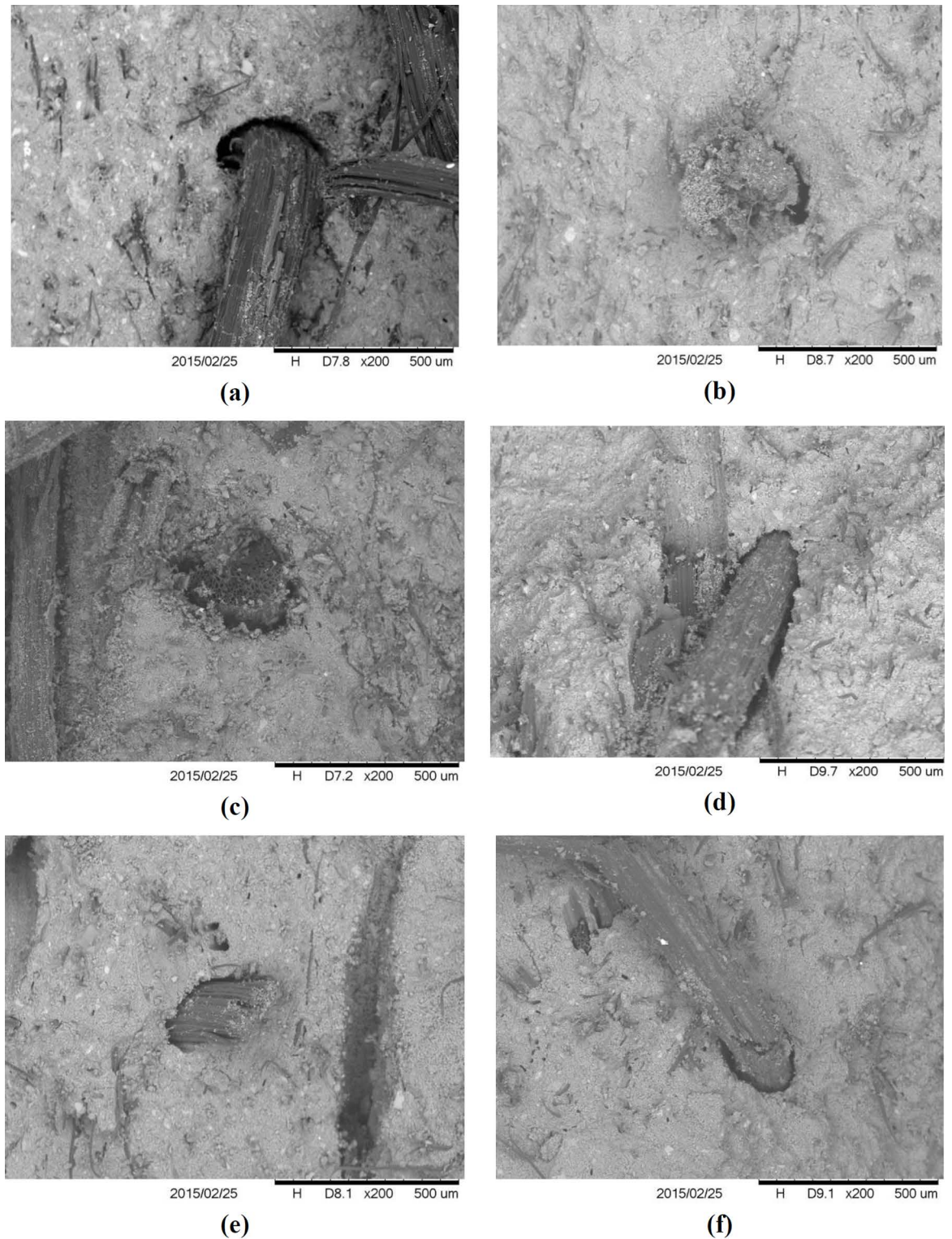
### 3.6 Scanning Electron Microscopy (SEM)

The micrographs in Figure 8 show that chemical treatment did not alter the original structure of sisal fibres. However, the surface morphology of the sisal fibres underwent some minor changes compared to the original, showing slight signs of deterioration, visible from the peeling and shredding on the surface of the fibres.

The composites' rupture section and the interface between the fibre and cementitious matrix can be observed in Figure 9.



**Figure 8.** (a) Natural sisal fibre, (b) modified fibre with lauroyl chloride and DMF, (c) modified fibre with stearoyl chloride and toluene, (d) modified fibre with stearoyl chloride and DMF, (e) modified fibre with octanoyl chloride and toluene, and (f) modified fibre with octanoyl chloride and DMF.



**Figure 9.** Fibre-matrix interface at age of 28 days: (a) natural fibre, (b) modified fibre with lauroyl chloride and toluene, (c) modified fibre with stearoyl chloride and toluene, (d) modified fibre with stearoyl chloride and DMF, (e) modified fibre with octanoyl chloride and toluene, and (f) modified fibre with octanoyl chloride and DMF.

Micrographs of the rupture section of composites in flexural testing at the age of 28 days were obtained.

It was observed that the stress generated in the bending of natural fibre composite was insufficient to fracture the fibres, which can be seen pulled out from the matrix in the micrograph in Figure 9a. However, in composites of fibres treated with toluene as solvent, the fibres underwent further deterioration of mechanical properties: notice that the fibres were broken during the composite bending test (Figures 9b, 9c, and 9e). In the rupture section of the composites with fibres treated with DMF as solvent (Figures 9d and 9f), pulled out fibres and fractured fibres can be seen. This behaviour shows a better performance of these fibres among the modified ones, as noted in the fibres' mechanical properties. There is a gap between the fibres and the matrix in all of the analysed composites; however, in treated fibre composites, the space between the fibres and the matrix has been reduced, probably by reducing the hydrophilicity of the treated fibres, also reducing the dimensional variation of the fibres. This has been observed on all micrographs analyzed in which are presented in Figure 9 only a typical example obtained for each composite.

#### 4 . Conclusions

The treatments that give the greatest modification of the fibres were those using toluene as solvent, which resulted in inferior moisture absorption of the fibres. However, these treatments resulted in further deterioration of the fibre mechanical properties. The fibre micrographs showed that chemical treatments did not change the original morphology significantly but revealed some signs of surface deterioration.

In the studied composites, it was observed that at 28 days of age, the natural fibre composite showed better properties than composites with treated fibres. However, the toughness of natural fibre composite decreased by 50% at the age of 90 days, which was not observed for the composite with octanoyl chloride and DMF treated fibres, which maintained its toughness. This conservation of toughness is indicative of the better preservation of the treated fibres in the matrix with age.

The composites with treated fibres presented lower initial toughness but have presented smaller loss with age. The researches have shown total loss of toughness with the aging of the composites with the untreated sisal fibres. The 90 days of age have shown this tendency, but only the natural aging for longer will allow to definitively conclude on the effectiveness of the treatment to improve the durability of the composites. This aging is in progress and the results will be published soon.

#### 5. Acknowledgements

The authors acknowledge CAPES for the financial support and for providing the periodicals portal ([www.periodicos.capes.gov.br](http://www.periodicos.capes.gov.br)). Dantas thanks CNPq for Scientific Initiation scholarship and Vieira thanks CAPES for Post-Doctoral scholarship. The authors also acknowledge to Machining Research Laboratory of the Faculty of Mechanical Engineering by the use of the Scanning Electron Microscope.

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