Colloidal silica to improve the interface between lignocellulosic fibre and matrix in extruded cement based composites

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ABSTRACT

The macro mechanical properties of extruded cement based composites depend on transition zone between fibre and matrix. The nanotechnology in construction materials is a research area with high potential. The objective of this work is to evaluate the treatment of colloidal silica on lignocellulosic fibre surface to improve mechanical performance of fibre-cement composites. In this study the ²⁹Si SSNMR (solid-state nuclear magnetic resonance) technique was used to evaluate the effectiveness of treatment of lignocellulosic fibres with colloidal silica. It was also observed some regions of the fibre where colloidal silica was impregnated by scanning electron microscopy micrographs (SEM). Fibre-cement composites reinforced with sisal fibres and bleached Eucalyptus Kraft pulps were produced by the extrusion process. Mechanical behaviour of the fibre-cement composites was evaluated by means of modulus of rupture and energy of fracture based on load-displacement curves (L-d curves) under continuous loading and 3-point bending arrangement. The average values of modulus of rupture and energy of fracture of the fibre-cement increased about 29% and 35%,
respectively, with application of the colloidal silica treatment. The use of colloidal silica improved the interface bond. The results of this study show an important way to control the adhesion of lignocellulosic fibre at cement matrix.

KEYWORDS: Extruded composites, nuclear magnetic resonance, nanoparticles, sisal fibre, Eucalyptus pulp.

1. INTRODUCTION

The purpose of the fibre reinforcement is to improve mechanical properties of a given cement based material, which would be otherwise (if not reinforced) unsuitable for several practical applications. However, the production of synthetic fibres consumes a large amount of energy and chemicals and petrochemicals raw material. Within the context of sustainable economy and innovative construction, lignocellulosic fibres, from wood and non-wood sources, are widely available in most developing countries as suitable reinforcement materials for brittle matrix. Besides, lignocellulosic fibres have many advantages over most synthetic fibres such as low density, low cost, excellent specific strength and high specific modulus [1]-[2].

The possibility of applications for the lignocellulosic fibres has stimulated the interest to modify their surfaces to avoid degradation processes such as loss of adhesion by the oscillation of the cross section when fibre is submitted to wetting and drying cycles. It is crucial to maintain of the dimensional stability of these fibres. Therefore, the fibre surface modification is an essential requisite to improve the interfacial compatibility between fibre and matrix (improving adhesion) and thus yielding enhanced mechanical performance of the fibre-cement [1],[3]. The use of nanotechnology as strategy to modify the surface of lignocellulosic fibres is a reality.

As the most widely used nanomaterial for cement-engineering, nano-SiO$_2$ (colloidal silica) has been studied intensively. A recent contribution to the development of building materials comprises adding synthetic colloidal silica to concrete, cement mortars and fibre-cements, whereby the resulting product displays improved properties with regard to strength gain, sulphate attack and alkali-silica reactions. Due to the high specific surface area for the nanometer sized colloidal silica particles they constitute a highly reactive siliceous material [4]-[7].
There are few works that addressed in the study of the influence of colloidal silica in the adhesion between lignocellulosic fibres and cement matrix and, consequently, in the mechanical behaviour of the fibre-cement. Santos et al. [6] evaluated the effects of the content of colloidal silica (in range 0% and 10% w/w of colloidal silica suspension) in the mechanical behaviour of the fibre–cement reinforced with Kraft pulp and produced by the slurry dewatering technique followed by pressing. The significant increase in the average $\gamma_{\text{WoF}}$-value (approximately 37%) of the composite with a 10% w/w colloidal silica suspension suggested that toughening mechanisms such as pull-out were promoted by a balanced physical–chemical adhesion between the fibres and the cement matrix.

Another interesting strategy for achieving low cost reinforcement of cement based composites is the use of the extrusion process that is presented itself is an efficient process method in the following aspects: low energy consumption, varied geometry of products and lower cost of investment for a new plant, the use of simpler machines for continuous production, the possibility of the use many types of mineral additions and colloidal silica without loss of these materials in the process, and the possibility of using low water/cement ratio, which promotes greater compaction of the composite generated [8]-[10].

The objective of this work is to evaluate the treatment of colloidal silica on sisal fibres and unbleached Eucalyptus Kraft pulp surfaces to improve mechanical performance of extruded fibre-cement composites.

2. MATERIALS AND METHODS

2.1. Analyses and preparation of materials

The quantitative chemical analysis of the ordinary Portland cement (OPC) and ground limestone filler was carried out by X-ray fluorescence equipment PANalytical Axios Advanced. The oxide compositions are listed in Table 1. The loss on ignition is related with the quantity of CO$_2$ in the raw materials.
Table 1 – X-ray fluorescence chemical analysis of the particulate raw material (% by mass).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Ordinary Portland cement CP V-ARI</th>
<th>Limestone filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.40</td>
<td>9.04</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.11</td>
<td>2.16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.30</td>
<td>1.25</td>
</tr>
<tr>
<td>MnO</td>
<td>----</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>MgO</td>
<td>3.13</td>
<td>8.90</td>
</tr>
<tr>
<td>CaO</td>
<td>63.50</td>
<td>39.10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.24</td>
<td>0.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.09</td>
<td>0.41</td>
</tr>
<tr>
<td>TiO₂</td>
<td>----</td>
<td>0.15</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>----</td>
<td>0.16</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.97</td>
<td>----</td>
</tr>
<tr>
<td><strong>Loss on ignition (1000°C)</strong></td>
<td>3.26</td>
<td>38.58</td>
</tr>
</tbody>
</table>

For the preparation of fibre-cement was used the unrefined bleached eucalyptus cellulosic pulp produced by Fibria Celulose S. A. The pulp was analyzed by a PulptecTM MFA-500 Morphology Fibre and Shive Analyser – MorFiTrac. The mainly parameters are the Canadian Standard Freeness (CSF) about 664 mL, as well as the length fibres of 0.83 ± 0.05 mm.

The sisal fibres used in this work are residues of the baler twine industry, donated by the Association for the Sustainable Development of the Sisal Producing Region (APAEB - Valente), Bahia state, Brazil, which were tested as received without any prior conditioning or treatment. The specific density of residual sisal fibres was 1.44 ± 0.01 g/cm³, which was measured by means of gas pycnometer (QuanTahrome, Ultrapycnometer 1000). However, the residual sisal fibres, from the cordage production, present a broad and irregular size variation. Fig. 1 shows that the cutting process in a knife mill promoted a length and diameter distributions of sisal fibres using stereoscopy (Zeiss, Stemi 2000-C) and optical microscopy (Zeiss, AxioImager.A2m), respectively. About 100 measurements were performed. The fibre length distribution was situated in the range between 1 and 14 mm, whereas the fibre diameter varied between 100 and 600 µm.
2.2. Colloidal silica treatment

The commercial dispersed suspension of colloidal silica (Bindzil® CC310) was used to apply the chemical treatment. The suspension of concentrations used in the treatment of the lignocellulosic pulp and fibres was 10% w/w in 500 mL of deionized water. Initially, the fibres were immersed in suspension for 18 h. at ambient temperature (25 °C ± 2 °C). After soaking, they were dried at 60 °C in the drying oven for 3 h.

2.3. NMR Experiments

In this study the \(^{29}\text{Si}\) SSNMR technique was used to evaluate the effectiveness of treatment of lignocellulosic fibres with colloidal silica. The \(^{29}\text{Si}\) NMR spectra of vegetable fibres treated and untreated samples were compared to show the effectiveness of the treatment used.

We can take the example of silicon that has three natural isotopes being \(^{30}\text{Si}\), \(^{29}\text{Si}\) and \(^{28}\text{Si}\), whose natural abundances are by 92.23%, 4.67% and 3.1% respectively. However, the silicon isotope having nonzero spin magnetic moment is \(^{29}\text{Si}\) in this way the signal obtained in an experiment \(^{29}\text{Si}\) NMR is proportional to only 4.67% of all silicon atoms in the sample under study.

The high resolution \(^{29}\text{Si}\)-NMR spectra were obtained in a magnetic field strength of 8.1 T in Varian UNITY Inova spectrometer. Measurements were carried out under magic-angle sample spinning (MAS) of up to 5 kHz, using a 7 mm wide-body CP/MAS probe from Varian and 7 mm zirconia rotors. The spectra were obtained from Free Induction Decay (FID) signals after \(\pi/2\) pulses of 4.5 µs length. For each samples, it was verified that the pulse recycling time was long enough to avoid saturation, resulting in recycling times up to 400 s. The resonance line of a polycrystalline kaolinite sample was used as external standard for referencing chemical shifts (-91.2 ppm with respect to tetrametilsilano, TMS).
2.4. Specimen preparation

The mix design was inspired by the formulations for air cured sheets produced by the Hatschek method (changing polymer for sisal fibre) as listed in the Table 2. Brazilian ordinary Portland cement type CP V-ARI (high initial strength), correspondent to ASTM-C150, Type I [11], was chosen because of its finer particle size and higher reactivity in comparison to other blended cements available in the Brazilian market. The water soluble polymers, hydroxypropyl methylcellulose with 86,000 average molecular weight and 5.39 cP viscosity (at 2% concentration in water at 20 °C), provided by Aditex and high range water reducer polyether carboxylic (commercially named ADVA 190 and provided by Grace) were used as rheological modifiers to promote pseudo-plastic behaviour of the composite. Each additive was applied in the proportion representing 1% of the total mass of the particulate raw materials, and was required to enable the extrusion process.

Table 2 – Mix design of the cellulosic fibre-cement composites.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Content (% by mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary Portland cement (CP V-ARI)</td>
<td>53</td>
</tr>
<tr>
<td>Limestone filler</td>
<td>42</td>
</tr>
<tr>
<td>Unrefined bleached eucalyptus pulp*</td>
<td>3</td>
</tr>
<tr>
<td>Sisal fibres</td>
<td>2</td>
</tr>
</tbody>
</table>

*Fibria S/A

The mixture was homogenized in a mechanical Amadio planetary mixer (capacity of 20 L) during 5 min at 125 rpm, 5 min at medium speed (220 rpm) and finally 5 min at high speed (450 rpm). The water-cement (w/c) ratio was 0.41. The mixture was transferred to a Gelenski MVIG-05 laboratory extruder following the procedures adjusted in previous work. The linear speed of the extruder was approximately 4 mm/s and cross section die width/height ratio was 3.3. The mixture was re-circulated into the extruder for 5 min before tailoring the samples. Samples of 15 mm x 50 mm x 200 mm were extruded and immediately transferred to the steel plates for hardening and initial curing.

2.5. Mechanical tests

Mechanical tests in equilibrium with the temperature and air humidity of the laboratory were performed about 20 days after curing for non-aged composites, using a servo-hydraulic mechanical testing machine MTS model 370.02 controlled by MultiPurpose TestWare System. Prismatic
specimens were prepared using a diamond saw blade, prior to grinding and final polishing of the specimen sides and having nominal dimensions of 12 mm x 16 mm x 80 mm. The three-point bending test configuration with span of 64 mm, eight specimens and specific type of specimen and parameters of test were used for each mechanical propriety: modulus of rupture, fracture toughness and energy of fracture. The fracture toughness and energy of fracture were determined using the single-edge notch bend SENB-type specimens.

Modulus of rupture values (MOR) were obtained using prismatic specimens, without notch, but with the same dimensions and finishing and three-point bending test configuration as mentioned previously as well as cross-head speed of 5 mm/min.

Fracture toughness, $K_{IC}$, was determined to evaluate the initial crack growth resistance in cement matrix. The prismatic specimens were prepared, with a centred flat notch with depth equal to 10% of the specimen height and notch tip profile in the shape of a “V”, with angle of about 30° using a diamond disc of 0.5 mm thick to simulate a sharp crack in order to establish the critical defect size and catastrophic fracture. A cross-head speed of 15 mm/min was applied. The calculation of the value of $K_{IC}$ was done according to Santos et al. [12].

The values of the maximum load, $P_{max}$, from load-displacement curves were applied in the calculation of the value of $K_{IC}$ using the following equation:

$$K_{IC} = \frac{P_{max}}{b \cdot w^{1/2}} \cdot y(\alpha)$$

(1)

where $y(\alpha)$ is a geometric factor. The ratio $\alpha = a/w$ of initial notch length to specimen height was 0.1 (or 10% as mentioned before). The factor $y(\alpha)$ is written as:

$$y(\alpha) = \frac{S}{w} \cdot \left[ \frac{3^{1/2}}{2(1-\alpha)^{3/2}} \right] \cdot \left[ 1.99 - 1.33\alpha - (3.49 - 0.68\alpha + 1.35\alpha^2) \cdot \frac{(1-\alpha)}{(1+\alpha)^2} \right]$$

(2)

where $S$ is the span and $\alpha$ is the relative length of the notch, which, in turn, is the ratio of the original length of the notch, $a_0$, and the height of the specimen, $w$.

The fracture energy was obtained to evaluate the influence of toughening mechanisms promoted by vegetable fibres, such as pull-out and bridging, on mechanical performance of the composites. The fracture energy test was performed with the SENB-type specimen. The specimens with a centred flat notch with 30% of specimen height and notch tip in “V” with angle of about 30°
were prepared using diamond disc of 0.5 mm thick. A cross-head speed of 10 µm/min was adopted and controlled by the actuator displacement to guarantee stable growth of the crack.

The work done by the machine to completely propagate the crack along the specimen divided by two times the projected area of the fracture surface (cross-section of the specimen) was used to obtain the fracture energy, $\gamma_{\text{WoF}}$. The integration of the force-displacement curve was made up to the point where the force decreased to 5% of its maximum value reached during the test.

3. RESULTS AND DISCUSSION

Until the present time few studies [13]-[15] report the use of $^{29}$Si NMR in the analysis of plant fibres treated with colloidal silica. Gonçalves et al. used $^{29}$Si NMR in the study of plant fibre cellulose that were given the modified surface using hydrolysis of tetraethoxysilane (TEOS), octyltrimethoxysilane (OTMS) or phenyltrimethoxysilane (PTMS), followed by the layer-by-layer deposition of previously synthesized TiO$_2$ nanoparticles and observed that the NMR technique was effective in the study of plant fibre cellulose surface modified where it was possible to identify the different chemical environments of the silicon present in the sample. In two recent reports Souguir et al. [14]-[15] used in the study $^{29}$Si NMR degraded cellulosic materials reinforced with the use of diamine alkylalkoxysilane where demonstrated the existence of in situ polymerization in the samples through the use of NMR technique.

In Fig. 2 are shown $^{29}$Si NMR spectra for cellulose pulp and sisal fibres treated and untreated samples with colloidal silica, the spectrum for the colloidal silica are shown with both sets of samples for the purpose of demonstrate the efficacy of the treatment. In Fig. 2a) can observe that the sample of untreated cellulose pulp has a higher signal intensity in the region between -90 and -100 ppm, however the sample treated pulp have higher signal intensity in the region of -105 to -115 ppm, this region coincides with the most intense peak at -112 ppm for the colloidal silica used in the treatment of vegetable fibres. The same behaviour could be observed for the sisal fibres (Fig. 2b). This increase in intensity of the NMR signal in the region between -105 and -115 ppm for samples of vegetable fibre shows that the treatment using colloidal silica was effective.
Figure 2: $^{29}$Si-NMR spectra for: (a) Cellulose Pulp and (b) Sisal. The spectrum of colloidal silica is plotted with both sets of samples.

The mechanical behaviour of the fibre-cement with untreated and treated fibres and pulp can be observed initially in Fig.3. The average MOR-values showed a significant increase of 39% in the case of the composite with treated sisal fibres and pulp, if compared to untreated fibre-cement.

Figure 3. Average values and standard deviations of modulus of rupture (MOR) of the fibre–cement reinforced with untreated and treated lignocellulosic fibres.

However, the average $K_I$-value has non-significant decreased, due to superposition of the standards deviation (Fig. 4), i.e. maintained the initial crack growth resistance, resulting in the same resistant matrix to the crack propagation after treatment of the lignocellulosic fibres.
Figura 4. Average values and standard deviations of fracture toughness (K<sub>IC</sub>) of the fibre–cement reinforced with untreated and treated lignocellulosic fibres.

The fibre-matrix interactions are strongly dependent on physical and chemical adhesion, shear stress resistance and overall complex geometry and orientation effects of the cellulosic fibres. Indeed these parameters are reflected on mechanical behaviour of the fibre-cement. The average values of energy of fracture of the treated composite increased approximately 53% (Fig. 5). The fracture process has been changed due to the contribution of the colloidal silica in the interface between fibre-matrix [6]. This indicates that a balanced physical-chemical adhesion between fibre and matrix was partially maintained without a significant destruction of macromolecular chains during the hydration in the curing process. This degradation of the fibres occurs by the easy movement of the pore water towards the surface of the fibres. Other mechanism that was probably inhibited is a gradual process of filling up the inner cores of the vegetable fibres with the hydration products that leads to the embrittlement of the reinforcement [16].
Figura 5. Average values and standard deviations of energy of fracture of the fibre–cement reinforced with untreated and treated lignocellulosic fibres.

These results support the effects of the adsorption of colloidal silica onto surfaces fibres. However, it is necessary to focus on better understanding of the complex interfacial interactions between colloidal silica, lignocellulosic fibres and cement matrix. A strategy is a long-term plan to study directly the adsorption of the colloidal silica on surface sisal fibres and unbleached Eucalyptus Kraft pulps in the media with high pH.

4. CONCLUSIONS

From this experimental study, the following comments can be made:

This increase in intensity of the NMR signal in the region between -105 and -115 ppm for samples of vegetable fibre shows that the treatment using colloidal silica was effective.

The results indicated that the colloidal silica treatment on surface fibres increased the average value of the modulus of rupture and energy of fracture, as well as maintained the initial crack growth resistance of the fibre–cement composite.

The remarkable affinity of the cement matrix with treated lignocellulosic fibres is encouraging to design composites with interesting mechanical performances.
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