Analysis of variance: content and length of curauá fibers on mechanical behavior of extruded cementitious composites

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ABSTRACT

The use of composite materials in construction has grown considerably in recent years, such as cementitious matrices and concrete reinforced with fibers. The vegetable fibers have become an alternative due to its abundance, low cost and low energy consumption for its production, and appropriate properties mechanical. Curauá fiber is a plant native from Amazonas harvested manually in commercial farming and it is used in the manufacture of ropes and baskets or as reinforcement in composite with organic matrix of components for cars, buses and trucks. On the other hand, the extrusion process can produce composites with high-density matrix with fibers, low permeability and good interface between fiber and matrix. This process is also compatible with the use of vegetable fibers as raw materials in the production of cost-effective construction elements such as ceiling panels and drywalls. The objective of this research was use the analysis of variance (ANOVA) for evaluating the content and length of curauá fibers on the mechanical behavior of the extruded cementitious composites. Composites without fibers and reinforced with 1% and 2% by mass of fibers as well as 6 mm and 10 mm of length these curauá fibers were evaluated. The composites with fibers of 10 mm have showed better mechanical results. Besides, the composites with fibers curauá after 200 accelerated aging cycles were better than one non-aging.

Keywords: Mechanical of fracture; extrusion process; lignocellulosic fiber; Amazonian fiber.

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1. INTRODUCTION

Fiber-cement products had been widely used in the world due to their versatility as corrugated and flat roofing materials, cladding panels, and water containers presented in large number of building and agriculture applications [1,2].

In order to improve the sustainability of construction materials, part of the global strategy is to use regional, recyclable and renewable materials from agroindustrial resource and environmentally appropriate technologies for civil construction. Recent years new technologies using lignocellulosic fiber have arisen enabling the use of composites with less environmental impact, low cost and low power consumption, allowing replace partially synthetic fibers, such as polypropylene or polyvinyl alcohol [1,3–5].

The incorporation of lignocellulosic fibers mostly co-product of agriculture and agro-industries, allows a valorization of these residues and a limitation of environmental damages [1,6]. The curauá fiber is a plant native from Amazon and a hydrophilus species belongs to pineapple/bromeliad family. It is a lignocellulosic fiber that has mechanical properties comparable to synthetic polymeric fiber [7–10].

As part of the global strategy to produce regional and environmental-friendly materials the extrusion technology has been successfully as an economical, efficient and processing method for manufacturing sustainable fiber-reinforced cement based composites [11,12]. Other advantage of the extrusion process is its capacity of producing not only flat shapes, but also structural and complex shapes. Besides, this process allows the use of a variety of materials that have been successfully incorporated such as lignocellulosic fiber, including, sugar cane fiber [4] and sisal fiber [13].

However, It is known the problem of reduction of lignocellulosic fiber durability caused mainly by the alkaline (pH around 12) environment of the cement matrix and, consequently causing a destruction of the macromolecular chains during the partial alkaline hydrolysis, initially the lignin after that the cellulose, which decrease of the degree of polymerization of the both phases [14–16]. Other mechanism is the gradual filling of the inner cores of the lignocellulosic fibers with the cement hydration products, leading to the embrittlement of the fibers. These mechanisms could affect some important properties of the reinforced composites, such as toughness mechanisms and other mechanical properties of the fiber-cement in the long-term. [1,17].

The degradation of the composite can be studied by accelerated tests, whose advantage is to provide results in a smaller time interval [18,19]. The durability test (accelerating aging) of the cementitious
composites shows their performance in the presence of wet/dry cycling and therefore may be recommended for both internal and external building applications [16,20].

In this study was evaluated statically, with analysis of variance (ANOVA), mechanical behavior of extruded fiber-cement composites reinforced with curauá fiber with different content and lengths, before and after accelerated aging.

2. EXPERIMENTAL

2.1. Raw materials

Curauá fibers (CF) (Ananas erectifolius) used in this study was obtained from the Pematec Triangel Industry in Pará/PA, Brazil. Mechanical and physical properties and chemical composition of the fiber are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1 – Mechanical, chemical and physical properties of the curauá fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
</tr>
<tr>
<td>α-Cellulose 1 (% by mass)</td>
</tr>
<tr>
<td>Lignin 2 (% by mass)</td>
</tr>
<tr>
<td>Hemicellulose 3 (% by mass)</td>
</tr>
<tr>
<td>Average length (mm)</td>
</tr>
<tr>
<td>Cross section (mm²)</td>
</tr>
<tr>
<td>Thickness (µm)</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
</tr>
<tr>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>

1 TAPPI T 204 CM-97 [21]; 2 Zimmermann et al., [22]; 3 TAPPI T 222 OM-02 [23].

The results of the chemical composition of the curauá fibers were similar found in the literature. For example, It was found a range between 73% by mass and 71% by mass of cellulose and 7.5% by mass to 13% by mass of lignin [24,25]. It is important to consider that there is a natural variation in the analysis of chemical composition of vegetable fibers by means of quantification methods and characteristics of the fibers of a specific region and harvested at different times throughout the season.

Figure 1a shows a surface roughness of the curauá fiber and Figure 1b shows its cross section, approximately elliptical shape. These characteristics help to anchor better in cementitious matrix. Besides, in Figure 1b, it is possible to observe unit cells and lumens (cavities) of the fiber cross section.
Unbleached unrefined eucalyptus (*Eucalyptus grandis*) Kraft pulp was provided by Fibria S/A, Brazil. The cellulose pulp was collected directly from the mill, prior to drying and pressing. It was extensively washed with water and centrifuged to remove any residual chemicals from the pulping processes.

Ordinary Portland cement (OPC) type CP-V-ARI, corresponding to ASTM C 150 [27], Type I was selected because of its finer particle size and higher reactivity. Additionally, this type of cement contains higher levels of tricalcium silicate (C₃S) and dicalcium silicate (C₂S) for the formation of C–S–H. The cement and limestone filler particles distributions were evaluated by a laser particle size analyzer (Malvern Mastersizer S long bed, version 2.19). The particle size distributions of the raw materials are depicted in Figure 2. Figures 2a and 2b show the discrete particle size distributions and the cumulative percentage finer than (CPFT) of the cement and limestone filler, respectively. Cement and limestone particles showed 50% of its mass less than 11.89 and 12.38 µm, respectively. Both raw materials exhibit similar particle distributions.
The quantitative chemical analysis was performed of the OPC and limestone using PANalytical Axios Advanced X-ray fluorescence equipment. The oxides are listed in Table 2. The specific surface area (determined using the BET method) and specific density of raw materials were measured. The OPC presented value of specific density of 3.10 g/cm$^3$ and specific surface area of 1.10 m$^2$/g and for limestone 2.80 g/cm$^3$ and 1.14 m$^2$/g, respectively. The similar values of the specific surface area may be important to avoid competition of water between the raw materials in the system.

Table 2 – Chemical analysis by means of X-ray fluorescence of the particulate raw materials (% by mass).

<table>
<thead>
<tr>
<th>Oxides compositions</th>
<th>Ordinal Portland cement (OPC) CP-V-ARI</th>
<th>Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (%)</td>
<td>14.70</td>
<td>9.40</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>67.20</td>
<td>39.10</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (%)</td>
<td>4.07</td>
<td>2.16</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (%)</td>
<td>3.50</td>
<td>1.25</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>3.13</td>
<td>8.90</td>
</tr>
<tr>
<td>P$_2$O$_5$ (%)</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>SO$_3$ (%)</td>
<td>5.23</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$O (%)</td>
<td>0.75</td>
<td>0.41</td>
</tr>
<tr>
<td>MnO (%)</td>
<td>-</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>TiO$_2$ (%)</td>
<td>-</td>
<td>0.15</td>
</tr>
</tbody>
</table>

### 2.2. Formulation and preparation of composites cementitious

The composite is composed of CP-V-ARI cement and limestone filler. The water-soluble polymers, high range water reducer (HRWR) provided by Aditex and polyether carboxylic provided by Grace was used as lubricant, representing 1% of cement mass. Hydroxypropylmethylcellulose (HPMC)
with an average molecular weight of 86,000 and a viscosity of 5.39 cps (at a concentration of 2% in water at 20 °C) and carboxylate polyether (surfactant) commercially called ADVA 170, were used as rheological modifiers to promote pseudo plastic behavior of the composite. As curauá fibers present higher real density (1.42 g/cm³), the fiber contents were set in relation to polypropylene fibers (0.92 g/cm³) to maintain the same volume reinforcement. The mix design used in this work is in Table 3.

### Table 3 – Formulations used in the production of cementitious composite

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Content [% by mass] / length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland cement [CP-V-ARI]a</td>
<td>Ref 69.95 / 1% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>66.87 / 2% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>67.79 / 1% / 10 mm</td>
</tr>
<tr>
<td></td>
<td>66.87 / 2% / 10 mm</td>
</tr>
<tr>
<td>Limestone filler b</td>
<td>27.08 / 1% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>26.66 / 2% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>26.54 / 1% / 10 mm</td>
</tr>
<tr>
<td></td>
<td>26.66 / 2% / 10 mm</td>
</tr>
<tr>
<td>Eucalyptus cellulosic pulp</td>
<td>2.98 / 1% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>2.93 / 2% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>2.89 / 1% / 10 mm</td>
</tr>
<tr>
<td></td>
<td>2.93 / 2% / 10 mm</td>
</tr>
<tr>
<td>Curauá fiber (CF)</td>
<td>- 1.53 / 1% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>3.08 / 2% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>1.53 / 1% / 10 mm</td>
</tr>
<tr>
<td></td>
<td>3.08 / 2% / 10 mm</td>
</tr>
<tr>
<td>Water/cement ratio</td>
<td>0.33 / 1% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>0.34 / 2% / 6 mm</td>
</tr>
<tr>
<td></td>
<td>0.36 / 1% / 10 mm</td>
</tr>
<tr>
<td></td>
<td>0.34 / 2% / 10 mm</td>
</tr>
</tbody>
</table>

(a) ASTM C-150 [27]; (b) Provided by Infibra Ltda; (c) volume fraction of fibers in study: 3% and 6%, respectively.

The sequence of mixing was powder/water [28]. The cement, limestone, curauá fiber (CF) and HRWR (by dry mass) were mixed and homogenized at low speed (mixture distributive), in a mechanical Eirich intensive mixer (capacity of 10 L) for 5 min. After this stage, water and carboxylate polyether was added fractionally for 2 min. All raw materials was mixed at high speed for another 5 min. to achieve a high shear mixing to break down the agglomeration generated in wet mixing stage. Before composites production, the composite was re-homogenized in the extruder itself, feeding it and taking two times the mass.

Composites with 15 mm thick were extruded, according to Figures 3a and 3b. An extrusion helical screw equipment (Auger type), Verdes, model 051, was used. The equipment contains a motor speed regulator that was maintained by 4 mm/s during extrusion. Pads with 200 mm x 50 mm x 15 mm were cured at water vapor saturated environment (in sealed plastic bags) at 25 ± 2 °C for two days. Subsequently, the specimens were maintained in a water vapor saturated environment (in sealed plastic bags) and placed in a chamber at 45 °C for five days (thermal curing) totalizing 7 days of cure [13].
2.3. Mechanical characterization of the composites

Mechanical characterization tests were adopted according to Santos et al., [13]. The fiber-cement composites were tested using a servo-hydraulic mechanical testing machine MTS (810 series) controlled by the TestStar II system. Prismatic specimens were prepared using a diamond cut-off wheel before grinding and final polishing of the specimen sides. The specimens had nominal dimensions of 80 mm x 20 mm x 13 mm for all of the mechanical tests of the fiber-cement composite. The modulus of rupture (MOR) was calculated by equation 1 and determined using a three-point bending configuration with a span of 64 mm and cross-head speed of 5 mm min⁻¹.

\[
\text{MOR} = \left( \frac{3 \cdot P_{\text{max}} \cdot L_v}{2 \cdot b \cdot h^2} \right)
\]  

where \( P_{\text{max}} \) is maximum load, \( b \) is width, \( h \) is height and \( L_v \) is span between inferior supports.

The fracture toughness (\( K_{\text{IC}} \)) is the critical stress intensity fracture value for crack growth in the material during mode-I failure, which evaluates the initial crack growth resistance, was also used to characterize the cement based composites reinforced with curauá fiber. The SENB-type (single-edge notch bend) specimens were prepared to establish the critical defect size and catastrophic fracture [1]. The test configuration was the three-point bending. Prismatic specimens were prepared with a centered plan notch with a depth equal to 10 % of the specimen height and notch tip profile in the shape of a “\( V \)” with an angle of approximately 30° using a diamond disk of 0.5 mm thickness to simulate a sharp crack. A cross-head speed of 15 mm min⁻¹ was used. The values of the maximum load, \( P_{\text{max}} \), from the load-displacement curves were applied in the calculation of the value of \( K_{\text{IC}} \) using the following equation, according to Santos et al., [13]:
\[ K_{IC} = \frac{P_{\text{max}}}{bw^{1/2}} y(\alpha) \]  

(2)

where \( y(\alpha) \) is the geometric factor and accounts for both shape of crack and loading geometry, the tensile stress at fracture, and \( a_0 \) the crack size. The ratio \( \alpha = a_0/w \) of the initial notch length to specimen height was 0.1 (or 10% as mentioned before).

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

(3)

where \( S \) is the span of 64 mm, 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 (FE) test was performed with the SENB type specimen and three-point bending configuration, but the centered plan notch was of 30% of the specimen height. The span was of 64 mm. A cross-head speed of 10 \( \mu \)m min\(^{-1} \) was used to guarantee stable growth of the crack and to measure the energy required for extending this crack over a unit area [30].

The work performed 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, \( A \)) was used to determine the fracture energy, \( \gamma_{WF} \). The integration of the force–displacement curve was performed up to the point where the force decreased to 5% of its maximum value reached during the test, according to equation 4:

\[ \gamma_{WF} = \frac{1}{2A} \int P d\delta \]  

(4)
Figure 4 – Schematic illustration of a typical load–displacement curve divided into two regions: initial work and work of crack propagation [13].

Additionally, a mechanical parameter was obtained the “relative work of crack-propagation” [31]. This mechanical parameter is obtained by dividing the work of crack propagation by the initial work (elastic energy stored). The initial work is that performed from zero up to the point of the maximum load (Figure 4). Although up to this point, some crack propagation could already occur, it is easy to determine. This ratio considers all of the work performed for the effective crack propagation related to the elastic energy stored in the system. Therefore, a higher value of this relative work indicates that the material is more resistant to propagation of a crack [31].

2.4. Physical characterization tests

Water absorption (WA) apparent porosity (AP) and bulk density (BD) values were obtained from the average of five specimens for each formulation, following procedures specified by ASTM C 948 [32], Standards.

2.5. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used with secondary electron (SE) detector, operated at 5.0 kV accelerating voltage, for observation of the morphologies on the fractured surface of composites generated in the mechanical tests. A back- scattered electron (BSE) detector operated at around 15.0 kV and 20.0 kV was applied for viewing cut and polished surfaces. The BSE image was used to study the fiber–matrix transition zone. Energy dispersive X-ray spectroscopy (EDS) analyses were also conducted. These were performed on the same flat surface specimens in an effort
to obtain semi-quantitative compositional information. The preparation of specimens for BSE and EDS was accomplished with vacuum (80 kPa gauge) impregnation using cyanoacrylate ester resin. BSE EDS samples were semi-automatic ground with silicon carbide abrasive paper with sequential grit sizes of 320, 600, 1200 and 2000 for 2 min each, using alcohol as lubricant. A final preparation was carried out using in turn 8–4, 4–2 and 1–0 µm diamond polishing compound during 4, 2 and 1 min each size respectively. Fractured and polished samples were gold coated in a Bal-Tec Med020 coating system before being analyzed in a Hitachi TM 3000 microscope.

2.6. Accelerated aging testing

The accelerated aging testing involved a comparative analysis of physical and mechanical performance of the composites, before and after 200 soak/dry cycles. Specimens were successively immersed in water at 20 ± 5 °C during 170 min, followed by the interval of 10 min, and then exposed to temperature of 70 ± 5 °C for 170 min in a ventilated oven and with the final interval of 10 min. This procedure was based on recommendations of the EN 494 [33], Standards. Each soak/dry set represents one cycle and was performed for 200 cycles (200C) [4].

2.7. Statistical analysis

The physical and mechanical properties evaluated were: water absorption (WA), apparent porosity (AP), apparent density (BD), modulus of rupture (MOR), fracture energy (FE), fracture toughness (KIC) and relative work of crack propagation (RWP). The factors and levels investigated consisted of curauá fiber fractions (% F) [1, 2%], fiber length (FL) [6, 10 mm] and curing type (Cr) [7d (0), 200C (1)]. The product of the three factor levels along with the reference conditions [Ref] (0% fiber and 7 days cure [Tr1], 0% fiber resulted in an experimental design consisting of 9 treatments, as explained in Table 4. It should be noted that the treatment Tr1 (reference) was used in the manufacture of materials for the determination of physical and mechanical properties.

Table 4 – Experimental treatments.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Treatment (Tr)</th>
<th>%F</th>
<th>FL</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>Tr1</td>
<td>0</td>
<td>0</td>
<td>7 days (0)</td>
</tr>
<tr>
<td>1% / 6 mm</td>
<td>Tr2</td>
<td>1%</td>
<td>6 mm</td>
<td>7 days (0)</td>
</tr>
<tr>
<td>1% / 10 mm</td>
<td>Tr3</td>
<td>1%</td>
<td>10 mm</td>
<td>7 days (0)</td>
</tr>
<tr>
<td>2% / 6 mm</td>
<td>Tr4</td>
<td>2%</td>
<td>6 mm</td>
<td>7 days (0)</td>
</tr>
<tr>
<td>2% / 10 mm</td>
<td>Tr5</td>
<td>2%</td>
<td>10 mm</td>
<td>7 days (0)</td>
</tr>
<tr>
<td>1% / 6 mm</td>
<td>Tr6</td>
<td>1%</td>
<td>6 mm</td>
<td>200C (1)</td>
</tr>
<tr>
<td>1% / 10 mm</td>
<td>Tr7</td>
<td>1%</td>
<td>10 mm</td>
<td>200C (1)</td>
</tr>
<tr>
<td>2% / 6 mm</td>
<td>Tr8</td>
<td>2%</td>
<td>6 mm</td>
<td>200C (1)</td>
</tr>
<tr>
<td>2% / 10 mm</td>
<td>Tr9</td>
<td>2%</td>
<td>10 mm</td>
<td>200C (1)</td>
</tr>
</tbody>
</table>
The methodology of Experimental Planning (DOE), using Minitab® software version 14, was used to establish the relationship between the properties (physical and mechanical) and the factors evaluated, to understand the effects and to identify the factors and interactions considered significant and to identify the treatments that resulted in the extreme values of the properties estimated by the models. The analysis of variance (ANOVA) of regression models (Equation 5) was evaluated at the 5% level of significance ($\alpha$), considering the non-significance (P-value <0.05) of the models and coefficients as null hypothesis (H0) and significance as an alternative hypothesis (H1). For the validation of the regression models, the normality of the generated residues was tested with the aid of the Anderson-Darling normality test, also at the 5% level of significance, and for the hypotheses formulated, P-value greater than or equal to 0.05 implies in the normality of the waste distribution, validating the ANOVA model.

$$Y=\beta_0+\beta_1\cdot%F+\beta_2\cdot FL+\beta_3\cdot Cr+\beta_4\cdot%F\cdot FL+\beta_5\cdot%F\cdot Cr+\beta_6\cdot FL\cdot Cr+\beta_7\cdot F\cdot Cr +\epsilon$$  (5)

From Equation 5, Y denotes the estimated physical and mechanical properties, $\beta_i$ are the coefficients obtained from the least squares method and $\epsilon$ consists of the random error. The coefficient of determination ($R^2$) was used to measure the quality of the adjustments obtained, and it should be noted that the reference conditions are not incorporated in the regression models. In planning involving the 9 treatments after understood the effects of factors and interactions between them on each property investigated. It can be noted that 6 or more determinations were obtained by treatment and property investigated, totaling 382 determinations.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

Figure 5 shows the mechanical properties (modulus of rupture (MOR), fracture toughness ($K_{IC}$), fracture energy (FE), and relative work of crack propagation (RWP)) of extruded cementitious composite (ECC) cured at 7 days (7d), after accelerated aging (200C), the confidence intervals of the mean (at the 95% confidence level) and the range of variation of the coefficient of variation (CV). Table 5 lists the respective average values and standard deviations of the mechanical properties and physical characteristics. The P-values of the Anderson-Darling normality test of the ANOVA residues for the four mechanical properties (MOR, $K_{IC}$, FE and RWP, respectively) evaluated ranged from 0.265 to 0.781, validating the ANOVA model, and by the results of the determination coefficients [79.72%; 99.02%], it is verified the good estimation of the properties
provided by the models, being all considered significant by ANOVA. Equations 6 and 7 expresses
the regression model obtained in the estimation of the MOR and $K_{IC}$ values, respectively, and also
the coefficients of determination ($R^2$) and the numerical intervals of this property are presented.
Equations 6 and 7, the outliers were excluded from the set of results, and the terms considered non-
significant by ANOVA of the regression models were underlined.

$$
\text{MOR} = 1.39775 + 9.30425\cdot%F + 1.55238\cdot FL + 2.0527\cdot Cr - 1.05938\cdot%F\cdot FL - 14.2959\cdot%F\cdot Cr + 1.23217\cdot FL\cdot Cr + 1.14854\cdot%F\cdot FL\cdot Cr
$$

(R$^2$ = 79.72%); $\text{MOR} = [12.19; 23.18]$ (6)

$$
\text{K}_{IC} = 0.878467 - 0.0865817\cdot%F - 0.0040055\cdot FL + 0.438194\cdot Cr + 0.0117967\cdot%F\cdot FL - 0.332244\cdot%F\cdot Cr - 0.0522791\cdot FL\cdot Cr + 0.0312871\cdot%F\cdot FL\cdot Cr
$$

(R$^2$ = 81.65%); $\text{K}_{IC} = [0.64; 1.08]$ (7)

ECC reinforced with 2% of curauá fiber (CF) at 7d showed a significant increase of MOR values in
relation to the ECC with 1% of CF and reference (Ref), according the ANOVA test shown in
Equation 6 and Figure 5a. However, the results of fiber length did not differ significantly between
the formulations. The MOR is the tensile strength in bending as well as it is influenced by
interaction and distribution of stresses between fiber-matrix and matrix porosity. The inclusion of
fibers increases the toughness and the reinforcement of composites, but also increases the porosity
because the dispersion deficiency of the fibers in cementitious matrix and, consequently, generating
lack of stress transfer between the fibers and matrix. After 200C, Figure 5a, the MOR values of the
ECC increased due to the combined effect better adhesion (increase in chemical bonding) of CF in
the cementitious matrix, the continued hydration process in the fiber-matrix interface and
petrification or mineralization these fibers [34].

According Melo Filho et al., [17], the mineralization occurs under conditions in which the cement
hydration products migrate to the more porous regions within the fibers (surface pores and lumens).
From the interaction between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length
(FL) [6, 10 mm] and curing type (Cr) [7d, 200C]), the highest value occurs from the combination
with 2% of fibers, 10 mm in length and after 200C.

MOR values found in this study are around 16 MPa to 7d and 20 MPa after 200C for the
formulation 1% / 10 mm. These MOR values were higher than those found in previous studies with
ECC reinforced with sisal and sugarcane fibers, with respective content of 1% by mass and 1.5% by
mass and the distribution of lengths between 15 mm to 18 mm and 10 mm to 15 mm that showed,
respectively, MOR values of 8 MPa to 11 MPa for 28 days (28d) and 4 MPa to 15 MPa after 200C
[4,35].
Figure 5 – Average values and standard deviation (MOR) modulus of rupture (a) and (KIC) fracture toughness (b).

The individual statistical interactions as the higher content (%F) and fiber length (FL) decrease KIC values, i.e., initial crack growth resistance in cement matrix, according to ANOVA, as calculated by the equation 7 and whose values are shown in Figure 5b. The KIC value of the reference composites (1.05 MPa.m\(^{1/2}\)) suggests that these results may be related to distribution of defects in the matrix produced by several factors such as the difficulty in packaging fiber in the matrix with particles and negative interference in cement hydration process caused by absorption of water by CF. However,
the statistical combination of 2% by mass of fiber with 10 mm length after 200C increases the $K_{IC}$ values. It indicates that the matrix was improved mainly after 200 cycles of immersion and drying. The results of fracture toughness of the composites reinforced with CF are similar than the results obtained by Santos et al., [13]. The authors produced cement composites, reinforced with 3% eucalyptus pulp and 2% of sisal fibers, produced by the extrusion method and subjected to accelerated carbonation curing in the supercritical condition. The authors also analyzed the composite before and after 200 cycles of immersion and drying. The average results obtained was 0.9 MPa.m$^{1/2}$ and 0.85 MPa.m$^{1/2}$, for the unaged and aged composites, respectively.
Table 5 – Average values and standard deviations of modulus rupture (MOR), fracture toughness ($K_{IC}$), fracture energy (FE), relative work of propagation (RWP), water absorption (WA), bulk density (BD) and apparent porosity (AP) of the extruded cementitious composite (ECC) reinforced with curauá fiber (CF), 6 mm and 10 mm of length in the conditions at 7 days (7d) of curing and after 200 accelerated aging cycles (200C).

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Condition</th>
<th>MOR (MPa)</th>
<th>$K_{IC}$ (MPa·m$^{1/2}$)</th>
<th>FE (J/m$^2$)</th>
<th>RWP</th>
<th>WA (%)</th>
<th>BD (g/cm$^3$)</th>
<th>AP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference (Ref)</td>
<td>7d</td>
<td>18.75 ± 0.75</td>
<td>1.05 ± 0.04</td>
<td>187.61 ± 16.07</td>
<td>9.77 ± 4.22</td>
<td>16.14 ± 0.28</td>
<td>1.702 ± 0.013</td>
<td>27.47 ± 0.34</td>
</tr>
<tr>
<td>1% / 6 mm</td>
<td>7d</td>
<td>13.82 ± 0.57</td>
<td>0.83 ± 0.02</td>
<td>108.20 ± 13.58</td>
<td>3.21 ± 0.67</td>
<td>16.49 ± 0.20</td>
<td>1.708 ± 0.007</td>
<td>28.16 ± 0.29</td>
</tr>
<tr>
<td>1% / 10 mm</td>
<td>7d</td>
<td>15.85 ± 1.66</td>
<td>0.88 ± 0.03</td>
<td>309.98 ± 15.98</td>
<td>14.65 ± 5.59</td>
<td>17.22 ± 0.15</td>
<td>1.729 ± 0.055</td>
<td>29.78 ± 0.84</td>
</tr>
<tr>
<td>2% / 6 mm</td>
<td></td>
<td>16.01 ± 1.92</td>
<td>0.78 ± 0.08</td>
<td>102.05 ± 9.05</td>
<td>3.66 ± 0.80</td>
<td>18.48 ± 0.72</td>
<td>1.726 ± 0.016</td>
<td>31.90 ± 0.96</td>
</tr>
<tr>
<td>2% / 10 mm</td>
<td></td>
<td>15.21 ± 2.26</td>
<td>0.92 ± 0.10</td>
<td>245.09 ± 89.49</td>
<td>14.04 ± 3.13</td>
<td>17.04 ± 0.24</td>
<td>1.720 ± 0.031</td>
<td>29.31 ± 0.59</td>
</tr>
<tr>
<td>1% / 6 mm</td>
<td>200C</td>
<td>19.52 ± 1.63</td>
<td>0.82 ± 0.03</td>
<td>45.67 ± 4.28</td>
<td>1.41 ± 0.42</td>
<td>16.73 ± 0.14</td>
<td>1.740 ± 0.009</td>
<td>29.10 ± 0.23</td>
</tr>
<tr>
<td>1% / 10 mm</td>
<td>200C</td>
<td>20.45 ± 2.17</td>
<td>0.77 ± 0.03</td>
<td>56.75 ± 5.83</td>
<td>1.43 ± 0.63</td>
<td>17.41 ± 0.10</td>
<td>1.754 ± 0.044</td>
<td>30.54 ± 0.72</td>
</tr>
<tr>
<td>2% / 6 mm</td>
<td>200C</td>
<td>15.16 ± 1.27</td>
<td>0.70 ± 0.06</td>
<td>20.18 ± 2.51</td>
<td>0.61 ± 0.25</td>
<td>17.77 ± 0.27</td>
<td>1.725 ± 0.008</td>
<td>30.66 ± 0.40</td>
</tr>
<tr>
<td>2% / 10 mm</td>
<td>200C</td>
<td>18.08 ± 2.77</td>
<td>0.78 ± 0.05</td>
<td>41.75 ± 3.89</td>
<td>1.67 ± 1.17</td>
<td>17.59 ± 0.19</td>
<td>1.723 ± 0.027</td>
<td>30.31 ± 0.39</td>
</tr>
</tbody>
</table>
Figures 6a to 6d shows the micrographs of ECC with polished surface, Ref and reinforced with CF at 7d and 200C respectively, that it showed a homogenous microstructure of the cement matrix at 7d and more densified after 200C. The composite reinforced with CF, (Figure 6c and 6d) content high porosity in the fiber-matrix interface, i.e., it has a low adhesion which do not lead to expressive values of MOR and $K_{IC}$ in relation to the Ref. In the mixing process, the ECC with CF consumed more water, which promotes the formation of porosity and interferes strongly in the w/c ratio (water/cement) and the packaging of the raw materials in the matrix. Figure 6d indicates that the vegetable fiber suffer a dimensional variation because it tends to lose water to the system of the cementitious matrix which in turn is submitted to a rehydration process. This dimensional variation process of the fiber promotes detachment of it in the cementitious matrix, consequently, it affects the mechanical behavior of the cement composite [19].

Figure 6 – SEM of the composites at 7d and after 200C, respectively. (a) and (b) reference composite and (c) and (d) composite reinforced with CF.
The average values of fracture energy values (FE) and relative working crack propagation (RWP) of the composite at 7d and after 200°C are shown in Figures 7a and 7b, respectively. Equations 8 and 9 expresses the regression analysis obtained in the estimation of the FE and RWP values, and the coefficients of determination ($R^2$) and the numerical intervals of these properties are also presented, respectively. A regression analysis generates an equation to attempts to explain the statistical relationship between one or more predictors and the response variable.

\[
FE = -314.084 + 113.851 \times \%F + 384.347 \times FL + 70.6381 \times Cr - 19.6163 \times \%F \times FL - 155.064 \times \%F \times Cr - 70.4887 \times FL \times Cr + 22.2370 \times \%F \times FL \times Cr \quad (R^2 = 99.02\%); \quad FE = [16.68; 391.23] \quad (8)
\]

\[
RWP = -21.7027 + 4.75874 \times \%F + 4.01494 \times FL + 25.4552 \times Cr - 0.686908 \times \%F \times FL - 7.11968 \times \%F \times Cr - 4.27127 \times FL \times Cr + 0.946910 \times \%F \times FL \times Cr \quad (R^2 = 98.21\%); \quad RWP = [0.33; 19.23] \quad (9)
\]

The outliers were excluded from the set of results, and the terms considered non-significant by ANOVA of the regression models were underlined.

FE is the energy per unit area needed to completely fracture the composite in quasi stable crack propagation process in order to record the contribution of all toughness mechanisms mainly promoted by the fibers. The RWP is the ratio of the plastic working and the elastic work i.e. indicates the degree of pseudoplastic deformation, that is, it shows that capability of the cement composite to absorb energy.

The ECC reinforced with 2% of fibers presented a significant statistical FE value in relation to ECC with 1% at 7d and after accelerated aging (200°C), based on Equation 8 and Figure 7a. According to Rodrigues and Montardo [36] and Bentur and Mindess [37], the fiber content provides greater post-cracking energy and smaller size of the cracks, since the fibers help to absorb the elastic energy necessary to propagate cracks, which occur between fiber fractions. Regarding the fiber length, the average value of FE of the composite with fiber of 10 mm is higher than one with fibers of 6 mm, according to the ANOVA, as calculated by Equation 9 and demonstrated in Figure 7b, before accelerated aged. However, FE values of composites with fibers of 10 mm presented major standard deviations than ones with fibers of 6 mm. Fiber with length of 6 mm has a higher number of filaments per mass, but fiber of 10 mm presented more efficiency in relation to pullout mechanism that increased average values of the FE and RWP. Fiber with 10 mm has a better degree of adhesion in the cementitious matrix between the different lengths of fibers, i.e. there is a greater probability of shorter fibers be pulled without an effective frictional energy. For a surface shear stress applied
to the fiber, this will be more efficient if its length is capable of allowing the shear stress permits the development of a tensile stress equal to its tensile strength [37,38]. From the individual statistical factors, increases in fiber content and length promote increases in FE and RWP values and the best type of cure is 7d, however, the interaction between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length (FL) [6, 10 mm] and curing type (Cr) [7d, 200C]), the highest value for FE and RWP occurs from the combination with 2% of fibers, 10 mm in length and after 200C.

Figure 7 – Average values and standard deviation (FE) Fracture energy (a) and (RWP) relative work of crack propagation (b) in the composite extruded.
ECC reinforced with 1% / 10 mm length presented the highest average FE value of 310 J/m² and 57 J/m², at 7d and after 200°C, respectively. The value of FE at 7d was higher than one determined by Santos et al. (2015), which produced extruded composite reinforced with 2% by mass of eucalyptus cellulosic pulp and 3% by mass of sisal fibers with a length distribution between 1 mm and 14 mm, 7 days cure and exposed to supercritical carbonation. It presented average value of FE approximately 230 J/m². Correia et al., [39] worked with extruded composites reinforced with hybrid cellulosic fibers (8% cellulosic fibers + 1% bamboo nanofibers) that presented FE value around 430 J/m² at 28 days of cure, but it decreased for 271 J/m² after accelerated aging of 200°C. The reduction of the FE value after accelerated aging indicates that degradation of the fibers in the ECC caused debonding and breakage of fibers as illustrated in Figures 8a and 8b.

(a) 
(b) 
Figure 8 - SEM micrographs of composite extruded at 7d (a) the arrow shows deboning fiber from cement matrix after 200 cycles (b) breaked fiber

3.2. Physical Characterization

In Figure 9 are shown the graphs with the average values of the physical parameters: water absorption (WA), bulk density (BD) and apparent porosity (AP) of the composites at 7 days and after 200°C between level fiber fraction and lengths of curauá fiber (CF). The confidence intervals of the mean (at the 95% confidence level) and the range of variation of the coefficient of variation (CV). The P-values of the Anderson-Darling normality test of the ANOVA residues for the three physical properties (WA, BD and AP) evaluated ranged from 0.109 to 0.918, validating the ANOVA model. Although the coefficient of determination obtained for the estimation of apparent porosity (AP) was 33.22%, all regression models were considered significant by ANOVA.
Equations 10, 11 and 12 expresses the regression analysis obtained in the estimation of the WA, BD and AP values, and also the coefficients of determination ($R^2$) and the numerical intervals of this property are presented, respectively.

\[ WA = 10.0648 + 5.32864 \times \%F + 0.743583 \times FL - 0.560438 \times \%F \times FL - 2.83893 \times \%F \times Cr + 0.341080 \times FL \times Cr + 0.329509 \times \%F \times FL \times Cr \] (R$^2$ = 92.09%); WA $= [16.24; 18.47]$ (10)

\[ BD = 17.5215 + 8.65426 \times \%F + 1.21420 \times FL + 5.76981 \times Cr - 0.883184 \times \%F \times FL - 4.71053 \times \%F \times Cr - 0.506878 \times FL \times Cr + 0.486204 \times \%F \times FL \times Cr \] (R$^2$ = 84.44%); BD $= [27.86; 31.98]$ (11)

\[ AP = 1.61519 + 0.0700806 \times \%F + 0.0122749 \times FL + 0.160396 \times Cr - 0.00855097 \times \%F \times FL - 0.0935377 \times \%F \times Cr - 0.0158791 \times FL \times Cr + 0.0100770 \times \%F \times FL \times Cr \] (R$^2$ = 33.22%); AP $= [1.67; 1.82]$ (12)

Equations 10 to 12, the outliers were excluded from the set of results, and the terms considered non-significant by ANOVA of the regression analysis were underlined.

ECC reinforced with 2% of curauá fiber (CF) presented higher values of WA in relation to the formulation with 1% by mass showed in Equation 10 and Figure 9a, possibly due to the greater number of fibers per unit volume conducting to inefficient packaging of the matrix, aspect ratios of the fibers, CF (80 and 133, respectively for lengths of 6 mm and 10 mm) and, consequently more defects appears in the interface fiber and matrix [40,41]. The results of fiber length and type of cure did not differ significantly between the formulations according the ANOVA. The interaction between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length (FL) [6, 10 mm] and curing type (Cr) [7d, 200C]), the highest value occurs from the combination with 2% of fibers, 6 mm or 10 mm in length at 7d or after 200C.

Composites with 2% by mass of fibers after 200C presented an increase significant of the BD values showed in Equation 11 and Figure 9b, which can be attributed the filling of the matrix pores by the continued hydration process during accelerated aging cycles in formation of calcium hydroxide (Ca(OH)$_2$), calcium silicate hydrate (CSH) and calcium carbonate (CaCO$_3$) [13]. These phenomena were found in several studies that have been applied accelerated aging cycles in composites cementitious, such as Soto et al., [35]; Dias et al., [42] and Teixeira [4]. The only individual factor statistical that did not affect the bulk density (BD) values was the fiber length.

Thus, the interaction between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length (FL) [6, 10 mm] and curing type (Cr) [7d, 200C]), the highest value occurs from the combination with 2% of fibers, 6 mm or 10 mm in length and after 200C.
(a) WA (%)

CV=[0.86; 3.91%]

(b) BD (g/cm³)

CV=[0.41; 3.18%]
According to the ANOVA, considering the individual statistical factors and the interaction, only the accelerated aging (200°C) promoted significant differences in the values of the apparent porosity (AP) of the composites shown in Equation 12 and Figure 9c. It is believed that the immersion and drying cycles caused higher incidence of pores as result of microcracks caused by the aging cycles [39]. At the initial period of the immersion cycles, lignocellulosic fiber could absorb the water from the cementitious microstructure since the surrounding water concentration is greater than within the fibers. At a later stage of drying cycles, the moisture content within the fibers dry out and thus, fibers shrink to a smaller size. The shrinkage of the fiber generates microcracks between the fiber and cement matrix, creating voids that explain the low results of FE and RWP in the transition zone [29,39]. From the interaction between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length (FL) [6, 10 mm] and curing type (Cr) [7d, 200C]), the highest value occurs from the combination with 1% or 2% of fibers, 6 mm or 10 mm in length at 7d.

3.3. Micrographic electronic scanning SEM

Figure 10 shows the micrographs (SEM) with EDS in the composites reinforced with CF detaching the points of chemical elements in cementitious structures. The dark areas in the image (associated with low atomic number of the predominant chemical elements) correspond to the longitudinal sections of the fibers.

In point 1, identifies the grain with a high calcium index from the formulation used about 27% of
limestone in the mix. In point 2, detaching the anhydrous grain that was not completely hydrated, predominantly Si and Ca elements.

Point 3 clearly shows a grain formed cement constituents. In point 4, the cellulose pulp with a high calcium content and silicon are shown, indicating that the fiber absorbed cement hydration water, which was similar to that presented by Tonoli et al., [43] and Teixeira et al., [29], who studied eucalyptus cellulosic pulp.
Figure 10 – (a) Image Scanning electron microscopy (SEM-BSE) polished surfaces of composites reinforced with CF and points of EDS analyzes that are marked on the images (1 to 4): (1) limestone; (2) anhydrous grain; (3) cementitious matrix and (4) cellulosic pulp

In Figure 11a, it is observed a resulted of the dimensional variation of fiber according to its humidity content. Resulting pores lead to higher water absorption, greater porosity and low resistance.

Savastano and Agopyan [44], explain that the best performance is achieved by better adhesion of the fiber-matrix. The improved adherence is achieved by reducing the porosity and the lowest concentration of Portlandite (calcium hydroxide crystals) approximately the fiber.
In Figure 11b, after 200 cycles, there is better adhesion of the fiber in the matrix. Point 1 shows that, in the central part of the fiber were not found cement hydration products as indicated by the EDS, the large presence of C. However, at point 2, the border of the fiber presents the main chemical elements of cement, silicon and calcium \([19,45]\). They can also be observed by EDS, chemical elements, such as, Al, S, and Mg. This phenomenon can be associated with mineralization fibers as indicated by Bentur and Akers [46]. On immersion in water, free ions formed by the dissolution of the cementitious phases of Portland cement penetrated into the lumen of the fibers, leading to the formation of ettringite/monosulfates and calcium hydroxide \(\text{Ca(OH)}_2\) [29,45]. Batic et al., [47] showed that the re-precipitation of ettringite in microcracks and pores of the cementitious composite may occur under normal conditions (ambient temperature) curing. Such training has previously been suggested as one of the degradation mechanisms of the fibers within the concrete matrix [14,15].

4. CONCLUSIONS

The curauá fiber suffered mineralization process during curing (water absorption of the cement hydration products) which consequently carried the fiber to decreased its properties. The fiber content directly influenced the mechanical performance and fibers with lengths greater showed better mechanical results for modulus of rupture (MOR) and fracture energy (FE) according to ANOVA. Cementitious composites reinforced with fibers curauá showed superior mechanical performance compared to available research literature. The modulus of rupture (MOR), fracture energy (FE) and relative working crack propagation (RWP) results of the composites reinforced...
with fibers curauá after 200 accelerated aging cycles were better in relation of the composites at 7
days, because of the cement hydration, which filled the pores, densified its structure, which
improved the transition zone fiber matrix. On the other hand, the aging promoted mineralization of
the fiber, which reduced the mechanical performance of composites with curauá compared with
literature researches. Thus, the best results were obtained for composites reinforced with 2% of
curauá fiber with 10 mm of length after 200C.

In the physical results, the composite with 2% of fiber increased by water absorption and bulk
density due to the greater number of fibers per unit volume and the filling of the matrix pores by the
continued hydration process during accelerated aging cycles (200C) in formation of calcium
hydroxide (\(\text{Ca(OH)}_2\)), calcium silicate hydrate (CSH) and calcium carbonate (\(\text{CaCO}_3\)) respectively.
Considering the individual statistical factors and the interaction, only the accelerated aging (200C)
promoted significant differences in the values of the apparent porosity (AP). It is believed that the
immersion and drying cycles caused higher incidence of pores as result of microcracks caused by
the aging cycles. According to the ANOVA, the only individual factor statistical that did not affect
the physical values was the fiber length. Thus, the interaction between the three statistical factors,
the highest value occurs from the combination with 2% of curauá fibers, 6 mm or 10 mm in length
after 200C.

Scanning electron microscopy of the fracture surface of curauá fibers showed chemical elements
from the cement inside the fiber. Also showed detachment of the fibers from the cement matrix
indicating low mechanical performance.

These results encourage us to use composites reinforced with curauá fiber in constructions in indoor
environments as ceiling and partitions. New tests should be used to optimize results.

5. ACKNOWLEDGEMENTS
The authors acknowledge the financial support provided by Brazilian Agencies: Fundação de
Amparo à Pesquisa do Estado de São Paulo (FAPESP, Grant nº 2013/03823-8 and 2012/51467-3);
Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, Grant nº 3886/2014); and
Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Grant nº 406429/2015
and 312151/2016-0). The authors thank the Brazilian companies Fibria S.A., Infibra S.A. and
Imbralit Ltda. for technical support to the development of this work.

6. REFERENCE


