1 **Analysis of variance: content and length of curauá fibers on mechanical**

2 **behavior of extruded cementitious composites**

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19 **ABSTRACT**

20 The use of composite materials in construction has grown considerably in recent years, such as

21 cementitious matrices and concrete reinforced with fibers. The vegetable fibers have become an

22 alternative due to its abundance, low cost and low energy consumption for its production, and

23 appropriate properties mechanical. Curauá fiber is a plant native from Amazonas harvested

24 manually in commercial farming and it is used in the manufacture of ropes and baskets or as

25 reinforcement in composite with organic matrix of components for cars, buses and trucks. On

26 the other hand, the extrusion process can produce composites with high-density matrix with

27 fibers, low permeability and good interface between fiber and matrix. This process is also

28 compatible with the use of vegetable fibers as raw materials in the production of cost-effective

29 construction elements such as ceiling panels and drywalls. The objective of this research was

30 use the analysis of variance (ANOVA) for evaluating the content and length of curauá fibers on

31 the mechanical behavior of the extruded cementitious composites. Composites without fibers

32 and reinforced with 1% and 2% by mass of fibers as well as 6 mm and 10 mm of length these

33 curauá fibers were evaluated. The composites with fibers of 10 mm have showed better

34 mechanical results. Besides, the composites with fibers curauá after 200 accelerated aging

35 cycles were better than one non-aging.

36 **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

69 composites shows their performance in the presence of wet/dry cycling and therefore may be

70 recommended for both internal and external building applications [16,20].

71 In this study was evaluated statically, with analysis of variance (ANOVA), mechanical behavior of

72 extruded fiber-cement composites reinforced with curauá fiber with different content and lengths,

73 before and after accelerated aging.

74

75 **2. EXPERIMENTAL**

76 *2.1. Raw materials*

77 Curauá fibers (CF) (*Ananas erectifolius*) used in this study was obtained from the Pematec Triangel

78 Industry in Pará/PA, Brazil. Mechanical and physical properties and chemical composition of the

79 fiber are listed in Table 1.

80

81 Table 1 – Mechanical, chemical and physical properties of the curauá fiber

	Curauá fiber (CF)
Ultimate tensile strength (MPa)	550
Young's modulus (GPa)	64
α-Cellulose [1] (% by mass)	68
Lignin [2] (% by mass)	14
Hemicellulose [3] (% by mass)	10
Average length (mm)	6.00 ± 0.88 and 10.00 ± 0.46
Cross section (mm^2)	0.1136
Thickness (µm)	~75
Density (g/cm^3)	1.42
Aspect Ratio	~80 and ~133

82 1 TAPPI T 204 CM-97 [21]; 2 Zimmermann et al., [22]; 3 TAPPI T 222 OM-02 [23].

83

84 The results of the chemical composition of the curauá fibers were similar found in the literature. For

85 example, It was found a range between 73% by mass and 71% by mass of cellulose and 7.5% by

86 mass to 13% by mass of lignin [24,25]. It is important to consider that there is a natural variation in

87 the analysis of chemical composition of vegetable fibers by means of quantification methods and

88 characteristics of the fibers of a specific region and harvested at different times throughout the
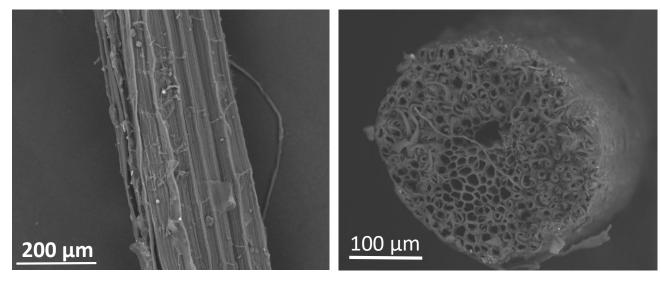
89 season.

90 Figure 1a shows a surface roughness of the curauá fiber and Figure 1b shows its cross section,

91 approximately elliptical shape. These characteristics help to anchor better in cementitious matrix.

92 Besides, in Figure 1b, it is possible to observe unit cells and lumens (cavities) of the fiber cross

93 section.

94

(a)   (b)

Figure 1 – Morphological characteristics of CF observed by scanning electron microscopy. (a) Lateral surface and (b) cross-section detaching the irregular lumens [26].

95

96   Unbleached unrefined eucalyptus (*Eucalyptus grandis*) Kraft pulp was provided by Fibria S/A,

97   Brazil. The cellulose pulp was collected directly from the mill, prior to drying and pressing. It was

98   extensively washed with water and centrifuged to remove any residual chemicals from the pulping

99   processes.

100 Ordinary Portland cement (OPC) type CP-V-ARI, corresponding to ASTM C 150 [27], Type I was

101 selected because of its finer particle size and higher reactivity. Additionally, this type of cement

102 contains higher levels of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) for the formation of

103 C–S–H. The cement and limestone filler particles distributions were evaluated by a laser particle

104 size analyzer (Malvern Mastersizer S long bed, version 2.19). The particle size distributions of the

105 raw materials are depicted in Figure 2. Figures 2a and 2b show the discrete particle size

106 distributions and the cumulative percentage finer than (CPFT) of the cement and limestone filler,

107 respectively. Cement and limestone particles showed 50% of its mass less than 11.89 and 12.38 µm,

108 respectively. Both raw materials exhibit similar particle distributions.
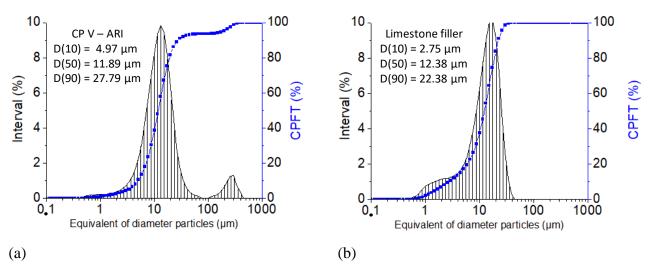
109

Figure 2 – (a) Particle size distribution of ordinary Portland cement and (b) limestone filler. The legend indicates the maximum equivalent diameter for each accumulated percentage of particles

110

111 The quantitative chemical analysis was performed of the OPC and limestone using PANalytical

112 Axios Advanced X-ray fluorescence equipment. The oxides are listed in Table 2. The specific

113 surface area (determined using the BET method) and specific density of raw materials were

114 measured. The OPC presented value of specific density of 3.10 g/cm^3 and specific surface area of

115 1.10 m^{2}g^{-1} and for limestone 2.80 g/cm^3 and 1.14 m^{2}g^{-1}, respectively. The similar values of the

116 specific surface area may be important to avoid competition of water between the raw materials in

117 the system.

118

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

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

121

122 **_2.2. Formulation and preparation of composites cementitious_**

123 The composite is composed of CP-V-ARI cement and limestone filler. The water-soluble polymers,

124 high range water reducer (HRWR) provided by Aditex and polyether carboxylic provided by Grace

125 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

Raw material	Content [% by mass] / length				
	Ref	1% / 6 mm	2% / 6 mm	1% / 10 mm	2% / 10 mm
Portland cement [CP-V-ARI][a]	69.95	68.87	67.79	68.87	67.79
Limestone filler[b]	27.08	26.66	26.54	26.66	26.54
Eucalyptus cellulosic pulp	2.98	2.93	2.89	2.93	2.89
Curauá fiber (CF)	-	1.53	3.08	1.53	3.08
Water/cement ratio	0.33	0.34	0.36	0.34	0.36

(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 ºC 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 ºC for five days (thermal curing) totalizing 7 days of cure [13].

(a)   (b)

Figure 3 – (a) Front view of the vacuum extruder machine and (b) side view illustrating the composite exiting of the die [29].

152

153   ### 2.3. Mechanical characterization of the composites

154   Mechanical characterization tests were adopted the according to Santos et al., [13]. The fiber–

155   cement composites were tested using a servo-hydraulic mechanical testing machine MTS (810

156   series) controlled by the TestStar IIs system. Prismatic specimens were prepared using a diamond

157   cut-off wheel before grinding and final polishing of the specimen sides. The specimens had nominal

158   dimensions of 80 mm x 20 mm x 13 mm for all of the mechanical tests of the fiber-cement

159   composite. The modulus of rupture (MOR) was calculated by equation 1 and determined using a

160   three point bending configuration with a span of 64 mm and cross-head speed of 5 mm min^{-1}.

161

$$MOR = \left(\frac{3 * P_{max} * L_V}{2 * b * h^2}\right) \tag{1}$$

162

163   where P_{max} is maximum load, b is width, h is height and Lv is span between inferior supports.

164   The fracture toughness (K_{IC}) is the critical stress intensity fracture value for crack growth in the

165   material during mode-I failure, which evaluates the initial crack growth resistance, was also used to

166   characterize the cement based composites reinforced with curauá fiber. The SENB-type (single-

167   edge notch bend) specimens were prepared to establish the critical defect size and catastrophic

168   fracture [1]. The test configuration was the three-point bending. Prismatic specimens were prepared

169   with a centered plan notch with a depth equal to 10 % of the specimen height and notch tip profile

170   in the shape of a ''V'' with an angle of approximately 30º using a diamond disk of 0.5 mm

171   thickness to simulate a sharp crack. A cross-head speed of 15 mm min^{-1} was used. The values of the

172   maximum load, P_{max}, from the load–displacement curves were applied in the calculation of the

173   value of K_{IC} using the following equation, according to Santos et al., [13]:

174

$$K_{IC} = \frac{P_{max}}{bw^{1/2}}\, y(\alpha) \tag{2}$$

175

176   where $y(\alpha)$ is the geometric factor and accounts for both shape of crack and loading geometry, the

177   tensile stress at fracture, and a_0 the crack size. The ratio $\alpha = a_0/w$ of the initial notch length to

178   specimen height was 0.1 (or 10% as mentioned before).

179

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

180

181   where S is the span of 64 mm, and α is the relative length of the notch, which, in turn, is the ratio of

182   the original length of the notch, a_0, and the height of the specimen, w.

183   The fracture energy (FE) test was performed with the SENB type specimen and three-point bending

184   configuration, but the centered plan notch was of 30% of the specimen height. The span was of

185   64 mm. A cross-head speed of 10 µm min^{-1} was used to guarantee stable growth of the crack and to

186   measure the energy required for extending this crack over a unit area [30].

187   The work performed by the machine to completely propagate the crack along the specimen divided

188   by two times the projected area of the fracture surface (cross section of the specimen, A) was used

189   to determine the fracture energy, γ_{WoF}. The integration of the force–displacement curve was

190   performed up to the point where the force decreased to 5% of its maximum value reached during

191   the test, according to equation 4:

192

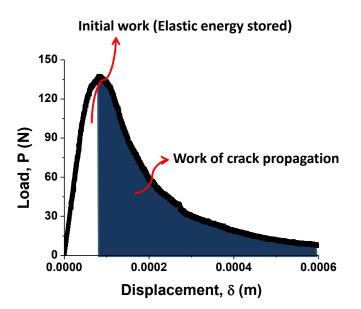193 $\gamma_{WoF} = \frac{1}{2A}\int P d\delta$ (4)

194

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

195

196   Additionally, a mechanical parameter was obtained the ''relative work of crack-propagation'' [31].

197   This mechanical parameter is obtained by dividing the work of crack propagation by the initial

198   work (elastic energy stored). The initial work is that performed from zero up to the point of the

199   maximum load (Figure 4). Although up to this point, some crack propagation could already occur, it

200   is easy to determine. This ratio considers all of the work performed for the effective crack

201   propagation related to the elastic energy stored in the system. Therefore, a higher value of this

202   relative work indicates that the material is more resistant to propagation of a crack [31].

203

204   **2.4. Physical characterization tests**

205   Water absorption (WA) apparent porosity (AP) and bulk density (BD) values were obtained from

206   the average of five specimens for each formulation, following procedures specified by ASTM C

207   948 [32], Standards.

208

209   **2.5. Scanning electron microscopy (SEM)**

210   Scanning electron microscopy (SEM) was used with secondary electron (SE) detector, operated at

211   5.0 kV accelerating voltage, for observation of the morphologies on the fractured surface of

212   composites generated in the mechanical tests. A back- scattered electron (BSE) detector operated at

213   around 15.0 kV and 20.0 kV was applied for viewing cut and polished surfaces. The BSE image

214   was used to study the fiber–matrix transition zone. Energy dispersive X-ray spectroscopy (EDS)

215   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 grinded 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 (K_{IC}) 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.

Formulation	Treatment (Tr)	%F	FL	Cr
Ref	Tr1	0	0	7 days (0)
1% / 6 mm	Tr2	1%	6 mm	7 days (0)
1% / 10 mm	Tr3	1%	10 mm	7 days (0)
2% / 6 mm	Tr4	2%	6 mm	7 days (0)
2% / 10 mm	Tr5	2%	10 mm	7 days (0)
1% / 6 mm	Tr6	1%	6 mm	200C (1)
1% / 10 mm	Tr7	1%	10 mm	200C (1)
2% / 6 mm	Tr8	2%	6 mm	200C (1)
2% / 10 mm	Tr9	2%	10 mm	200C (1)

243 The methodology of Experimental Planning (DOE), using Minitab® software version 14, was used

244 to establish the relationship between the properties (physical and mechanical) and the factors

245 evaluated, to understand the effects and to identify the factors and interactions considered

246 significant and to identify the treatments that resulted in the extreme values of the properties

247 estimated by the models. The analysis of variance (ANOVA) of regression models (Equation 5) was

248 evaluated at the 5% level of significance (α), considering the non-significance (P-value <0.05) of

249 the models and coefficients as null hypothesis (H0) and significance as an alternative hypothesis

250 (H1). For the validation of the regression models, the normality of the generated residues was tested

251 with the aid of the Anderson-Darling normality test, also at the 5% level of significance, and for the

252 hypotheses formulated, P-value greater than or equal to 0.05 implies in the normality of the waste

253 distribution, validating the ANOVA model.

254

$$Y=\beta 0+\beta 1\cdot\%F+\beta 2\cdot FL+\beta 3\cdot Cr+\beta 4\cdot\%F\cdot FL+\beta 5\cdot\%F\cdot Cr+\beta 6\cdot FL\cdot Cr+\beta 7\cdot\%F\ FL\cdot Cr+\varepsilon \qquad (5)$$

255

256 From Equation 5, Y denotes the estimated physical and mechanical properties, βi are the

257 coefficients obtained from the least squares method and ε consists of the random error. The

258 coefficient of determination (R^2) was used to measure the quality of the adjustments obtained, and it

259 should be noted that the reference conditions are not incorporated in the regression models.

260 In planning involving the 9 treatments after understood the effects of factors and interactions

261 between them on each property investigated. It can be noted that 6 or more determinations were

262 obtained by treatment and property investigated, totaling 382 determinations.

263

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

266 Figure 5 shows the mechanical properties (modulus of rupture (MOR), fracture toughness (K_{IC}),

267 fracture energy (FE), and relative work of crack propagation (RWP)) of extruded cementitious

268 composite (ECC) cured at 7 days (7d), after accelerated aging (200C), the confidence intervals of

269 the mean (at the 95% confidence level) and the range of variation of the coefficient of variation

270 (CV). Table 5 lists the respective average values and standard deviations of the mechanical

271 properties and physical characteristics. The P-values of the Anderson-Darling normality test of the

272 ANOVA residues for the four mechanical properties (MOR, K_{IC}, FE and RWP, respectively)

273 evaluated ranged from 0.265 to 0.781, validating the ANOVA model, and by the results of the

274 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.

$$MOR=1.39775+9.30425 \cdot \%F+1.55238 \cdot \underline{FL}+20.7527 \cdot Cr-1.05938 \cdot \%F \cdot FL-14.2959 \cdot \%F \cdot Cr$$
$$1.23217 \cdot FL \cdot Cr+1.14854 \cdot \%F \cdot FL \cdot Cr \ (R^2=79.72\%); \ MOR = [12.19; 23.18] \tag{6}$$

$$K_{IC}=0.878467-0.0865817 \cdot \%F-0.0040055 \cdot FL+0.438194 \cdot Cr+0.0117967 \cdot \%F \cdot FL$$
$$0.332244 \cdot \%F \cdot Cr-0.0522791 \cdot \underline{FL \cdot Cr}+0.0312871 \cdot \%F \ FL \cdot Cr \ (R^2=81.65\%); \ K_{IC} = [0.64; 1.08] \tag{7}$$

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].

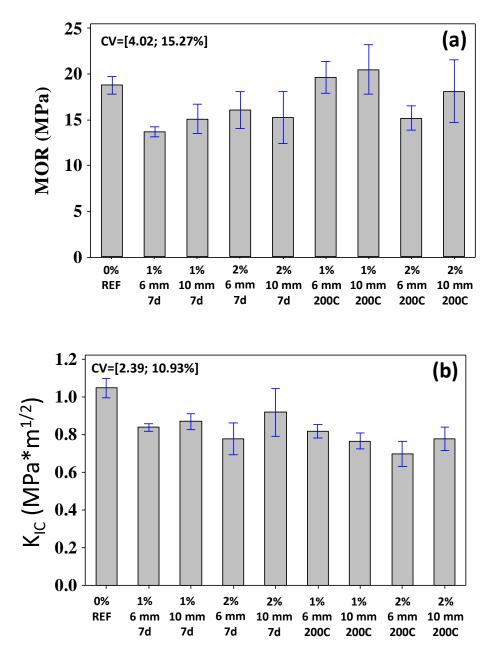Figure 5 – Average values and standard deviation (MOR) modulus of rupture (a) and (K_{IC}) fracture toughness (b).

304

305 The individual statistical interactions as the higher content (%F) and fiber length (FL) decrease K_{IC}

306 values, i.e., initial crack growth resistance in cement matrix, according to ANOVA, as calculated by

307 the equation 7 and whose values are shown in Figure 5b. The K_{IC} value of the reference composites

308 (1.05 MPa.m$^{1/2}$) suggests that these results may be related to distribution of defects in the matrix

309 produced by several factors such as the difficulty in packaging fiber in the matrix with particles and

310 negative interference in cement hydration process caused by absorption of water by CF. However,

311   the statistical combination of 2% by mass of fiber with 10 mm length after 200C increases the K_{IC}

312   values. It indicates that the matrix was improved mainly after 200 cycles of immersion and drying.

313   The results of fracture toughness of the composites reinforced with CF are similar than the results

314   obtained by Santos et al., [13]. The authors produced cement composites, reinforced with 3%

315   eucalyptus pulp and 2% of sisal fibers, produced by the extrusion method and subjected to

316   accelerated carbonation curing in the supercritical condition. The authors also analyzed the

317   composite before and after 200 cycles of immersion and drying. The average results obtained was

318   0.9 MPa.m$^{1/2}$ and 0.85 MPa.m$^{1/2}$, for the unaged and aged composites, respectively.

319 Table 5 – Average values and standard deviations of modulus rupture (MOR), fracture toughness (K_{IC}), fracture energy (FE), relative work of
320 propagation (RWP), water absorption (WA), bulk density (BD) and apparent porosity (AP) of the extruded cementitious composite (ECC) reinforced
321 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).
322

Formulations	Condition	MOR (MPa)	K_{IC} (MPa.m$^{1/2}$)	FE (J/m^2)	RWP	WA (%)	BD (g/cm^3)	AP (%)
Reference (Ref)	7d	18.75 ± 0.75	1.05 ± 0.04	187.61 ± 16.07	9.77 ± 4.22	16.14 ± 0.28	1.702 ± 0.013	27.47 ± 0.34
1% / 6 mm		13.82 ± 0.57	0.83 ± 0.02	108.20 ± 13.58	3.21 ± 0.67	16.49 ± 0.20	1.708 ± 0.007	28.16 ± 0.29
1% / 10 mm	7d	15.85 ± 1.66	0.88 ± 0.03	309.98 ± 15.98	14.65 ± 5.59	17.22 ± 0.15	1.729 ± 0.055	29.78 ± 0.84
2% / 6 mm		16.01 ± 1.92	0.78 ± 0.08	102.05 ± 9.05	3.66 ± 0.80	18.48 ± 0.72	1.726 ± 0.016	31.90 ± 0.96
2% / 10 mm		15.21 ± 2.26	0.92 ± 0.10	245.09 ± 89.49	14.04 ± 3.13	17.04 ± 0.24	1.720 ± 0.031	29.31 ± 0.59
1% / 6 mm		19.52 ± 1.63	0.82 ± 0.03	45.67 ± 4.28	1.41 ± 0.42	16.73 ± 0.14	1.740 ± 0.009	29.10 ± 0.23
1% / 10 mm	200C	20.45 ± 2.17	0.77 ± 0.03	56.75 ± 5.83	1.43 ± 0.63	17.41 ± 0.10	1.754 ± 0.044	30.54 ± 0.72
2% / 6 mm		15.16 ± 1.27	0.70 ± 0.06	20.18 ± 2.51	0.61 ± 0.25	17.77 ± 0.27	1.725 ± 0.008	30.66 ± 0.40
2% / 10 mm		18.08 ± 2.77	0.78 ± 0.05	41.75 ± 3.89	1.67 ± 1.17	17.59 ± 0.19	1.723 ± 0.027	30.31 ± 0.39

323   Figures 6a to 6d shows the micrographs of ECC with polished surface, Ref and reinforced with CF

324   at 7d and 200C respectively, that it showed a homogenous microstructure of the cement matrix at

325   7d and more densified after 200C. The composite reinforced with CF, (Figure 6c and 6d) content

326   high porosity in the fiber-matrix interface, i.e., it has a low adhesion which do not lead to expressive

327   values of MOR and K_{IC} in relation to the Ref. In the mixing process, the ECC with CF consumed

328   more water, which promotes the formation of porosity and interferes strongly in the w/c ratio

329   (water/cement) and the packaging of the raw materials in the matrix.

330   Figure 6d indicates that the vegetable fiber suffer a dimensional variation because it tends to lose

331   water to the system of the cementitious matrix which in turn is submitted to a rehydration process.

332   This dimensional variation process of the fiber promotes detachment of it in the cementitious

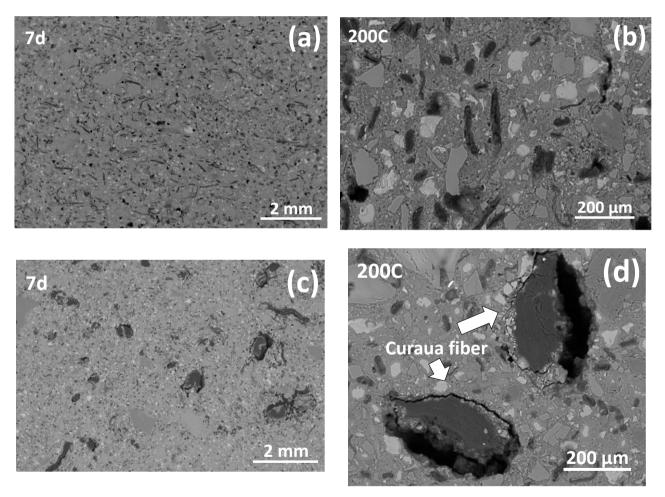333   matrix, consequently, it affects the mechanical behavior of the cement composite [19].

334

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.

335

336 The average values of fracture energy values (FE) and relative working crack propagation (RWP) of

337 the composite at 7d and after 200C are shown in Figures 7a and 7b, respectively. Equations 8 and 9

338 expresses the regression analysis obtained in the estimation of the FE and RWP values, and the

339 coefficients of determination (R^2) and the numerical intervals of these properties are also presented,

340 respectively. A regression analysis generates an equation to attempts to explain the statistical

341 relationship between one or more predictors and the response variable.

342

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

$$RWP = -21.7027 + 4.75874 \cdot \%F + 4.01494 \cdot FL + 25.4552 \cdot Cr - 0.686908 \cdot \underline{\%F \cdot FL} - 7.11968 \cdot \underline{\%F \cdot Cr} - 4.27127 \cdot FL \cdot Cr + 0.946910 \cdot \%F \ FL \cdot Cr \ (R^2 = 98.21\%); \ RWP = [0.33; 19.23] \tag{9}$$

343

344 The outliers were excluded from the set of results, and the terms considered non-significant by

345 ANOVA of the regression models were underlined.

346 FE is the energy per unit area needed to completely fracture the composite in quasi stable crack

347 propagation process in order to record the contribution of all toughness mechanisms mainly

348 promoted by the fibers. The RWP is the ratio of the plastic working and the elastic work i. e.

349 indicates the degree of pseudoplastic deformation, that is, it shows that capability of the cement

350 composite to absorb energy.

351 The ECC reinforced with 2% of fibers presented a significant statistical FE value in relation to ECC

352 with 1% at 7d and after accelerated aging (200C), based on Equation 8 and Figure 7a. According to

353 Rodrigues and Montardo [36] and Bentur and Mindess [37], the fiber content provides greater post-

354 cracking energy and smaller size of the cracks, since the fibers help to absorb the elastic energy

355 necessary to propagate cracks, which occur between fiber fractions. Regarding the fiber length, the

356 average value of FE of the composite with fiber of 10 mm is higher than one with fibers of 6 mm,

357 according to the ANOVA, as calculated by Equation 9 and demonstrated in Figure 7b, before

358 accelerated aged. However, FE values of composites with fibers of 10 mm presented major standard

359 deviations than ones with fibers of 6 mm. Fiber with length of 6 mm has a higher number of

360 filaments per mass, but fiber of 10 mm presented more efficiency in relation to pullout mechanism

361 that increased average values of the FE and RWP. Fiber with 10 mm has a better degree of adhesion

362 in the cementitious matrix between the different lengths of fibers, i.e. there is a greater probability

363 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.
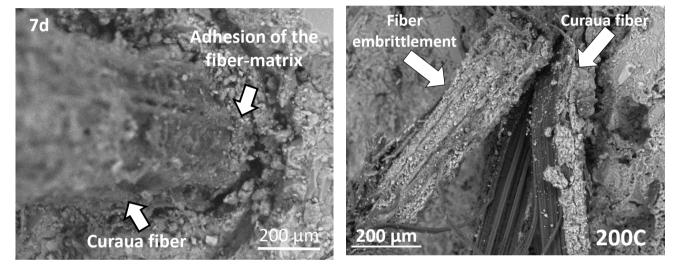

Figure 7 – Average values and standard deviation (FE) Fracture energy (a) and (RWP) relative work of crack propagation (b) in the composite extruded.

372   ECC reinforced with 1% / 10 mm length presented the highest average FE value of 310 J/m^2 and

373   57 J/m^2, at 7d and after 200C, respectively. The value of FE at 7d was higher than one determined

374   by Santos et al. (2015), which produced extruded composite reinforced with 2% by mass of

375   eucalyptus cellulosic pulp and 3% by mass of sisal fibers with a length distribution between 1 mm

376   and 14 mm, 7 days cure and exposed to supercritical carbonation. It presented average value of FE

377   approximately 230 J/m^2. Correia et al., [39] worked with extruded composites reinforced with

378   hybrid cellulosic fibers (8% cellulosic fibers + 1% bamboo nanofibers) that presented FE value

379   around 430 J/m^2 at 28 days of cure, but it decreased for 271 J/m^2 after accelerated aging of 200C.

380   The reduction of the FE value after accelerated aging indicates that degradation of the fibers in the

381   ECC caused debonding and breakage of fibers as illustrated in Figures 8a and 8b.

382

(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

383

384   ### 3.2. Physical Characterization

385   In Figure 9 are shown the graphs with the average values of the physical parameters: water

386   absorption (WA), bulk density (BD) and apparent porosity (AP) of the composites at 7 days and

387   after 200C between level fiber fraction and lengths of curauá fiber (CF). The confidence intervals of

388   the mean (at the 95% confidence level) and the range of variation of the coefficient of variation

389   (CV). The P-values of the Anderson-Darling normality test of the ANOVA residues for the three

390   physical properties (WA, BD and AP) evaluated ranged from 0.109 to 0.918, validating the

391   ANOVA model. Although the coefficient of determination obtained for the estimation of apparent

392   porosity (AP) was 33.22%, all regression models were considered significant by ANOVA.

393 Equations 10, 11 and 12 expresses the regression analysis obtained in the estimation of the WA, BD

394 and AP values, and also the coefficients of determination (R^2) and the numerical intervals of this

395 property are presented, respectively.

396

$$WA=10.0648+5.32864\cdot\%F+0.743583\cdot\underline{FL}+3.14206\cdot\underline{Cr}-0.560438\cdot\%F\cdot FL-2.83893\cdot\underline{\%F\cdot Cr}-$$
$$0.341080\cdot FL\cdot Cr+0.329509\cdot\%F\ FL\cdot Cr\ (R^2=92.09\%);\ WA = [16.24;\ 18.47] \tag{10}$$

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

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

397 Equations 10 to 12, the outliers were excluded from the set of results, and the terms considered non-

398 significant by ANOVA of the regression analysis were underlined.

399 ECC reinforced with 2% of curauá fiber (CF) presented higher values of WA in relation to the

400 formulation with 1% by mass showed in Equation 10 and Figure 9a, possibly due to the greater

401 number of fibers per unit volume conducting to inefficient packaging of the matrix, aspect ratios of

402 the fibers, CF (80 and 133, respectively for lengths of 6 mm and 10 mm) and, consequently more

403 defects appears in the interface fiber and matrix [40,41]. The results of fiber length and type of cure

404 did not differ significantly between the formulations according the ANOVA. The interaction

405 between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length (FL) [6, 10 mm] and

406 curing type (Cr) [7d, 200C]), the highest value occurs from the combination with 2% of fibers, 6
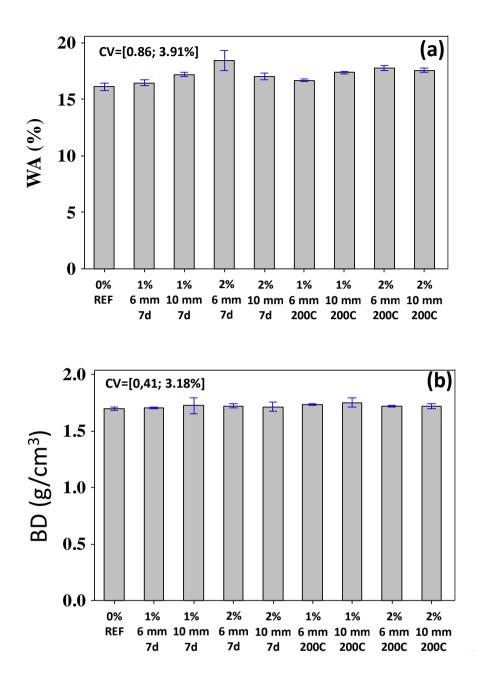
407 mm or 10 mm in length at 7d or after 200C.

408 Composites with 2% by mass of fibers after 200C presented an increase significant of the BD

409 values showed in Equation 11 and Figure 9b, which can be attributed the filling of the matrix pores

410 by the continued hydration process during accelerated aging cycles in formation of calcium

411 hydroxide ($Ca(OH)_2$), calcium silicate hydrate (CSH) and calcium carbonate ($CaCO_3$) [13]. These

412 phenomena were found in several studies that have been applied accelerated aging cycles in

413 composites cementitious, such as Soto et al., [35]; Dias et al., [42] and Teixeira [4]. The only

414 individual factor statistical that did not affect the bulk density (BD) values was the fiber length.

415 Thus, the interaction between the three statistical factors (fiber fractions (% F) [1, 2%], fiber length

416 (FL) [6, 10 mm] and curing type (Cr) [7d, 200C]), the highest value occurs from the combination

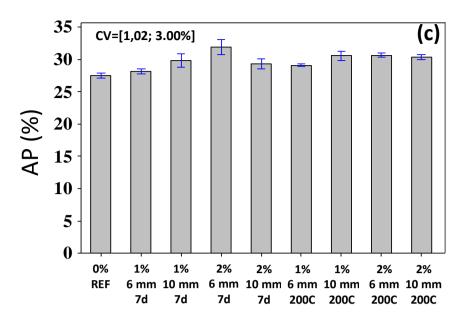417 with 2% of fibers, 6 mm or 10 mm in length and after 200C.

(a)

CV=[0.86; 3.91%]

WA (%)

0% REF | 1% 6 mm 7d | 1% 10 mm 7d | 2% 6 mm 7d | 2% 10 mm 7d | 1% 6 mm 200C | 1% 10 mm 200C | 2% 6 mm 200C | 2% 10 mm 200C

(b)

CV=[0,41; 3.18%]

BD (g/cm^3)

0% REF | 1% 6 mm 7d | 1% 10 mm 7d | 2% 6 mm 7d | 2% 10 mm 7d | 1% 6 mm 200C | 1% 10 mm 200C | 2% 6 mm 200C | 2% 10 mm 200C

Figure 9 - Results of the physical properties: (WA) water absorption (a); (BD) bulk density (b) and (AP) Apparent porosity (c).

According to the ANOVA, considering the individual statistical factors and the interaction, only the accelerated aging (200C) 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.
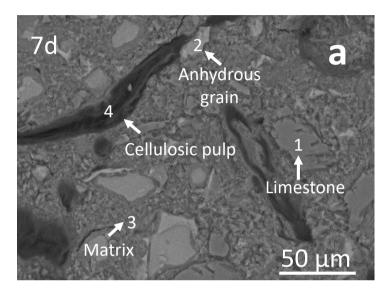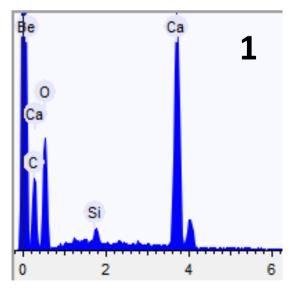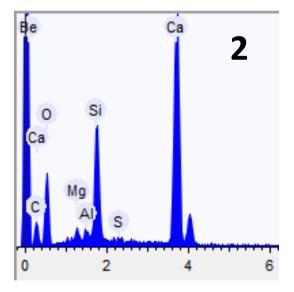
3.3. Micrographic electronic scanning SEM

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

438   limestone in the mix. In point 2, detaching the anhydrous grain that was not completely hydrated,

439   predominantly Si and Ca elements.

440   Point 3 clearly shows a grain formed cement constituents. In point 4, the cellulose pulp with a high

441   calcium content and silicon are shown, indicating that the fiber absorbed cement hydration water,

442   which was similar to that presented by Tonoli et al., [43] and Teixeira et al., [29], who studied
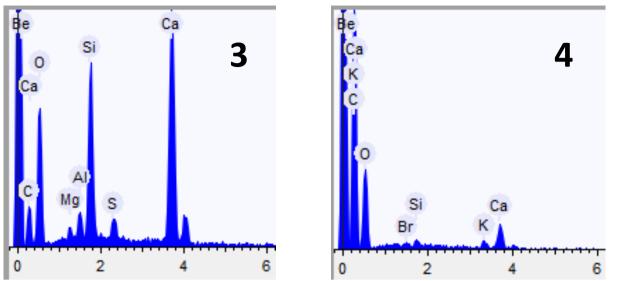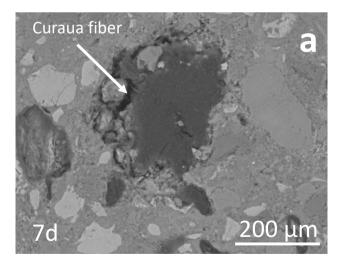
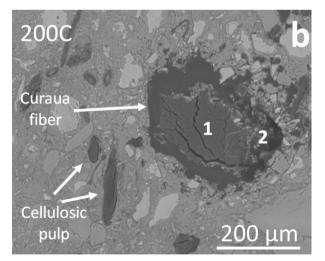443   eucalyptus cellulosic pulp.

444

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

445

446   In Figure 11a, it is observed a resulted of the dimensional variation of fiber according to its

447   humidity content. Resulting pores lead to higher water absorption, greater porosity and low

448   resistance.

449   Savastano and Agopyan [44], explain that the best performance is achieved by better adhesion of

450   the fiber-matrix. The improved adherence is achieved by reducing the porosity and the lowest

451   concentration of Portlandite (calcium hydroxide crystals) approximately the fiber.
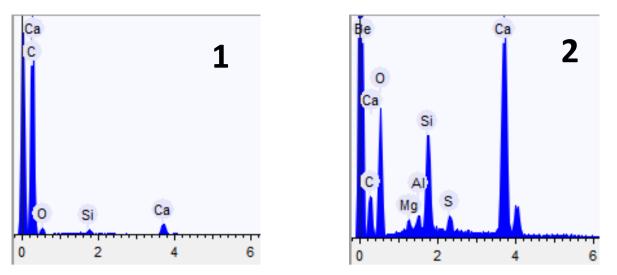
452

Figure 11 – Micrograph of scanning electron microscopy (SEM-BSE) polished surfaces of composites reinforced with CF: (a) CF (arrow indicates adhesion fiber-cement) and (b) CF after 200C with points of EDS analysis that is signaled the image (point 1 and 2).

453

454 In Figure 11b, after 200 cycles, there is better adhesion of the fiber in the matrix. Point 1 shows that,

455 in the central part of the fiber were not found cement hydration products as indicated by the EDS, the

456 large presence of C. However, at point 2, the border of the fiber presents the main chemical elements

457 of cement, silicon and calcium [19,45].

458 They can also be observed by EDS, chemical elements, such as, Al, S, and Mg. This phenomenon can

459 be associated with mineralization fibers as indicated by Bentur and Akers [46]. On immersion in

460 water, free ions formed by the dissolution of the cementitious phases of Portland cement penetrated

461 into the lumen of the fibers, leading to the formation of ettringite/monosulfates and calcium hydroxide

462 Ca(OH) [29,45]. Batic et al., [47] showed that the re-precipitation of ettringite in microcracks and

463 pores of the cementitious composite may occur under normal conditions (ambient temperature)

464 curing. Such training has previously been suggested as one of the degradation mechanisms of the

465 fibers within the concrete matrix [14,15].

466

467 **4. CONCLUSIONS**

468 The curauá fiber suffered mineralization process during curing (water absorption of the cement

469 hydration products) which consequently carried the fiber to decreased its properties. The fiber

470 content directly influenced the mechanical performance and fibers with lengths greater showed

471 better mechanical results for modulus of rupture (MOR) and fracture energy (FE) according to

472 ANOVA. Cementitious composites reinforced with fibers curauá showed superior mechanical

473 performance compared to available research literature. The modulus of rupture (MOR), fracture

474 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 ($Ca(OH)_2$), calcium silicate hydrate (CSH) and calcium carbonate ($CaCO_3$) 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.

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