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BAMBOO CELLULOSIC PULP PRODUCED BY THE ETHANOL/WATER PROCESS FOR REINFORCEMENT APPLICATIONS

POLPA CELULÓSICA DE BAMBU PRODUZIDA PELO PROCESSO ETANOL/ÁGUA PARA APLICAÇÕES DE REFORÇO

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ABSTRACT

Organosolv pulping is the clean chemical process of using organic solvents to aid in the removal of lignin and hemicellulose from lignocellulosic raw materials. This method provides facility for solvent recovery at the end of the process. In this work, it was to produce bamboo cellulosic pulp by the organosolv process evaluating different temperatures and reaction times, and the pulps were analyzed aiming their future application in the reinforcement of composites. The production of bamboo pulp by the organosolv process was studied varying the cooking conditions at 1, 2 and 3 h and 150, 170 and 190ºC of temperature, in order to achieve the ideal conditions of yield, chemical and morphological characteristics of the pulp for its potential application in the reinforcement of composites. The best results for delignification (kappa number of 38), with relatively lower fiber degradation (viscosity of 625 cm^3 g^{-1}), aspect ratio of 40.4 and the index zero-span of 204 Nm g^{-1}, were achieved for the pulping process at 190ºC for 2 h. These pulping conditions can be considered as the more appropriate in the range of time intervals evaluated in this work. The higher mechanical strength and the lower incidence of morphological defects in the fiber (6.0% of *curls* and 10.6% of *kinks*) can demonstrate the potential of organosolv bamboo pulp as a reinforcing element.
Keywords: cellulose; bamboo; organosolv pulping; ethanol.

RESUMO

A polpação organossolve é o processo químico limpo que utiliza solventes orgânicos para remoção de lignina e hemicelulose de matérias-primas lignocelulósicas. Esse método proporciona a facilidade de recuperação do solvente no final do processo. Neste trabalho foi produzida polpa celulósica de bambu pelo processo organossolve, avaliando diferentes temperaturas e tempos de reação, e as polpas foram analisadas visando à futura aplicação para reforço de compósitos. A produção de polpa de bambu pelo processo organossolve foi estudado variando as condições de cozimento de 1, 2 e 3 h a 150, 170 e 190° C, a fim de alcançar as condições ideais de rendimento e características químicas e físicas da polpa para a potencial aplicação em reforço de compósitos. Os melhores resultados para a deslignificação (número de kappa 38), com a degradação da fibra relativamente baixa (viscosidade de 625 cm^3 g^{-1}), razão de aspecto de 40,4 e o índice zero span de

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204 Nm g^{-1}, foram obtidos pelo processo de polpação a 190°C durante 2h. Essa condição de polpação pode ser considerada como a mais adequada em relação aos demais intervalos de tempo estudados no presente trabalho. A maior resistência mecânica e menor incidência de defeitos morfológicos na fibra (6,0% de *curls* e de 10,6% de *kinks*) podem demonstrar o potencial da polpa organossolve bambu como elemento de reforço.
Palavras-chave: celulose; bambu; polpação organossolve; etanol.

INTRODUCTION

The cellulosic pulp can be considered as a promising market for the reinforcement of polymeric materials, ceramic and cementitious composites in addition to the paper production (ALEMDAR; SAIN, 2008; SUNDAR et al., 2010). The use of cellulosic fibers as reinforcement in composite materials has been studied to replace synthetic fibers, especially glass fibers for different industrial applications such as packaging, automobiles (WAMBUA et al., 2003; SAIN; PANTHAPULAKKAL, 2006) and in the construction materials (KHEDARI et al., 2003;PACHECO-TORGAL; JALALI, 2011; CLARAMUNT et al., 2011).

Considering the vegetable fiber reinforced cementitious composites, the lignin present in these fibers has an amorphous structure with high solubility in the alkaline medium. Contrarily, cellulosic pulps contain negligible amounts of that compound and therefore it can result in a lower alkaline attack by cement to these pulps than fibers with higher lignin content (MOHR et al., 2005; LI et al., 2012).

There is a growing interest in the use of fibrous raw material derived from lignocellulosic materials such as annual plants and agricultural waste to cellulosic pulp production. The increasing environmental concerns, uncertain availability of wood fibers and potential increase in the wood costs justify the researches for alternative sources of fibers (LÓPEZ et al., 2010).

Non-wood lignocellulosic materials most used for cellulose production are distributed in 44% straw, 18% sugarcane bagasse, 14% reeds, 13% bamboo and 11% others (SRIDACH, 2010). Bamboo presents advantages such as rapid growth, short-term renewal and easily of spread that indicate it as a potential raw material for cellulosic pulp production. Although *Bambusa vulgaris* is commonly used for cellulosic pulp production in Brazil, the species *Bambusa tuldoides* has higher content of fibrous material (AZZINI et al., 1990; AZZINI; GONDIM-TOMAZ, 1996) compared to *Bambusa vulgaris* and *Dendrocalamus giganteus* that contribute to the higher cellulose yield.

The process of separation of macromolecular components, i.e. pulping process, comprises the delignification which is the solubilization of the lignin fragments resulted from the breakage of chemical bonds of protolignin (lignin "in situ") and is heavily influenced by the morphology of the different cells and the ultrastructure of plant tissues.

The most used pulping chemical processes are those alkaline such as kraft and those acidic such as sulfite (SRIDACH, 2010). Organic solvents solubilize lignin fragments in the organosolv process of pulping, usually associated with water in the 10% to 50% ratio (by volume). For the most organosolv process carried out at high temperatures (185 - 210ºC), there is not the need for acid addition since organic acids released from the biomass act as catalysts for the rupture of bonds of the lignin-carbohydrate complexes (DUFF; MURRAY, 1996).

The Alcell® method is a specific type of organosolv process that employs the ethanol-water mixture as solvent and cooking medium (PYE; LORA, 1991). Ruzene and Gonçalves (2003; 2007) produced sugarcane bagasse pulp by the organosolv process at 185°C for 3 h, 1:1 ethanol/water ratio and Joaquim et al. (2009) found the optimum condition for organosolv pulping of sisal at 190°C for 2 h, 1:1 ethanol/water ratio and 1:10 sisal/solvent. Based on this process, it is possible to produce pulps with high yield, low lignin content and high mechanical strength (SHATALOV; PEREIRA, 2004; SHATALOV; PEREIRA, 2008; YAWALATA; PASZNER, 2004).

The organosolv process has the advantage of using substances which are less harmful to the human health and the environment compared to

conventional processes (kraft and sulfite) that cause major problems of pollution (RUIZ et al. 2011). The organosolv pulping has economic and environmental advantages, since the use of organic solvents (ethanol, for instance) enables the operation of smaller and more compact plants, eliminates the need for the recovery of inorganic reagents and eliminates the sulfur emission. Additionally, the lignin removed can be recovered in the recycling operations of organic solvent, which involves stages of distillation and precipitation (AZIZ; SARKANEN, 1989; HERGET, 1998; SIDIRAS; KOUKIOS, 2004; RUIZ et al., 2011).

The recovered lignin has some commercial applications, such as additives in cement and concrete industry, animal feed, polymers industry and painting sector. Other applications are as binders and adhesives to replace phenolic resins and the production of particulate panels and as dispersants in pesticide industry, petroleum production sludge, in leather tanning and dye industry (STEWART, 2008; SENA-MARTINS et al., 2008).

The objective of this work was to produce bamboo cellulosic pulp by the organosolv process evaluating different temperatures and reaction times. The obtained pulps were analyzed by chemical, morphological and mechanical tests aiming their future application in composites.

MATERIALS AND METHODS

Ethanol/water pulping

The bamboo culms aged 1 year were obtained in Pirassununga, Sao Paulo state, Brazil. For the production of chips, dried bamboo culms were chopped in a wood chipper MA 680 Marconi brand. Chips with average dimensions of 26.02 mm x 2.02 mm were used for the production of pulps.

The cooking parameters were evaluated searching for a minimum time of reaction andmaximum lignin removal with minimal losses of mechanical strength of the pulps. The pulping variables were equally determined by observing an aspect ratio (the ratio between fiber length to fiber diameter) acceptable for reinforcing elements.

Temperatures, cooking times and ethanol/water ratio adopted in the experimental work were based on studies on the organosolv pulping developed for different raw materials (RUZENE; GONÇALVES, 2003; 2007; JOAQUIM et al., 2009). The above conditions for pulping served as a reference for those settings adopted in the present work that are shown in Table 1.

TABLE 1: Pulping parameters and conditions.
TABELA 1: Parâmetros e condições de polpação.

Parameters	Conditions
Weight of chips (g)	12
Chips/solvent ratio (weight:volume)	1:10
Ethanol/water ratio (volume: volume)	1:1
Pulping temperature(°C)	150, 170, 190
Pulping time (h)	1, 2 e 3

The pulping was carried out in a batch reactor with capacity of 150 mL. It took approximately 20 minutes for the reactors to achieve the pulping temperature. Consequently, the temperature rate varied from 7.5°C/min in the case of upper temperature equal 150°C until 9.5°C/min in the case of 190°C. After cooking, reactors were cooled in an ice container. After the cooling step, the bamboo chips treated were transferred to the defibrator where it was added 500 mL of 1% NaOH during 3 min, for the removal of the remaining lignin on the fibers. This mixture was transferred to a Buchner funnel, where it was filtered under vacuum and washed with another 500 mL 1% NaOH and then with distilled water until the washing liquid turned into neutral pH.

The non-depurated yield for all reactions was calculated by the Equation (1). Based on these results, the variables for a better pulp production were defined. Pulps produced from optimum conditions were subjected to chemical, morphological and mechanical analyses,

$$\% R = \frac{m_p}{m_c} \times 100 \quad (1)$$

Where % R is process yield, m_p is the dry mass of bamboo chips treated (g) and m_c is the dry mass of bamboo chips (g).

Chemical characterization of bamboo and pulps

The chemical characterization of bamboo and pulps was performed according to the methodologies presented in the Table 2. All analyses were performed in triplicate.

The bamboo and pulp crystallinity was

TABLE 2: Methodologies for the chemical characterization of bamboo and bamboo pulp.
TABELA 2: Metodologias para caracterização química do bambu e da polpa de bambu.

Parameters	Methodology
Kappa	ISO 302 (2004) e TAPPI T 236om (1999)
Klason Lignin	TAPPI T 222 om (1998)
Holocellulose	TAPPI T 19 m (1954)
α – Cellulose	TAPPI T 203cm (1999)
Cellulose	VAN SOESTAT (1987)
Hemicellulose	VAN SOESTAT (1987)
Extractives	ISO 624 (1974)
Viscosity	SCAN CM 15:88 (1998)

Bamboo and pulp crystallinity

determined by X-ray diffraction, carried out in the Rigaku Rotaflex Diffractometer, model RU 200B, with Cu-Kα radiation, rotational anode, horizontal goniometer. The generated voltage was 40 kV with 80 mA of current. The interval of scan between 5º to 40º (2Θ) with step of 0.02° and acquisition rate of 2°/min was adopted.

The crystallinity index (CrI) was determined by the empirical method as described by Segal et al. (1959) according toEquation (2).

$$CrI = 100 \times \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \quad (2)$$

Where, I_{002} is the value of the intensity of (002) reflections corresponding to22º – 23º(2 Θ), and I_{am}, diffraction intensity corresponding to 18º – 19º(2 Θ). The values were obtained directly from the XRD diffractogram of pulp samples (BROWNING, 1967; ZERONIAN; BUSCHLE-DILLER, 1992).

Fibers mechanical characterization

The mechanical characterization of fibers was carried out according to Tonoli et al. (2010) using sheets of cellulose prepared with the pulps obtained at different cooking times and the same temperature to evaluate the mechanical resistance of individual fibers. The sheets were shaped with the same weight (60g m^{-2}) using an automatic forming Pulmac ASF-C1.

Fiber mechanical strength was determined according to the methods TAPPI T 273 pm (1995) and TAPPI T 231 cm (1996) by means of a tensile tester Pulmac C1-Z2400. These methods are used to determine the index of average resistance of the longitudinal structure of individual fibers (Pasquini et al., 2008).

The tensile index, IT, was calculated from Equation (3).

$$IT = \frac{T}{G} \times 1000 \quad (3)$$

Where, T is the measure of zero – span strength and G is the weight.

Morphological characterization of fibers

The morphological characteristics that include length, diameter, *curls* and *kinks* (i.e. defects and distortions that occur in fibers during the pulping process and affect the resistance and break energy of the pulp) and the content of fines smaller than 0.2 mm were analyzed in Pulptec TM MFA-500 equipment - Morphology Fiber and Shive Analyser - MorFiTrac.

RESULTS AND DISCUSSION

The results of yield in the bamboo pulping process by the organosolv method using water and ethanol as solvent at 150, 170 and 190°C and for 1, 2 and 3 h are shown in Figure 1.

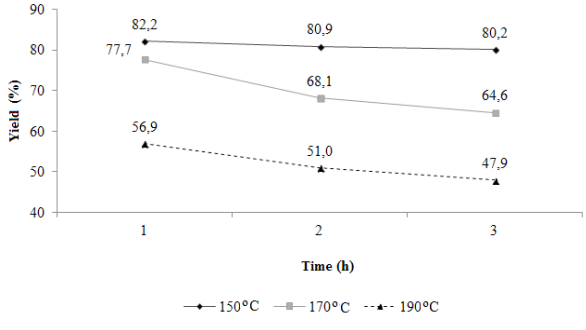

FIGURE 1: Organosolv bamboo pulping process yield at temperatures of 150, 170 e 190ºC, for 1, 2 and 3 h.
FIGURA 1: Rendimento do processo de polpação organossolve de bambu às temperaturas de 150, 170 e 190ºC, em 1, 2 e 3 h.

Figure 1 shows the decrease in the process yield with the increaseof temperature and pulping time. The decreased yield was expected since the removal of lignin and hemicelluloses becomes more effective under conditions where higher temperatures were combined with shorter time.With

the reduction of lignin and hemicellulose of the fibers there was an increase in the levels of cellulose. The fibers with lower lignin and hemicellulose have higher levels of cellulose as shown in Table 3. However, temperatures of 150°C and 170°C were insufficient for the delignification/pulping of bamboo chips during the 3 reaction times. Chips remained intact with minimal lignin dissolution and little disruption of fibers. Thus, pulping conditions were only considered at 190° C for 1, 2 and 3 h, as initially proposed.

Joaquim et al. (2009) also produced sisal pulp by the organosolv pulping process under the same conditions herein described. Yields were 60.9, 56.8 and 56.4% for times of 1, 2 and 3 h, respectively, at 190°C. For sugarcane bagasse pulping, also by the ethanol/water organosolv process in the same proportion adopted in this work and 3 h of cooking at 185°C, Ruzene and Gonçalves (2003) reached 54.5% in pulp yield.

The results presented in this study are compatible with the range found in the literature. The variation in such results can be attributed to the differences in chemical composition which is intrinsic to the raw materials used.

Chemical characterization of bamboo and pulps

As shown in Table 3, kappa number values, Klason lignin, hemicellulose and extractive were reduced by increasing the cooking time of bamboo chips.

The high extent of lignin solubilization (values measured by Kappa number and Klason lignin) confirms the efficiency and selectivity of the organosolv extraction.

According to De Groot et al. (1995) the delignification occurs in 3 stages: initial, dominant and residual. For the authors, the initial step removes high amount of hemicellulose and low amount of lignin. In the dominant step, there is higher removal of lignin and hemicelluloses and finally, the removal of lignin occurs slowly as a result of the higher inertia of the residual lignin in the residual phase. The process maintenance for longer reaction times may lead to the hydrolysis reactions and degradation of cellulose chains.

For bamboo organosolv pulping, 2 h comprised the dominant stage, based on the significant decrease in the lignin content and in the hemicellulose content in comparison to the 1 h cooking and raw material (Table 3) as previously discussed by De Groot et al. (1995). The residual step is considered in 3 h reaction, since the lignin solubilization and removal of extractives and hemicellulose occurred more slowly and there was further degradation of the cellulose chain, which can be confirmed by the viscosity results (Table 3).

According to Sridach (2010), for cooking non-wood raw materials by the organosolv process it is required temperatures between 165-195°C for at least 1 h. In conventional pulping processes, delignification takes place also in the range between 1 and 2 h, depending on the temperature and raw material.

Ciaramello (1970) produced bamboo pulp of *Bambusa tuldoides* by soda and sulphate processes for 2 h reaction at 160°C. The yields for soda and sulphate processes were 50.3% and

TABLE 3: Chemical characterization of bamboo and bamboo pulp obtained at 190°C and 1, 2 and 3 h of cooking.

TABELA 3: Caracterização química do bambu e da polpa organossolve de bambu obtida a 190°C em 1, 2 e 3 h de cozimento.

		Pulping time		
Parameters	Bamboo	1 h	2 h	3 h
Kappa number	--	76.3	38.0	25.2
Lignina Klason (%)	14.7	8.0	2.5	2.7
Holocellulose (%)	67.2	86.5	93.1	97.5
α – Cellulose (%)	35.2	76.8	86.6	91.2
Cellulose (%)	48.3	78.9	89.8	90.4
Hemicellulose (%)	22.0	7.5	4.5	4.0
Extractives (%)	--	3.4	2.3	2.3
Viscosity (cm^3/g)	--	982.0	625.0	382.0

55.0%, respectively and kappa number values were 30.0 and 31.4. The results indicate the organosolv process effectiveness for bamboo pulping, since the values of yield and kappa number are within the average found in reactions carried out by conventional methods.

The viscosity parameter is associated with the cellulose polymerization degree and may estimate the degree of degradation of this macromolecule in the processes of cellulosic pulping. Thus, overall, the higher viscosity value indicates greater carbohydrates preservation and cellulose in particular (VU et al., 2004).

Morphological and mechanical characteristics of pulps

The results of morphological and mechanical characterization of pulps obtained for 1, 2 and 3 hours of cooking time are shown in Table 4.

TABLE 4: Morphological and mechanical parameters of bamboo pulp obtained at 190ºC and 1, 2 and 3 h of cooking.
TABELA 4: Parâmetros físicos e mecânicos da polpa de bambu obtida a 190ºC e durante 1, 2 e 3 h de cozimento.

	Pulping time		
Parameters	1 h	2 h	3 h
Length weighted (mm)	1.2	0.8	0.8
Width (µm)	22.8	19.8	18.2
Aspect ratio (length/width)	52.6	40.4	43.9
Index *zero span* tensile (N.m/g)	162.0	204.0	184.0
Kinked fibers (%)	7.0	10.6	12.2
Curl (%)	5.1	6.0	6.4
Fines (%)	47.1	62.3	62.8
Length fines (µm)	60.5	56.5	55.0

Through the cellulose crystallinity index calculated from the amorphous and crystalline phases given in the X-ray diffractogram (see Figure 2), it is shown the increased pulp crystallinity index with the increasing of cooking time. The crystallinity index in bamboo and pulps produced at 1, 2 and 3 h were found to be 52.7, 79.2, 79.4 and 80.5%, respectively.

According to Evans et al. (1995) and Gümüskaya et al. (2003), there is an indirect proportional relationship between the pulping yield and cellulose crystallinity in pulp. This relationship can be observed by analyzing the pulp yields and the

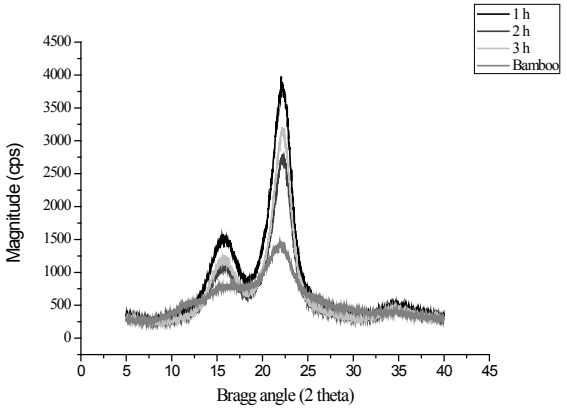

FIGURE 2: X-ray diffractogram of bamboo and organosolv bamboo pulp obtained after 1, 2 and 3 h of pulping at 190ºC.
FIGURA 2: Difratograma de raios-X do bambu e das polpas organossolve de bambu obtidas após 1, 2 e 3 h de polpação a 190º C.

values of crystallinity index for the 3 pulping times. Yields of pulp were reduced due to the removal of lignin, some carbohydrate fractions and impurities in bamboo during pulping.

The crystallinity index of cellulose increased as a result of the pulping time due to the removal of less-ordered amorphous cellulose portion. This removal can be seen in Table 3, which shows the reducing of lignin and hemicelluloses content and increase of cellulose, holocellulose and α-cellulose.

The length weighted reduced from 1.2 mm to 0.8 mm when reaction time increased from 1hour to 2 h, keeping constant at this value for 3 h reaction. The average width range also suffered decrease with the increase from 1 h to 2 h reaction by keeping it virtually constant for 3 h reaction. As expected, the reduction of length was more pronounced than the corresponding width reduction, resulting in the reduced aspect ratio as shown in Table 4. The length values obtained in this study (Table 4) were lower than those reported in the literature for bamboo cellulose fibers. The mean length determined by Coutts and Ni (1995) was 1.7 mm and 20.0 µm width for bamboo kraft pulp.

The size of pulp fibers change when determined by automatic optical analyzer. This is due to the projected length being smaller than the real one and the optical analyzer can measure broken fibers as full fibers (LEVLIN; SODERHJEM, 1999;

TREPANIER, 1998; BRAATEN; MOLTEBERG, 2004). According to the before mentioned authors, this breakdown occurs as a consequence of 3 factors. First, the raw material is chopped and this operation can cut fibers if not performed correctly. Second, pulping conditions alter fibers dimensions. During these processes, lignin and hemicelluloses are solubilized from the cell wall resulting on thinner and more flexible fibers. Third, during the processing of pulps,the mechanical and disintegration treatment deform the fiber and induce to gradual curvature (*curl*) and twisted curvature (*kink*) which has influenced on the fiber length.

The results of morphological characteristics of the fibers shown in Table 4 support the evidence that the damage to fibers were more intense between 1to 2h pulping. This can be verified by the reduced length and width, increased fine content and deformed fibers (*kink* and *curl*) and decreased length of fines. However the damage was more severe for 3hours, justified by the smaller dimensions, higher deflection and higher fine content, which can be correlated with the low viscosity described in the physico-chemical characterization.

When fibers are used as reinforcement in composites, the aspect ratio is an important parameter which affects significantly the amount of stress dissipated from the matrix to the embedded fibers (CLARAMUNT et al., 2011). Fibers with higher aspect ratios are more efficient to provide the reinforcing effect in the matrix for a predetermined threshold. The variation in the aspect ratio was due to the increased pulping time, mainly by the reducing of the length and width at 1 and 2 h cooking. As the length of fibers was constant between 2 h and 3hours and the width also decreased to a small extent, aspect ratio showed a slight increase.

It is observed the decreasing of tensile index of fibers with increasing pulping time from 2 to 3 h. The major degradation of cellulose chain to 3 h, indicated by the low viscosity, may be responsible for this drop in resistance. The fibers resistance may decrease with the chemical treatment if fiber components, especially cellulose, are degraded. The lower resistance for pulp obtained in 1 h can be explained by increased amount of lignin, hemicellulose and extractives.

The results for characterization of bamboo organosolv pulp are compatible with the pulp used as reinforcement in cementitious matrices reported by Almeida et al. (2013). In the work, the authors used eucalyptus pulp with 0.8 mm, 16.4μm, 51 and 8.6%, of length, width, aspect ratio and curls, respectively. Panthapulakkalet al., (2006) used wheat straw pulp as reinforcement of thermoplastic polyolefins. The pulp had 63.14% of cellulose, 5.57% of lignin, 2.7 mm, 76 μm of length and width, respectively, and 35 of aspect ratio. The results in the mentioned works show that cellulosic pulp from different raw materials can be used as reinforcement in different matrices and providing good mechanical and physical properties. The characteristics of bamboo organosolv pulp are similar to those mentioned in the cited works therefore the bamboo organosolv pulp can be considered as an alternative and used as reinforcing material.

CONCLUSION

The decreasing in pulp yield with the increasing temperature and pulping time can be observed, due to the removal of lignin and hemicelluloses.

The organosolv process for bamboo pulping is effective since the values of yield and kappa number are within the average found in conventional processes. The time of 1 h is insufficient to dissolve the lignin. There is a drop in the tensile index of fibers at 3 h due to the cellulose degradation, a reduction in fiber dimensions, fibers deformation, and increased amount of fines. Therefore, the 2 h cooking is considered appropriate at temperatures below 190°C. Associating the characteristics of residual lignin content in the pulp, aspect ratio, fiber damage and tensile index ensure that the best pulping time was 2 h at 190°C for its use as reinforcing element in composite materials for engineering applications.

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