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THERMAL ANALYSIS OF LESS COMMON LIGNOCELLULOSE FIBERS

A. L. F. S. d'Almeida[1], *D. W. Barreto*[1], *V. Calado*[1] *and J. R. M. d'Almeida*[2*]

[1]School of Chemistry, Universidade Federal o Rio de Janeiro, Centro de Tecnologia, Bl. E, Cidade Universitária
Rio de Janeiro, Brasil
[2]Materials Science and Metallurgy Department, PUC-Rio, Rua Marquês de São Vicente, 225
22453-900 Rio de Janeiro-RJ, Brasil

The thermal behavior of four unusual lignocellulose fibers – namely Caroa, Curaua, Piassava and Sponge gourd – is described. Caroa and Curaua fibers showed a more homogeneous thermal degradation, with a single peak dominating in the DTG curve. Piassava and Sponge gourd showed two separated peaks, revealing the more pronounced amounts of hemicellulose present at these fibers. All four fibers are, however, thermally stable up to temperatures of around 200°C. The activation energies for the thermal degradation of the fibers were similar, except for the Caroa fiber. The lower activation energy associated to this fiber was attributed to its higher hemicellulose to cellulose ratio.

Keywords: *activation energy, Caroa, Curaua, lignocellulose fibers, Piassava, Sponge gourd, TG, thermal analysis*

Introduction

Lignocellulose fibers are being increasingly used to reinforce polymer-matrix composite materials. The main advantages of these fibers over the synthetic ones are their biodegradability and the very important aspect of being neutral with respect to CO_2 emission [1].

Jute, sisal and flax can be included at the group of common lignocellulose fibers and many aspects of their use and properties are discussed on the literature [2–4]. Other fibers are, however, of interest, such as coir and hemp – just to cite a few – and many others are promising candidates to be used in composites.

In this last group Curaua (*Ananas erectifolius*) is a distinguished one, which is already being used in several composites [5] and also Piassava (*Attalea funifera*), Sponge gourd (*Luffa cylindrica*) and Caroa (*Neoglaziovia variegata*) fibers. Each of these fibers has its own characteristics in respect to their mechanical properties and structural features [6–8]. This work presents the thermal characteristics of these fibers.

Experimental

The thermal properties of the raw fibers was studied by thermogravimetric analysis (TG) using a PerkinElmer TGA-7 equipment. The analysis was performed from 30 to 700°C, using several heating rates: 5, 10, 15, 20, 30 and 40°C min^{-1}. The use of several heating rates was performed in order to evaluate the activation energy of the degradation process of the fibers using the method proposed by Kissinger [9]. This approach is based on the fact that when a reaction occurs upon heating it is indicated by a DTG peak. Therefore, and considering that the reaction rate is dependent on the peak temperature, the peak temperature will vary with the heating rate. It is possible then to evaluate the activation energy from a plot of the following equation [9]:

$$\ln\left(\frac{\phi}{T_\mathrm{m}^2}\right)=\ln\left(\frac{AR}{E}\right)-\frac{E}{R}\frac{1}{T_\mathrm{m}} \tag{1}$$

where ϕ is the heating rate, T_m is the peak temperature in degrees of Kelvin, A is the pre-exponential constant describing a solid→solid+gas reaction of order n, R is the universal gas constant (R= 8.314 J mol^{-1} K^{-1}) and E is the activation energy. All experiments were conducted under N_2 atmosphere with a gas flow of 20 mL min^{-1}. The average mass of the samples was of 5 mg and all the results presented are the average of 3 parallel measurements per fiber and heating rate.

Results and discussion

Figure 1 shows the TG and DTG curves for the lignocellulose fibers analyzed in this work. The initial low temperature mass loss corresponds to loss of humidity and it is a common feature observed for lignocellulose fibers [7, 10, 11]. The values of water loss obtained are listed in Table 1 in agreement with the

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[*] Author for correspondence: dalmeida@dcmm.puc-rio.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

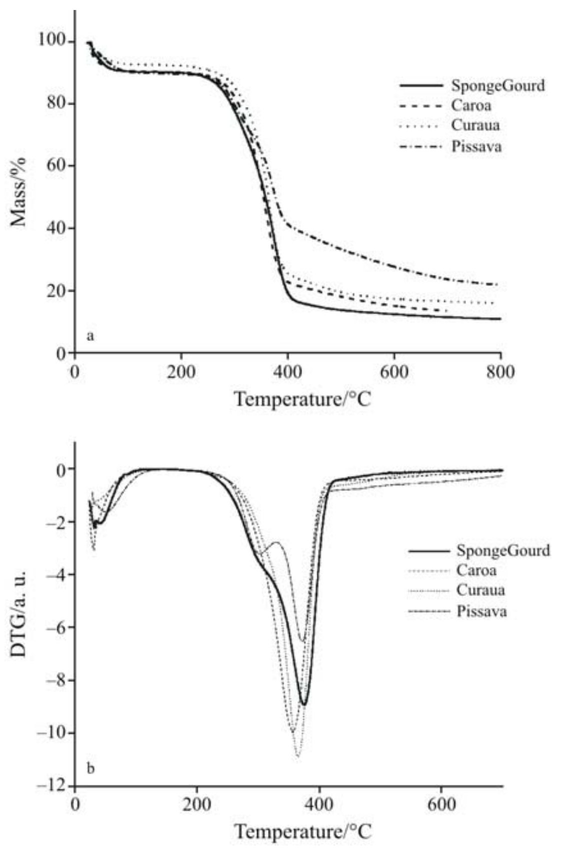

Fig. 1 a – TG, b – DTG curves for Curaua, Piassava, Sponge gourd and Caroa raw fibers

range of values reported for other raw lignocellulose fibers [7, 12]. The cumulative mass losses for higher temperatures are also listed in Table 1. It can be observed that until 200°C the fibers can be considered as thermally stable ones with minor mass losses apart from that attributed to humidity. This behavior is comparable to that shown by coir and sisal fibers where the onset of degradation occurs between 190 and 230°C [11].

The mass loss observed between 200°C and the peak temperature can be attributed to the thermal decomposition of hemicellulose and to the rupture of the glycoside link of the cellulose molecule [13, 14]. The rupture of α- and β-aryl-alkyl-ether linkages originated from the thermal degradation reactions of lignin also contribute to the mass loss behavior of these fibers [15]. The mass loss occurring at higher temperatures of this range involves the decomposition of cellulose oligomers evolving into levoglucosans and low molecular mass volatile compounds, like ketone, aldehydes, furans and pyrans [14]. The mass loss at 300°C for all the fibers here analyzed agrees very well but in fact are slight smaller than the value of 20 mass% reported for sisal fiber [13].

Table 2 lists the peak temperature obtained from the DTG curve, Fig. 1b. Curaua and Caroa showed a more homogeneous thermal behavior and displayed only a single peak with temperatures that can be associated to that of the thermal decomposition of α-cellulose [10]. Although both values are slightly higher than the value measured for jute fibers [10], one has to care that these temperatures are influenced by the specific interaction occurring between the different polysaccharides present in each fiber, as well as the different amounts of the fibers’ constituents.

Both Sponge gourd and Piassava showed two peaks at the DTG curves. This behavior was also observed previously [6, 7]. The lower temperature peak could be associated to the decomposition of hemicellulose, although the values obtained in this work are higher than those previously reported [6, 7] and also are higher than the usual range attributed to hemicellulose thermal decomposition – from 260 to 281°C [16, 17]. The higher temperature peak observed for both Sponge gourd and Piassava can also be associated to the thermal decomposition of α-cellulose (Table 2).

After completion of the main thermal degradation event found for all the fibers tested around 400°C the decomposition of cyclic rings begins and at higher temperatures carbonization of levoglucosan can occur [5]. From Table 1 it is apparent that on a percent basis

Table 2 DTG peak temperatures (°C) of the investigated samples

Fiber	t_1	t_2
Caroa	–	356.6
Curaua	–	365.0
Piassava	303.6	377.2
Sponge	303.4	373.7

Table 1 Cumulative mass loss (%) of the lignocellulose fibers analyzed

	Temperature/°C					
Fiber	100	200	300	400	500	600
Caroa	9.0±0.5	9.5±0.5	17.0±0.9	78.2±0.8	82.6±0.6	85.0±0.1
Curaua	7.7±0.1	8.6±0.2	15.7±0.12	74.2±1.0	80.6±0.2	82.6±0.3
Piassava	8.3±1.0	8.8±1.2	18.6±0.9	59.9±1.0	68.7±0.8	73.2±1.1
Sponge	7.7±0.2	8.0±0.2	14.5±1.0	68.8±2.9	86.0±0.2	87.7±0.1

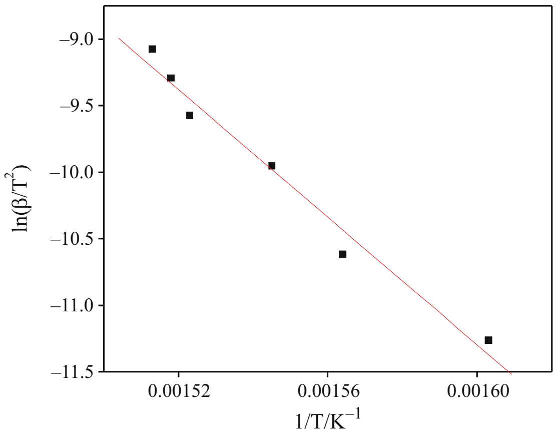

Fig. 2 Calculation of the activation energy in the example of Curaua fiber

the thermal decomposition of Piassava is less intense at higher temperatures. This agrees with the fact that Piassava is a lignin rich fiber with 45–48% of lignin content [6, 18].

Figure 2 shows an example of the plots obtained to evaluate the activation energy of the main decomposition process occurring in the fibers, i.e. the one related to the main peak at the DTG curve. The results for all the four fibers analyzed are shown in Table 3. The values obtained, except for Caroa correlates very well with reported data for flax (187 kJ mol^{-1} [14]), hemp (184.2 kJ mol^{-1} [19]), and even pure cellulose (203 kJ mol^{-1} [14]). It is worth to note however, that values of the activation energy of flax as low as 117.2 kJ mol^{-1} are also found on the literature [20].

Table 3 Activation energy of the investigated samples

Fiber	E/kJ mol^{-1}
Caroa	135
Curaua	199
Piassava	185
Sponge	165

The results obtained for Caroa may be related to its high hemicellulose to cellulose ratio (~0.5 [8]) as compared to the smaller ratios observed for Sponge gourd (0.33 [7]), Piassava (smaller than 0.33 [6]) or Curaua (~0.15 [5]) since hemicellulose decomposition occurs at a temperature range smaller than that of cellulose or lignin [16, 17, 21].

Conclusions

The thermal behavior of four less common lignocellulose fibers having great potential use as reinforcement in polymer-matrix composite materials was described. The fibers are thermally stable to at least 200°C, what is a good characteristic for their use with common thermoplastic matrices. Caroa and Curaua fibers showed a more homogeneous degradation behavior characterized by a single peak in the DTG curve. Piassava and Sponge gourd showed two peaks in the DTG curve.

Piassava, Sponge gourd and Curaua present activation energies similar to the ones reported for other lignocellulose fibers. The value obtained for Caroa fiber was smaller than the others, which was attributed to the higher hemicellulose to cellulose ratio present at this fiber in comparison to the ratios of the other three fibers analyzed in this work.

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