Studies on the thermal properties of sisal fiber and its constituents

Adriana R. Martin [a], Maria Alice Martins [b], Odilon R.R.F. da Silva [c], Luiz H.C. Mattoso [d],*

[a] Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, Rod. Washington Luís, Km 235, 13565-905, São Carlos, SP, Brazil
[b] Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brazil
[c] Embrapa Algodão, Rua Osvaldo Cruz 1143, C.P. 174, 58107-720 Campina Grande, PB, Brazil
[d] Embrapa Instrumentação Agropecuária, Laboratório de Nanotecnologia para o Agronegócio, Rua XV de Novembro 1452, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

ABSTRACT

In this work the thermal analysis of raw and defatted sisal fiber and its chemical constituents (cellulose, hemicellulose and lignin) was performed by thermogravimetric analysis, and differential scanning calorimetry under air and nitrogen atmospheres. The DSC studies showed that the degradation process depends on the atmosphere involved. In inert atmosphere, the DSC curves exhibited distinct peaks for sisal fiber and its constituents, whereas in air atmosphere the thermal curves presented two exothermic peaks for all the constituents. The degradation of cellulose in inert atmosphere occurred by endothermic processes whereas, in air atmosphere, it occurred by exothermic processes. TGA measurements corroborated the results obtained by DSC. It is shown that cellulose and hemicellulose degraded at lower temperatures than that of the raw sisal fiber, which can be attributed to the removal of lignin. The thermal decomposition of sisal fiber and its constituents was discussed and compared to jute and hemp fibers.

© 2010 Published by Elsevier B.V.

1. Introduction

In recent years there has been an increasing demand for natural fiber reinforced thermoplastic composites in a wide variety of industrial applications ranging from packaging and automotive to construction and aviation [1–4]. Lignocellulosic fibers such as sisal, jute and cotton have attracted interest as reinforcement due to renewable and biodegradable characteristics and have effectively been incorporated into several of thermoplastic and thermosetting polymers [5–9]. Many studies have been done on the thermal behavior of natural fibers and thermoplastic and thermosetting composites [10–13]. However, one of the drawbacks of natural fibers is that they can undergo degradation prior to the polymer during the processing at elevated temperatures, thus causing some limitations to select the polymeric matrix in common transforming processes. The literature shows thermal studies of natural fibers like jute, hemp and their constituents but it doesn't have studies regarding to thermal behavior of sisal fiber and constituents [14–16]. The knowledge of thermal properties of sisal fiber and their constituents can support the choice of polymeric matrix of composites due to elevated temperatures of processing.

Among Brazilian natural fibers, sisal is an especially important fiber not only due to its physico-chemical and mechanical properties, but also due to its socio-economical value [17–21]. Sisal fiber is a hard fiber extracted from the leaves of sisal plant [17,18]. Since this fiber is composed of cellulose, hemicellulose and lignin, as major constituents, in order to have a deeper comprehension of its decomposition process and the influence of each isolated constituent of sisal fiber in the thermal degradation process, it was carried out the thermal study of sisal fiber. In this work, it will be presented a detailed study of thermal stability of sisal fiber and its constituents carried out through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under inert and oxidative atmospheres. The thermal decomposition of sisal fiber and its constituents will be discussed and compared to jute and hemp fibers decomposition process [14–16].

2. Experimental part

2.1. Materials

Sisal fibers (*Agave sisalana* variety) were supplied by Embrapa – Cotton National Research Center in Brazil.

2.2. Methods

2.2.1. Separation of sisal fibers components
The fibers were milled and the extracts, waxes and fats, soluble in organic solvents, were separated using a Sohxlet apparatus

* Corresponding author. Tel.: +55 16 2107 2800; fax: +55 16 2107 2902.
 E-mail addresses: drimartin@yahoo.com.br (A.R. Martin),
a_martins1000@yahoo.com.br (M.A. Martins), mattoso@cnpdia.embrapa.br
(L.H.C. Mattoso).

for 48 h in a 1:1 cyclohexane:ethanol mixture, followed by water immersion during 6 h to access the water-soluble extractives, pectins. The samples were oven dried for 24 h at 105 °C, and then kept in a desiccator until the beginning of the thermal measurements.

The major chemical constituents isolated from defatted sisal are listed below:

Holocellulose: the defatted sisal fiber was delignified according to the sodium chloride method described in reference [22], to give holocellulose (hemicellulose and cellulose).
Cellulose: holocellulose was treated with a KOH solution (24 vol.%), according to the method described in the literature [22] to give cellulose.
Hemicellulose: holocellulose was treated with KOH solution (24 vol.%) for 2 h. The extract obtained by filtration was neutralized with acetic acid. Hemicellulose was precipitated from the neutral extract by addition of ethanol, followed by filtration, washing with ethanol, drying in an oven for 24 h and then kept in a desiccator until the beginning of thermal measurements.
Lignin: klason lignin was isolated from defatted sisal fibers by treatment with a sulfuric acid solution (72 vol.%), according to the method described in the literature [21,22]. The mass percentage of each fraction was calculated.

2.2.2. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument. Dynamic TG scans were conducted in a temperature range from 40 to 600 °C and heating rate of 10 °C min^{-1}. The experiments were carried out under nitrogen atmosphere at a flow rate of 20 mL min^{-1}. For both, DSC and TGA measurements, samples with approximately 6–11 mg, respectively, of raw and defatted sisal fiber and its constituents were used.

DSC measurements were carried out on a Shimadzu DSC-50 differential scanning calorimeter. Dynamic DSC scans were conducted in a temperature range from 40 to 600 °C, at a constant heating rate of 10 °C min^{-1}. The experiments were carried out separately, under nitrogen and air atmospheres, at a flow rate of 20 mL min^{-1}.

Table 1
Chemical components of sisal, jute and hemp fibers and their mass percentage (%) [2,16,17,21,23].

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Sisal	73.8	11.0	9.7
Jute	45–63	18–21	21–26
Hemp	58.7	14.2	6.0

Table 2
Thermoanalytical data from DSC thermal curves of sisal fiber and its constituents in nitrogen (10 °C min^{-1}).

Sample	Onset temperature (°C)	Peak temperature (°C)	ΔH (J/g)
Raw sisal	28	74	77
	234	297	22
	328	364	25
	387	415	10
Defatted sisal	33	60	50
	257	298	7
	326	365	124
Cellulose	28	60	69
	308	358	56
Hemicellulose	31	125	174
	241	282	130
	375	409	66
Lignin	29	66	208
	254	397	645

3. Results and discussion

The sisal fiber used in this study contains 73.8 wt% of cellulose, 11.0 wt% of hemicellulose and 9.7 wt% of lignin (Table 1) [17,23]. The chemical components percentages of sisal fiber are different compared with other natural fibers like jute and hemp [16,17,22]. This difference on chemical composition can result on different mechanical properties of natural fibers.

The DSC curves in nitrogen atmosphere of raw and defatted sisal fiber and its chemical constituents (hemicellulose, cellulose and lignin) are presented in Fig. 1A and their thermoanalytical data are summarized in Table 2. Fig. 1A shows that the DSC curve of raw sisal fiber presents three peaks of its major constituents (cel-
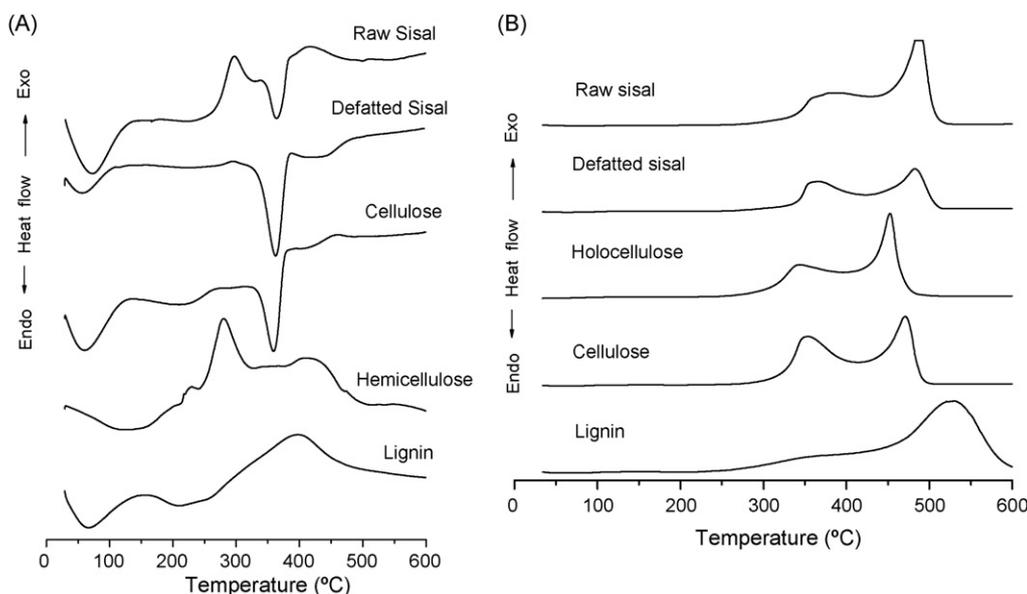
Fig. 1. DSC curves of raw and defatted sisal fiber and its chemical constituents (cellulose, hemicellulose and lignin) in nitrogen atmosphere (A) and in air atmosphere (B), 10 °C min^{-1}.

lulose, hemicellulose and lignin), which can also be observed in the thermal curves of the isolated constituents.

The endothermic peak (ca. 75 °C) observed in all the thermal curves, is due to the release of adsorbed water. The exothermic peak of raw sisal fiber, starting at 234 °C with maximum at 297 °C, is due to the degradation of hemicellulose, i.e., acetyl 4-o-methylglucuronoxylan of the sisal fiber [14]. For the defatted sisal fiber, this peak decreases in intensity and there is no significant shift in its position. Analyzing the DSC curve of isolated hemicellulose, it is possible to observe an exothermic peak starting approximately at 240 °C, with maximum at ca. 280 °C, which is absent in the curves of cellulose and lignin. The occurrence of the hemicellulose peak at 282 °C in the isolated hemicellulose sample (Table 2), compared with raw and defatted sisal fiber (both at 297 °C), is due to the easier accessibility to thermal degradation in the absence of lignin. Similar results were observed by Bhaduri et al. [14] in their studies on thermal degradation of jute fibers.

The endothermic peak at ca. 330 °C, with maximum at 365 °C for raw sisal fiber, is due to the degradation of cellulose, its predominant constituent. According to Shafizadeh and Bradburi [19] and Bhaduri et al. [14,15] this peak is attributed to dehydration and depolymerization of cellulose, leading to the formation of flammable volatile products. Chand et al. [24] on thermal studies of sisal fiber attributed it to the dehydration and splitting of hydroxyl groups of the cellulose molecule, resulting in the evolution of water. One can observe in Fig. 1A that the isolated lignin curve did not shows this endothermic peak, which confirms its relation with cellulose degradation and not lignin. Fairbridge and Ross [25] in thermal stability studies of cellulose carried out in nitrogen and atmospheric air, observed that the degradation of cellulose occurs by two competitive first-order reactions. One reaction is attributed to the generation of condensed fraction called volatiles, and the other is attributed to the production of ashes and gaseous substances including water, carbonic gas and carbon monoxide.

Delignification of defatted sisal fiber to produce cellulose shifts the endothermic peak (starting at 308 °C with maximum at 358 °C) to a lower temperature as compared to the thermal curves of raw and defatted sisal fiber (Fig. 1A). The presence of this endothermic peak at lower temperatures is due to the removal of lignin, the binding constituent of the fiber, which produces an easier accessibility for the thermal degradation of cellulose.

The weak exothermic peak starting at 387 °C with maximum at 415 °C, on the thermal curve of raw sisal fiber, is attributed to degradation of lignin. In this temperature range, a weak peak is observed for isolated hemicellulose (Fig. 1A), which is due to the association of small amounts of residual lignin with the isolated hemicellulose of the sisal fiber. The DSC curve of isolated klason lignin shows an exothermic peak with maximum at 397 °C, which occurs at lower temperatures as compared to raw sisal fiber. The results obtained by DSC analysis of sisal fiber and its constituents in nitrogen atmosphere are in accordance with those results achieved by Bhaduri et al. [14,15] on the thermal degradation studies of jute fiber and its constituents.

Fig. 1B displays the DSC curves, in air atmosphere, of raw and defatted sisal fiber and its chemical constituents. The thermoanalytical data are summarized in Table 3. The degradation of sisal fibers, in atmospheric air, does not display distinct peaks for each constituent due to the presence of oxygen that accelerates the degradation process, hindering peaks distinction. It is also observed that the peaks, for the isolated constituents of sisal fiber in atmospheric air, shifted to lower temperatures due to the easier accessibility to degradation, displaying therefore the same trend as for the experiments carried out with the isolated constituents in nitrogen atmosphere.

The DSC curves of raw sisal fibers degradation in air atmosphere show two exothermic peaks with maxima, respectively, at 376 and

Table 3
Thermoanalytical data from DSC thermal curves of the sisal fiber, and its constituents in air atmosphere (10 °C min^{-1}).

Samples	Initiation peak temperature (°C)	Peak[a] temperature (°C)	ΔH (J/g)
Raw sisal	240	376	452
	415	476	2790
Defatted sisal	225	359	852
	415	474	1750
Holocellulose	210	335	455
	385	447	2390
Cellulose	233	351	1790
	407	466	2390
Lignin	208	360	–
	411	528	6180

[a] All the peaks are exothermic.

476 °C (Fig. 1B). According to the literature [14,15,19,26], the first exothermic peak is attributed to oxidation of volatile products produced during degradation and the second one is attributed to the char oxidation.

The DSC curve of defatted sisal fiber shows that the peaks are shifted to lower temperatures as compared to raw sisal fiber, the first peak occurs at 359 °C and the second at 474 °C. The DSC curves of holocellulose and cellulose show that the maxima for both peaks are found at 335 and 447 °C, and 351 and 466 °C, respectively. The appearance of these exothermic peaks at lower temperatures for the holocellulose and cellulose constituents in oxidative atmosphere can be attributed to the removal of the binding fraction of sisal fibers, i.e., lignin. The removal of lignin from isolated holocellulose and cellulose cause the degradation of these constituents to occur at lower temperatures. The DSC curve of lignin shows an exothermic peak at 528 °C and a small shoulder at 360 °C.

These results are according to Rachini et al. [16] on degradation study of hemp fiber on air and argon atmospheres. DTA under air of natural hemp fibers presents two exothermic peaks above 380 °C, at 395 and 427 °C, and the weight loss (%) is about 27%. These peaks are attributed to the oxidative decomposition of the charred residue. Under argon, these peaks do not exist. This result concerns that under air, these two peaks are produced by the residue loss. Decomposition of natural hemp fiber under air was complete and proceeded at a lower temperature than under argon. The decomposition under argon is due to the presence of free radicals.

The thermogravimetric data of raw and defatted sisal fiber and its chemical constituents in nitrogen atmosphere are presented in Tables 4 and 5. Thermogravimetric analysis (TGA) and first derivative thermogravimetric (DTG) curves are presented in Figs. 2–4 and 6.

The TG curve of raw sisal (Fig. 2A, curve i) shows a weight loss of 2.9% in the temperature range of 32–221 °C, which is due to the loss of adsorbed water in the fiber (intra- and intermolecular dehydration reactions) [25]. Sisal fiber degradation starts at about 222 °C and proceeds very fast with temperature increase, showing a weight loss of 72% in the range of 222–415 °C. The weight losses at the temperature ranges of 222–365 °C and 365–415 °C are 39 and 33%, respectively. These results are an indication of a fast rate of fiber degradation that started at 222 °C and became faster at 365 °C. This behavior is shown by a slope change at ca. 365 °C. The weight loss between 416 and 520 °C is only 5.4%, due to the slow rate of char degradation. At 520 °C the char yield is 19.7%. This char yield occurs due to the condensation of the lignin component of fibers and formation of aromatic compounds in nitrogen atmosphere [27].

DTG curve (Fig. 2A, curve ii) shows two distinct peaks with maxima at 310 and 377 °C, indicating that the degradation of sisal

Table 4
Thermogravimetric data of raw and defatted sisal fibers and their chemical constituents in nitrogen atmosphere ($10\,^{\circ}C\,min^{-1}$).

Samples	Initial weight loss		Active pyrolysis		Char region	
	Temperature (°C)	Wt. loss (%)	Temperature (°C)	Wt. loss (%)	Temperature (°C)	Wt. loss (%)
Raw sisal	32–221	2.9	222–415	72.0	416–520	5
Def. sisal	32–230	2.8	231–415	76.3	416–520	4
Hemicellulose	33–185	3.2	186–401	67.4	402–600	24
Cellulose	33–206	5.2	207–404	67.4	405–600	27
Lignin	32–173	5.0	174–317	15.9	318–600	37

Table 5
Thermogravimetric data (DTG) of raw and defatted sisal fiber and its chemical constituents (hemicellulose, cellulose and lignin).

Samples	Initial degradation temperature (°C)	DTG maximum peaks (°C)	Char yield (%)
Raw sisal	222	310	19.5
Defatted sisal	231	318	16.5
Hemicellulose	186	348	9.0
Cellulose	207	353	0.5
Lignin	173	367	42.0

fiber occurs in two steps. The first peak is a shoulder on the main degradation peak, attributed to the hemicellulose degradation [20], which occurs between 220 and 328 °C. In the temperature range between 222 and 328 °C a slow degradation with weight loss of 17.7% takes place. Thermal degradation of cellulose occurs at higher temperatures compared with hemicellulose and at a faster degra-

dation rate. The main degradation peak starts at 328 °C and is completed at 416 °C with maximum at ca. 377 °C.

The thermal degradation behavior of defatted sisal fiber, Fig. 2B, has the same trend as that of the raw sisal fiber. TG curve (Fig. 2B) shows a weight loss of 2.8% in the temperature range from 32 to 230 °C, which is due to the loss of adsorbed water from the fiber. The slope change occurs at around 370 °C, indicating a fast degradation of the cellulose present in defatted sisal fiber. DTG curve (Fig. 2B) shows two peaks with maximum at 318 and 380 °C, indicating the degradation of hemicellulose and cellulose, respectively. At 520 °C the char yield is 16.5%.

TG curve of holocellulose (Fig. 3-i) shows weight loss of 3.2% up to 185 °C, due to loss of adsorbed water in the fiber. The cellulose degradation starts at around 186 °C, this temperature is lower than the initial degradation temperature of raw and defatted sisal fiber, this occurs due to delignification of fiber resulting on the higher
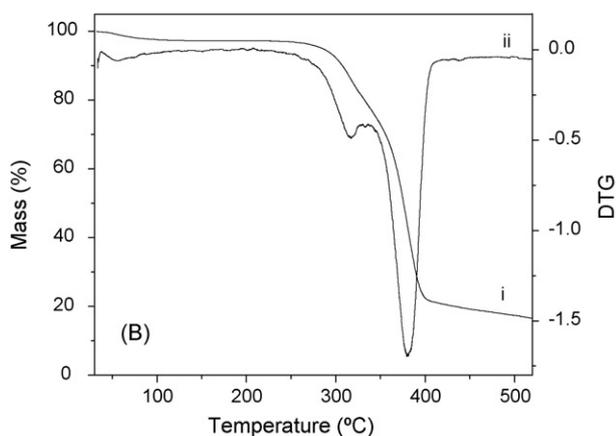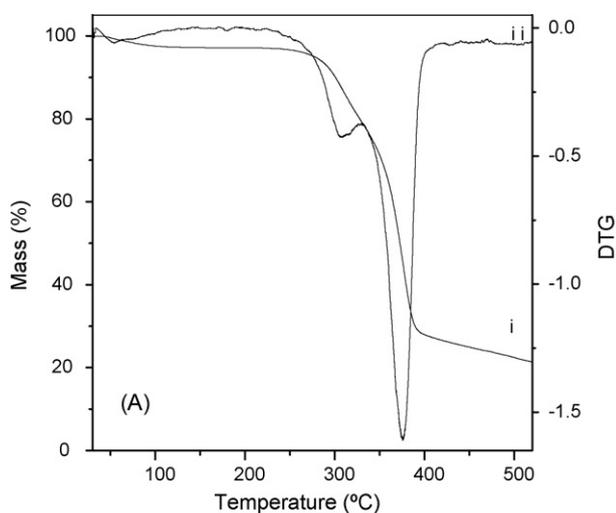
Fig. 2. TG (i) and DTG (ii) curves of raw sisal fiber (A), and defatted sisal fiber (B). Nitrogen atmosphere ($10\,^{\circ}C\,min^{-1}$).
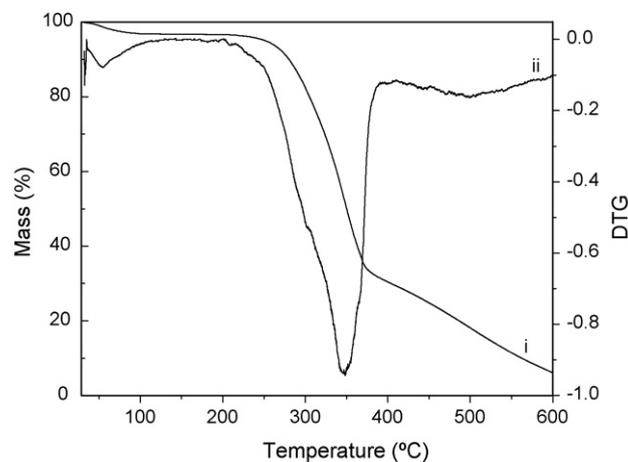
Fig. 3. TG (i) and DTG (ii) curves of holocellulose. Nitrogen atmosphere ($10\,^{\circ}C\,min^{-1}$).
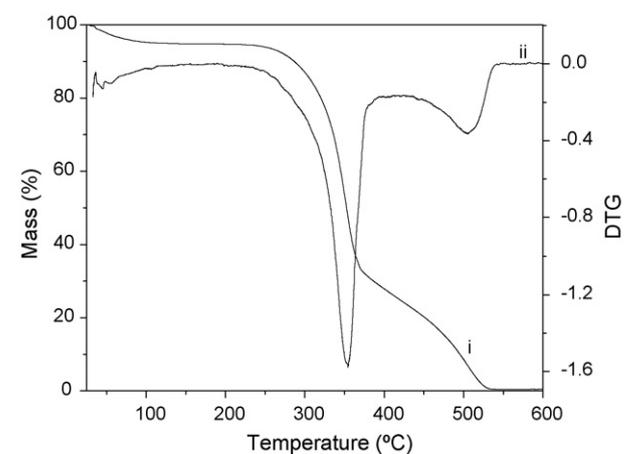
Fig. 4. TG (i) and DTG (ii) curves of cellulose. Nitrogen atmosphere ($10\,^{\circ}C\,min^{-1}$).

accessibility of the hemicellulose constituent to thermal degradation. At the first step of the thermal degradation (from 185 to 347 °C) the weight loss is 45.6%, which is higher than that of raw and defatted sisal fiber in the same temperature range. Hemicellulose degradation starts at 186 °C (Fig. 3-i) followed by cellulose degradation that ends at 401 °C. The weight loss in this temperature range (185–401 °C) is 67.4%. The weight loss between 402 and 600 °C is 23.9%, with a char yield of 5.5% at 600 °C. DTG curve of holocellulose (Fig. 3-ii) shows a peak with maximum at 348 °C. A small shoulder occurs at 297 °C due to slower hemicellulose degradation, while the peak at 348 °C is related to faster cellulose degradation.

Cellulose degradation starts at around 207 °C (Fig. 4-i) and continues at a very fast rate. The weight loss from 33 to 206 °C is 5.2%, which is attributed to the loss of adsorbed water from the fiber. The active pyrolysis region ends at around 404 °C, with a weight loss of 67.4%, and a char yield of 0.5% at 600 °C. DTG curve of cellulose (Fig. 4-ii) shows only a peak between 207 and 404 °C, with maximum at 353 °C. The small peak found in DTG curve for raw and defatted sisal fiber is not present here, due to the absence of hemicellulose constituent. Fairbridge and Ross [25], on degradation of cellulose carried out in nitrogen and air atmospheres, found that the maximum rate of cellulose degradation occurred at 350 and 330 °C, respectively in nitrogen and air atmosphere. Shafizadeh and Bradbury [19] carried out similar studies and found out that the maximum rate of weight loss occurred at 360 and 345 °C, respectively in nitrogen and air atmospheres. Therefore, the temperature at which the maximum rate of weight loss (ca. 353 °C) occurred, achieved in this study on the degradation of cellulose, is in accordance with the results found in the literature [19,26–31]. It can be also observed a peak at about 500 °C that can be attributed to oxidative degradation of the charred residues [20,21,26,27].

According to Shafizadeh and Bradbury [19] the activation energy values necessary to promote bond scission of cellulose molecules are 27 and 21 kcal mol^{-1}, respectively in nitrogen and air atmospheres. This can be explained because in atmospheric air the maximum rate of weight loss for cellulose degradation occurs at lower temperatures compared to nitrogen atmosphere, which is a consequence of the thermooxidative events occurring during the decomposition of the sample.

Fig. 5 shows a possible reaction mechanism for formation of the cellulose hydroperoxide and their decomposition in the atmospheric air [19,26]. In their work Shafizadeh and Bradbury [19] concluded that thermal degradation of cellulose is a first-order reaction at high temperatures. At lower temperatures there is an initiation period that is prolonged as temperature is lowered. The pyrolysis proceeds rapidly, at higher temperatures, via transglycosylation reactions. These processes overshadow the effect of oxygen
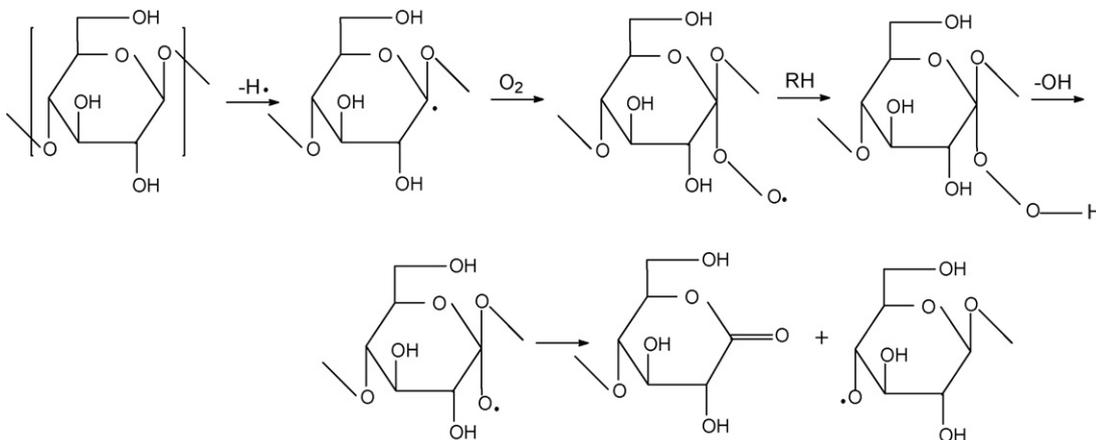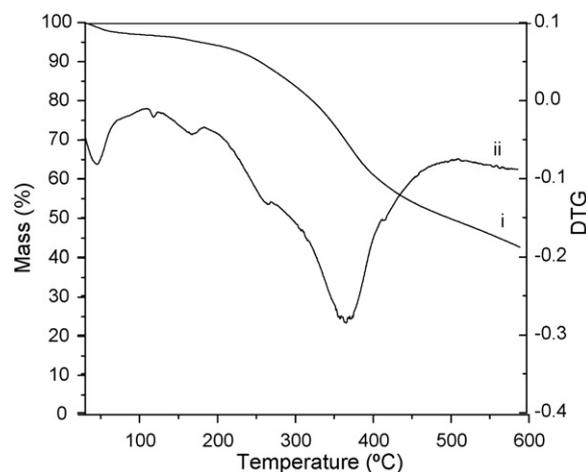
Fig. 6. TG (i) and DTG (ii) curves of klason lignin. Nitrogen atmosphere (10 °C min^{-1}).

or oxidative environment, whereas at lower temperatures, oxygen plays a dominant role and oxidative degradation progressively processed faster than pyrolysis in nitrogen. The initiation period of low-temperature reaction involves the production of free-radical initiators. Subsequent interaction of these initiators with oxygen can lead to thermal autoxidative reactions. In this oxidation mechanism, the abstraction of hydrogen occurs in C1 of D-glucopyranose molecule by radical-peroxide formation. Subsequent oxygen addition and hydrogen abstraction leads to a further hydroperoxide formation, which could split homolytically to give an alkoxyl and a hydroxyl radical (due to further hydrogen abstraction). A β-scission could then result in cleavage of the glycosidic bond and an alkoxyl radical is formed in the neighboring glucose unity.

TG curve of klason lignin (Fig. 6-i) shows a weight loss of 5.0% at 173 °C, due to the adsorbed water. The lignin degradation starts at around 174 °C and undergoes at a slow rate of degradation, yielding 41.7% of char residue at 600 °C. The thermal degradation of lignin occurs slowly because of the general stability of isolated lignin that is highly condensed. It can be observed that isolated lignin volatilizes only 58.3% at 600 °C, while 80.5% of sisal fiber was volatilized at the same temperature range under similar experimental conditions. This is due to the more complex aromatic structure of lignin as compared to cellulose and hemicellulose structures. The DTG curve of lignin (Fig. 6-ii) reveals a broad peak with maximum at 367 °C and shoulders at 119, 168, 264 and 418 °C, indicating that the thermal degradation of lignin occurs in multiple steps with the highest rate of degradation occurring at 367 °C.

Fig. 5. A possible reaction mechanism for cellulose hydroperoxide formation, and its decomposition in atmospheric air [19,26].

Table 5 presents the initial degradation temperature, DTG maximum peaks, and char content of raw and defatted sisal fiber and its chemical constituents. It can be observed that the DTG peaks of hemicellulose and cellulose shift to lower temperatures than those in raw and defatted sisal fibers. This is an indication that the maximum weight loss of isolated constituents occurs at lower temperatures than those for raw and defatted sisal fibers. TG studies (Table 5) revealed that defatted sisal fiber has the highest initial decomposition temperature and cellulose has the lowest char yield (0.5%) at 600 °C. This behavior points out that cellulose is the most reactive constituent of sisal fiber. Although, lignin presents the smallest initial decomposition temperature, it exhibited the highest char yield (42%); this is attributed to a higher thermal stability, which is a consequence of its aromatic structure. These TG results obtained for sisal fiber are in agreement to those obtain ed by Bhaduri et al. [14,15] on the thermal stability of jute fiber and its constituents.

The results obtained on DSC and TGA analyses to sisal fiber and its components are complementary because the temperature values of degradation on both analyses are on the same temperature range and are according to thermal degradation of natural fibers like jute and hemp [14–16,25,26]. According to results obtained on DSC and TGA analyses to sisal fiber and its components the polymeric matrix to produce composites reinforced by sisal fiber should be processed on temperatures under 185 °C due to degradation of holocellulose, hemicellulose and cellulose components, that starts at 186 °C. This limits the type of thermoplastics that can be used on composites.

Fung et al. [32] carried study on sisal fiber and polypropylene composites and it was observed that the specimens injection molded at temperature profile between 190 and 210 °C showed dark color and emission of empyreuma odor. The odor and dark color are due to degradation of sisal fiber components.

4. Conclusions

The DSC studies showed that the mode of degradation of sisal fiber depends on the atmosphere involved. In inert atmosphere, the DSC curves exhibited distinct peaks to each constituent of sisal fibers, whereas in air atmosphere two exothermic peaks are observed. The degradation of cellulose in inert atmosphere occurred by endothermic processes, whereas in oxidative atmosphere, it occurred by exothermic processes. The removal of lignin from fiber caused the thermal degradation of holocellulose and cellulose to occur at lower temperatures, in both inert and oxidant atmospheres, due to the easier thermal accessibility of these constituents. TG studies corroborated with the results obtained by DSC helping to elucidate the degradation behavior of sisal fiber and its constituents. It was concluded that the thermal degradation of sisal fiber and its constituents is similar to natural fibers like jute and hemp.

Also, it was concluded that the polymeric matrix to produce composites reinforced by sisal fiber and other natural fibers should be processed on temperatures under 185 °C due to degradation of holocellulose, hemicellulose and cellulose components, which starts at 186 °C.

References

[1] P.V. Joseph, K. Joseph, S. Thomas, Compos. Sci. Technol. 59 (1999) 1625–1640.
[2] A.K. Bledzki, J. Gassan, Prog. Polym. Sci. 24 (1999) 221–274.
[3] S. Mishra, A.K. Mohanty, L.T. Drzal, M. Misra, G. Hinrichsen, Macromol. Mater. Eng. 289 (2004) 955–974.
[4] K. Li, L.G. Tabil, S. Panigrahi, J. Polym. Environ. 15 (2007) 25–33.
[5] K. Joseph, S. Thomas, C. Pavithran, Polymer 37 (1996) 5139–5149.
[6] X. Li, Y. Mai, L. Ye, Compos. Sci. Technol. 60 (2000) 2037–2055.
[7] A.R. Martin, S. Manolache, F.S. Denes, L.H.C. Mattoso, J. Appl. Polym. Sci. 85 (2002) 2145–2154.
[8] A.R. Martin, F.S. Denes, R.M. Rowell, L.H.C. Mattoso, Polym. Comp. 24 (2003) 464–474.
[9] J.L. Lopez, M. Sain, P. Cooper, J. Appl. Polym. Sci. 5 (2006) 2570–2577.
[10] D.S. Varma, M. Varma, I.K. Varma, Thermochim. Acta 108 (1986) 199–210.
[11] H.S.S. Sharma, K. Kernaghan, Thermochim. Acta 132 (1988) 101–109.
[12] A.S. Luyt, M.E. Malunka, Thermochim. Acta 426 (2005) 101–107.
[13] B. Wielage, T. Lampke, G. Marx, K. Nestler, D. Starke, Thermochim. Acta 337 (1999) 169–177.
[14] S.K. Bhaduri, M.D. Mathew, A. Day, S.N. Pandey, Cell. Chem. Technol. 28 (1994) 391–399.
[15] S.K. Bhaduri, M.D. Mathew, A. Day, S.N. Pandey, Cell. Chem. Technol. 28 (1994) 595–603.
[16] A. Rachini, M.L. Troedec, C. Peyratout, A. Smith, J. Appl. Polym. Sci. 112 (2008) 226–234.
[17] A.R. Martin, Ph.D. Thesis, University of São Carlos, Brazil, 2001.
[18] M.A. Martins, L.A. Forato, L.H.C. Mattoso, L.A. Colnago, Carbohydr. Polym. 64 (2006) 127–133.
[19] F. Shafizadeh, G.W. Bradbury, J. Appl. Polym. Sci. 23 (1979) 1431–1442.
[20] M.A. Martins, I. Joekes, J. Appl. Polym. Sci. 89 (2003) 2507–2515.
[21] R.M. Rowell, R.A. Young, J.K. Rowell, Paper and Composites from Agro-Based Resources, Lewis Publishers, New York, 1997.
[22] B.L. Browning, Methods of Wood Chemistry, vol. 1, John Wiley & Sons, New York, 1967.
[23] A.R. Martin, M.A. Martins, O.R.R.F. Silva, L.H.C. Mattoso, Polímeros: Ciência e Tecnologia 19 (2009) 40–46.
[24] N. Chand, S. Verma, A.C. Khazanchi, J. Therm. Anal. 32 (1987) 595–599.
[25] C. Fairbridge, R.A. Ross, J. Appl. Polym. Sci. 22 (1978) 497–510.
[26] M.W. Sabaa, Polym. Degrad. Stab. 32 (1991) 209–217.
[27] C. Albano, J. Gonzáles, M. Ichazo, D. Kaiser, Polym. Degrad. Stab. 66 (1999) 179–190.
[28] S.L. Le Van, in: A.P. Schniewind (Ed.), Concise Encyclopedia of Wood and Wood-based Materials, Pergamon Press, Elmsford, New York, 1989, pp. 271–273.
[29] J. Scheirs, G. Camino, W. Tumiatti, Eur. Polym. J. 37 (2001) 933–942.
[30] P. Jandura, B. Riedl, B.V. Kokta, Polym. Degrad. Stab. 70 (2000) 387–394.
[31] A.M.A. Nada, M.L. Hassan, Polym. Degrad. Stab. 67 (2000) 111–115.
[32] K.L. Fung, X.S. Xing, R.K.Y. Li, S.C. Tjong, Y.W. Mai, Compos. Sci. Technol. 63 (2003) 1255–1258.