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Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior

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ABSTRACT

Cellulose nanowhiskers were prepared by sulfuric acid hydrolysis from coconut husk fibers which had previously been submitted to a delignification process. The effects of preparation conditions on the thermal and morphological behavior of the nanocrystals were investigated. Cellulose nanowhisker suspensions were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and X-ray diffraction. Results showed that it was possible to obtain ultrathin cellulose nanowhiskers with diameters as low as 5 nm and aspect ratio of up to 60. A possible correlation between preparation conditions and particle size was not observed. Higher residual lignin content was found to increase thermal stability indicating that by controlling reaction conditions one can tailor the thermal properties of the nanowhiskers.

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1. Introduction

Cellulose is an abundant and naturally occurring polymer that can be obtained from numerous resources (Klemm, Heublein, Fink, & Bohn, 2005). Its structure is organized into fibrils, which are surrounded by a matrix of lignin and hemicellulose (Hult, Larsson, & Iversen, 2000; Krassig, 1993). According Samir, Alloin, and Dufresne (2005), the first references to the existence of definite crystalline zones interposed in the amorphous structure of cellulose materials were made by Nageli and Schwendener (1877). The amorphous regions act as structural defects and are responsible for the transverse cleavage of the microfibrils into short monocrystals (Battista & Smith, 1962).

Nanometer-sized single crystals of cellulose, commonly referred to as whiskers, nanowhiskers or nanofibrils, can be obtained from various sources such as natural fibers, sea animals (Samir et al., 2005). The extraction of cellulose whiskers from renewable sources has gained more attention in recent years due to their exceptional mechanical properties (high specific strength and modulus), large specific surface area, high aspect ratio, environmental benefits and low cost (Orts et al., 2005; Medeiros, Mattoso, Bernardes-Filho, Wood, & Orts, 2008b; Medeiros et al., 2008a).

Different approaches have been applied to prepare cellulose nanowhiskers (Cranston & Gray, 2006; Favier, Chanzy, & Cavaille, 1996; Herrick, Casebier, Hamilton, & Sandberg, 1983; Heux, Dinand, & Vignon, 1999; Nakagaito, Iwamoto, & Yano, 2005; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006); all of them leading to different types of nanofibrillar material, depending on the cellulose raw material and its pre-treatment, and the disintegration process itself (Ahola, Osterberg, & Laine, 2008; Dong, Revol, & Gray, 1998).

Sulfuric acid hydrolysis of cellulose is a well-known process used to remove amorphous regions. However, it significantly decreases the thermal stability of cellulose whiskers. Since typical processing temperatures for thermoplastics rise above 200 °C, the thermal stability of these crystals is a key factor in order for them to be used as effective reinforcing materials (Tadmor & Gogos, 1979). The thermal stability can be recovered by partly neutralizing the sulfuric acid groups with strong bases such as sodium hydroxide (Roman & Winter, 2004).

A large amount of cellulosic waste is generated yearly by the agro-industries. There is a great demand to find other end uses for these "agricultural cellulosic wastes" (Alemdar & Sain, 2008; Dinand, Chanzy, & Vignon, 1996). Unripe coconut husk is an example of such agro-industrial by-products for which new end uses are needed (Rosa et al., 2009).

Coconut fiber is a lignocellulosic material, characterized by high toughness and durability due to its high lignin content, when it is

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compared with other natural fibers (Silva, Souza, Machado, & Hourston, 2000). Lignin, like cellulose and hemicelluloses, is a major component of plant materials and the most abundant form of aromatic carbon in the biosphere (Monties & Fukushima, 2001). Recently, investigations have shown a positive effect on thermal stability and on mechanical properties of blends and composites with lignin (Alexy et al., 2008; Cazacu et al., 2004). Besides, in polymer composites, lignin can play a role as dispersant, improving dispersion of cellulose whiskers (Thielemans, Can, Morye, & Wool, 2002).

This work assessed the effect of preparation conditions on thermal and morphological behavior of cellulose nanocrystals from coconut fibers to exploit their potential as reinforcement for nanocomposites. In order to elucidate the relationship between lignin content and properties of cellulose crystals extracted, delignification to two different levels was performed. To achieve optimal hydrolysis conditions, the effects of three hydrolysis conditions on nanowhiskers' properties were also determined and presented here. Fibers and cellulose nanocrystals were characterized by FTIR, X-ray diffraction and TGA. Morphological features of the fibers and nanostructures were studied with scanning and transmission electron microscopy, respectively.

2. Experimental

2.1. Materials

Unripe coconut husk fibers (37% lignin, 32.5% cellulose) were provided by Embrapa Agroindústria Tropical (Fortaleza, CE, Brazil). Fibrous cellulose powder CF1 and Kraft lignin were purchased from Whatman International Ltd. (Maidstone, Kent, UK). Reagent grade chemicals used for fiber surface modifications and bleaching, namely, sodium hydroxide, sodium chlorite and sulfuric acid were purchased from Sigma–Aldrich (Saint Louis, MO, USA) and used without further purification.

2.2. Pre-treatment of coconut fibers

Coconut fibers were subjected to a washing pre-treatment to remove impurities and waxy substances covering the external surface of fiber cell walls according to the method described by Dinand et al. (1996), modified by Malainine et al. (2003). First, fibers were chopped in a Wiley mill (Thomas Scientific, Swedesboro, NJ, USA) and sieved through a 40-mesh sieve. These fibers (100 g) were dispersed in distilled water (500 mL) for 10 min in a Waring Laboratory Blender (Waring Products, Inc., USA) at full speed. This suspension was stirred for 2 h at 50 °C and filtered in order to remove soluble extractives in water. This procedure was repeated once more. The residue was dispersed in 500 mL of a 2% NaOH solution and the suspension was stirred for 2 h at 80 °C, filtered and washed with water. After washing, the alkaline treatment was repeated once more, and the fibers were dried at 50 °C for 24 h.

As lignin hinders fiber separation by acid hydrolysis, partial delignification (bleaching) was performed in order to facilitate further whisker extraction. Partial delignification was carried out so that the remaining lignin would help improve the thermal properties of the acid-extracted whiskers. Delignification was carried out according to the method described by Wise, Murphy, and D'Addieco (1946) in two levels: a less strong one-stage (1B) and an aggressive multi-stage (4B) bleaching. First, 5 g of dried pre-treated fibers were heated between 60 and 70 °C in 150 mL of water containing 1.5 g $NaClO_2$ and 8–10 drops of glacial acetic acid. The mixture was stirred at frequent intervals for 1 h, then cooled in an ice bath, filtered quantitatively and washed with cold water. For stronger bleaching, this procedure was repeated three more times using the same conditions, i.e., treatment 1B was comprised of only one bleaching step while treatment 4B had four steps. In the end, the bleached pulps were treated with 0.05 N nitric acid solution for 1 h at 70 °C, sieved in a 120 μm mesh size sieve and washed extensively with water.

2.3. Sulfuric acid hydrolysis

Conditions were selected according to an earlier exploratory work and reports in the literature. Cellulose whiskers were prepared by sulfuric acid hydrolysis according to the literature methods (Cranston & Gray, 2006; Medeiros et al., 2008a, 2008b; Orts et al., 2005). In brief, the bleached fibers (1B and 4B samples) were treated in a concentrated sulfuric acid solution (64 wt% sulfuric acid in water) at 45 °C. The ratio of fibers to acid solution was 1–10 g/ml. Since the higher the ratio of nanowhiskers-to-microfibrils the better their dispersion and stability in the aqueous medium, in order to compare both treatments hydrolysis was performed for 120, 150, and 180 min, under constant stirring.

After treatment, the hydrolyzed cellulose samples were washed four times, separating the crystals from the solution by centrifugation (10,000 rpm, 10 min) after each washing step. The resultant precipitate was continuously dialyzed against water for 3 days until constant pH was reached. Subsequently, this precipitate was dispersed in water to obtain nanowhisker suspensions which were used for further characterization.

2.4. Characterization

Surface morphology of the fibers was characterized using a Hitachi Scanning Electron Microscope (Model S4700, Hitachi High-Technologies, Japan) at a voltage of 2 kV using samples which were previously deposited on carbon tape mounted on sample stubs.

In order to determine fiber length, width, aspect ratio (length-to-width) and to indicate the aggregation state of the whiskers, highly diluted samples of the hydrolyzed suspension were analyzed by transmission electron microscopy. The fibril solution was mixed in equal volumes with 2% aqueous uranyl acetate (UA). A 10 μL drop of the UA-fibril mixture was dispensed onto a 400 mesh copper grid, allowed to stand for 30–60 s and the excess fluid was wicked off with Whatman No. 1 filter paper. The grid was air dried and viewed in a CM12 scanning-transmission electron microscope (STEM) (FEI Co., Inc., Hillsboro, OR) operating in the bright field mode at 80 kV. Digital images were captured with the STEM's associated XR41 CCD camera system (AMT, Danvers, MA).

Fiber lengths and widths were measured directly from transmission electron micrographs using Image Pro Plus 6.3 (Media Cybernetics, Inc., Bethesda, MD). Data were collected and analyzed using Microsoft Excel 2003.

The distribution of particle lengths was measured on TEM images using specialized software (MeasureIT, version 5.0, Olympus Soft Imaging Solutions, GmbH). At least 50 measurements for each condition were used to determine average and standard deviation values.

FTIR experiments were conducted using a Perkin Elmer FTIR spectrometer (Model System 2000, Perkin Elmer, USA). Samples were dried, ground and pelletized using KBr and their spectra were recorded in the range from 4000 to 650 cm^{-1} at 4 cm^{-1} resolution and 50 scans for each sample. Absorption ratios were obtained by measuring peak heights and normalizing them in relation to the cellulose absorbance peak at 897 cm^{-1} due to C_1—H deformation of glucose rings. For non-hydrolyzed samples, FTIR spectra were recorded after the bleaching step but before the acid hydrolysis step, while from hydrolyzed samples, spectra were recorded after the acid hydrolysis step.

X-ray powder diffraction analyses were performed with a Philips 1820 diffractometer operated at 45 kV, 40 mA with graphite-filtered Cu-Ka radiation. Data were acquired in a 2θ scale from 5° to 40°. Besides coconut fibers and nanowhiskers, commercial cellulosic (fibrous cellulose powder CF1) and Kraft lignin samples were also examined. Crystallinity degree was calculated from X-ray diffraction curves by the ratio of the crystalline area to the total area.

Thermogravimetric analysis (TGA) was performed to study the degradation characteristics of the cellulose whiskers obtained by different treatments. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min and a nitrogen gas flow rate of 60 mL/min. The derivative of each TGA curve (DTG) was obtained using the Thermal Analysis Instruments Universal Analysis 2950 program, V 5.4A.

3. Results

Fig. 1 shows that the bleaching steps used were effective in removing lignin and that the more aggressive the bleaching process the whiter the fibers were. This confirms that the relative lignin content in the fibers could be controlled by bleaching conditions such as time and number of steps. Viscous aqueous suspensions of cellulose nanowhiskers were obtained for all samples, in

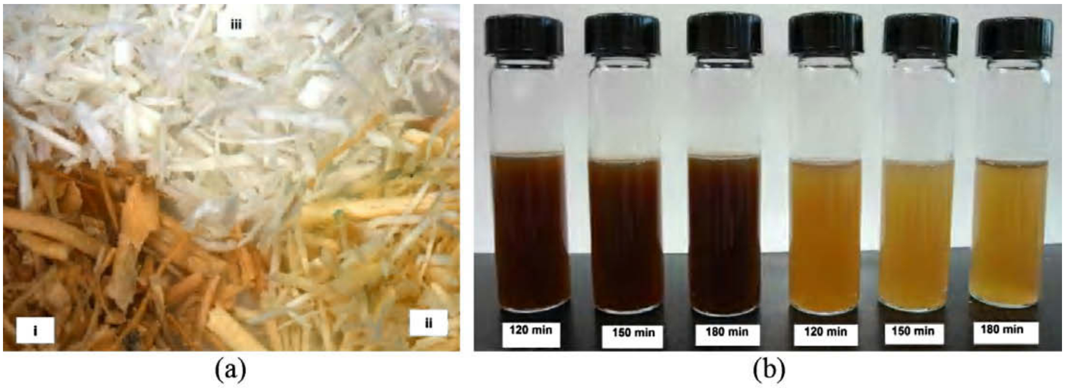


Fig. 1. (a) Optical microscopy micrograph of coconut husks (i) unbleached, (ii) after bleaching treatment 1B and (iii) after bleaching treatment 4B; and (b) vials containing nanowhisker suspensions obtained for different extraction times (1B = dark brown; 4B = yellowish brown). The dark brown color is due to the presence of remaining lignin in the samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

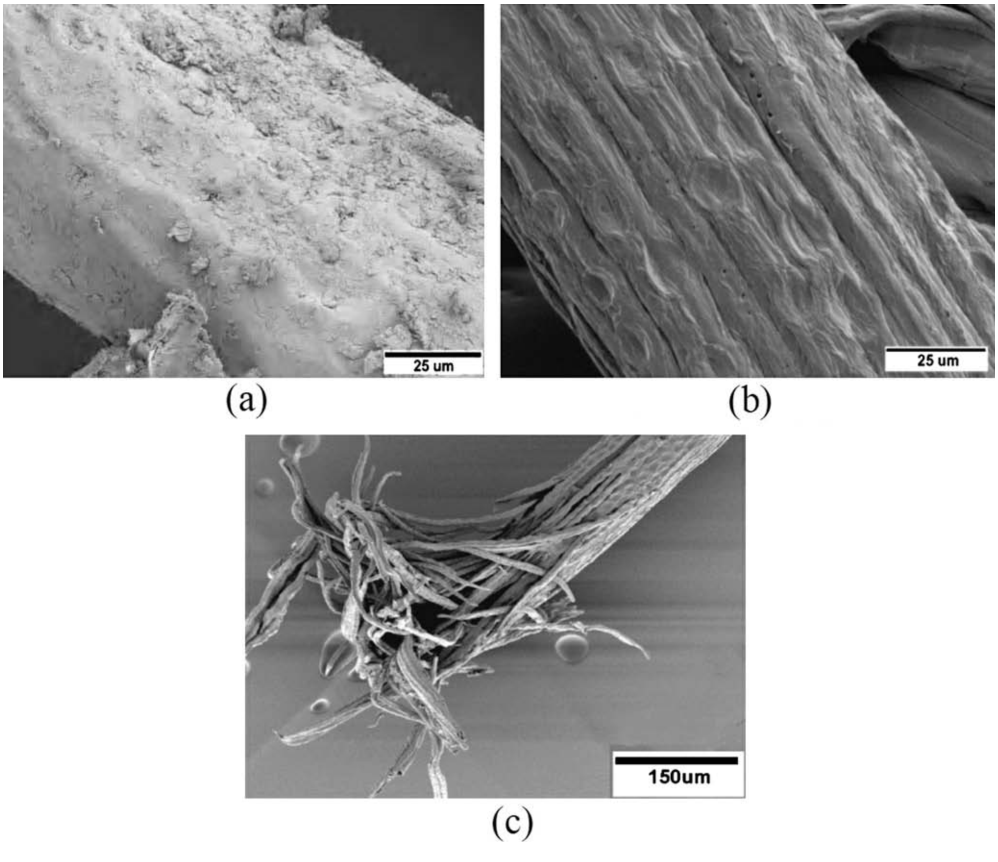


Fig. 2. Scanning electron micrographs of (a) untreated coconut fiber; (b) coconut fiber subjected to pre-treatment and (c) coconut fiber subjected to bleaching.

agreement with the results reported by Marchessault, Morehead, and Koch (1961). All dispersions presented brown color, indicating that there was still a significant amount of lignin, left from the raw material, after bleaching treatments. Moreover, these solutions, if concentrated to 4–5 wt%, form a gel due to particle–particle interaction similar to those reported in the literature (Battista, 1975; Battista & Smith, 1962).

3.1. Microscopical characterization

Fig. 2 shows SEM micrographs for untreated and treated coconut fibers prior to acid hydrolysis. TEM characterization of nanowhiskers is shown in Fig. 3. As pointed out by Alemdar and Sain (2008) working with wheat straw, these images suggest the partial removal of impurities, hemicelluloses, lignin and pectin after chemical treatment, which are the cementing components around the fiber-bundles. As can be seen in Fig. 2(c), bleaching resulted in partial defibrillation and opening of fiber-bundles. Partial removal of cementing components and defibrillations are important steps towards more efficient bleaching and subsequent steps of nanowhiskers hydrolysis. Each microfibril can be considered as a bundle of cellulose whiskers, linked along the microfibril by amorphous domains. The amorphous regions act as structural defects and are responsible for the transverse cleavage of the microfibrils into nanowhiskers, under acid hydrolysis (Battista & Smith, 1962).

These images evidenced the efficiency of the acid hydrolysis treatment, confirming that the aqueous suspensions contained coconut cellulose nanowhiskers consisting mostly of individual fibrils and some aggregates. This is consistent with the structural model proposed by Battista and Smith (1962) and the results reported by Lai-Kee-Him et al. (2002) and Azizi Samir, Alloin, and Dufresne (2005).

The effect of preparation conditions on the dimensions of cellulose nanowhiskers is shown in Table 1. The cellulose crystallites

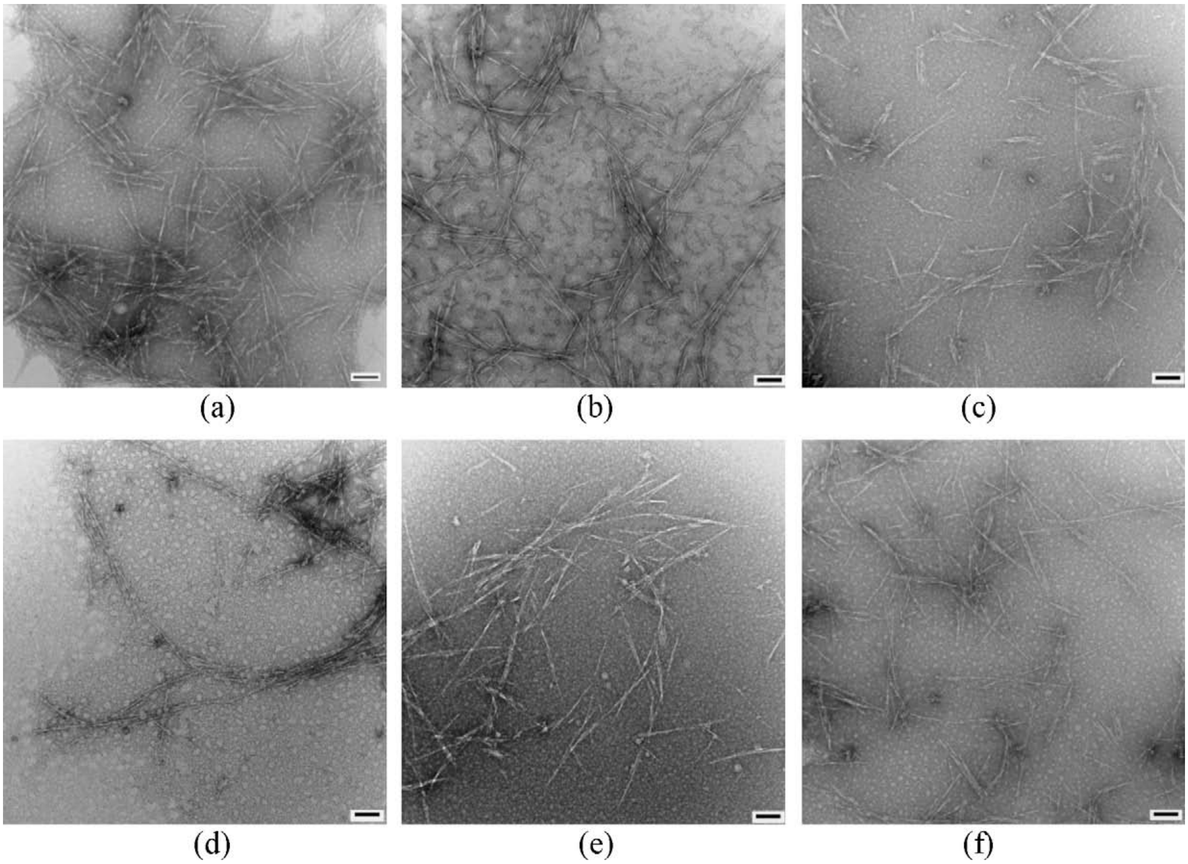


Fig. 3. Transmission electron micrographs of cellulose whiskers. (a) 1B (bleaching), 120 min (treatment time); (b) 1B, 150 min; (c) 1B, 180 min; (d) 4B, 120 min; (e) 4B, 150 min; (f) 4B, 180 min. Scale bars: 100 nm.

Table 1
Dimensions of cellulose nanowhiskers prepared by acid hydrolysis at different times (120, 150 and 180 min.), determined from TEM images.

Treatment	Hydrolysis time (min)	Length, L (nm)			Width, D (nm)[a]	Average aspect ratio[a] (L/D)
		min	max	Average[a]		
1B	120	85	374	194 ± 70	5.5 ± 1.5	39 ± 14
	150	58	447	179 ± 59	5.5 ± 1.4	36 ± 12
	180	58	322	204 ± 76	5.6 ± 1.3	41 ± 15
4B	120	74	408	210 ± 78	5.3 ± 1.3	42 ± 16
	150	75	515	218 ± 99	6.6 ± 1.7	44 ± 20
	180	73	409	177 ± 80	6.1 ± 1.7	35 ± 16

[a] Errors are the standard deviations of the distributions.

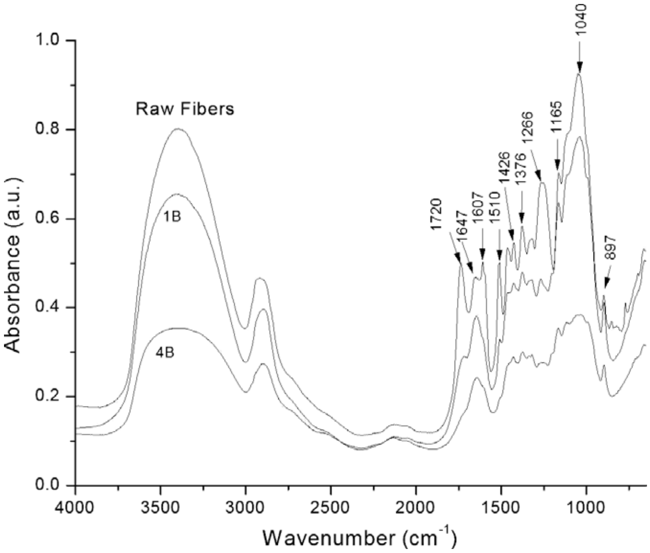


Fig. 4. FTIR spectra of bleached fibers (1B and 4B) compared with raw coconut fibers.

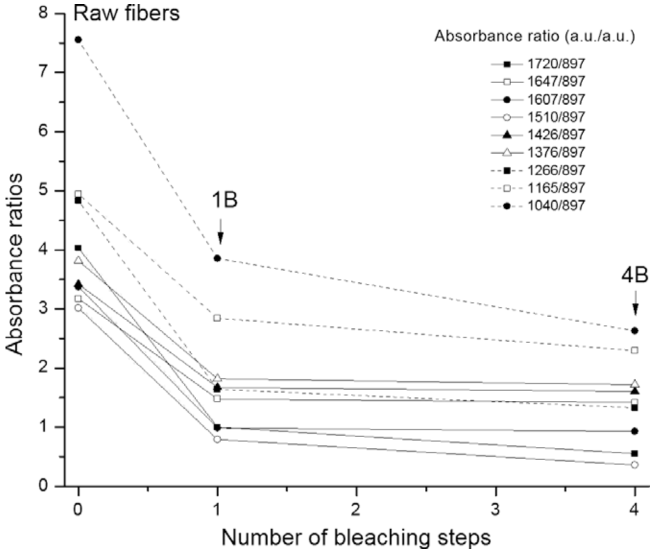


Fig. 5. Absorbance ratios normalized in relation to cellulose absorbance at 897 cm^{-1}.

were characterized by particle length (L), width (D) and aspect ratio (L/D). As pointed out by Dong et al. (1998), the conditions of preparation govern somewhat the properties of the cellulose particles. It is expected that the prolonged acid attack can not only "dissolve" amorphous molecules but also partly destroy crystalline zones of the fibrils, ultimately resulting in a shortening of nanowhisker length. However, the results show that, for the tested conditions, the values are nearly in the range of the deviation and there are no major differences between the lengths of nanowhiskers obtained from the different conditions of preparation.

Typically, coconut nanowhiskers had lengths ranging from 80 to 500 nm and widths of about 6 nm. A noteworthy observation is that the aspect ratio ranged from about 20 up to 60, with an average value of about 39 ± 16, which lies in the range of long nano-

Table 2
Vibrational frequencies (cm^{-1}) of coconut fibers with and without bleaching treatment (Fang, Sun, & Tomkinson, 2000; Hongzhang & Liying, 2007; Lawther & Sun, 1996; Pandey, 1999; Socrates, 2004; Stewart & Morrison, 1992; Sun, Lawther, & Banks, 1998).

Untreated (U)	Treatment 1B	Treatment 4B	Difference U-1B[a]	Difference U-4B[b]	Difference 1B–4B[c]	Peak assignments
3392	3413	3413	3371	3393	3413	O—H str.
2918	2900	2897	2943	2940	2932	C—H str.
			2844	2842^{sh}	2883	C—H str.
1736	1719^{sh}	1718^{sh}	1740	1740	1737	C=O str. of HC and L[d]
			1660	1661		C=O str. of L
1648	1643	1648			1656	O—H def. due to H_2O
						C=O str. of L
1609	1606^{sh}	1608^{sh}	1609	1609	1607^{brd}	C=C arom. skeletal vibr. of L
1596^{sh}			1595	1595		C=C arom. skeletal vibr. of L
1509	1513^{sh}	1509	1516	1515	1509	C=C arom. skeletal vibr. of L
1464	1466^{sh}	1465^{sh}	1464	1466	1468	C=C arom. skeletal vibr. (L); C—H def. (HC, L)
1427	1431	1427	1427	1424		C—H def. of C[d] and L
					1406	C—H and O—H bend. of HC & L
1377	1375	1376	1377	1378		C—H def. of HC, C and L
	1336		1332	1329	1329	O—H in-plane def. of C
1319	1321	1320	1313	1314		CH_2 wag of C
1267^{brd}		1268	1251^{brd}	1256^{brd}	1271	C—O str. of HC and L
	1202^{sh}	1202				O—H def. of C
1163	1166	1164	1163^{sh}	1162	1162	C—O—C asymmetric str. of HC, C and L
			1130	1126^{sh}		Aromatic C—H in-plane def. of L
1114^{sh}	1116	1113^{sh}	1104			Glucose ring str (C), arom. C—H in-plane def. (L)
	1061					C—O str. (C)
1050		1040	1052	1051	1040	C—O str. (HC, L)
	1034					C—O str. (C, L)
			916	918		C—H out of plane def. (L)
898	897	897			895	Glucose ring str., C_1—H def (HC, C)
852			852	852		C—H out of plane def. (L)
771			772	772		C—H out of plane def. (L)
698			699	699		Ring bend. (L)

sh, shoulder; and brd, broad peak; str, stretching; def., deformation; arom, aromatic; bend, bending; vibr, vibration.

[a] U-1B: material removed by treatment 1B.

[b] U-4B: total material removed by bleaching steps.

[c] 1B–4B additional material removed by treatment 4B.

[d] HC, hemicellulose; C, cellulose and L, lignin.

whiskers which have great potential to be used as reinforcing agents in nanocomposites. These results are consistent with other reports where nanowhiskers were extracted from different sources (Bondeson, Mathew, & Oksman, 2006; De Souza Lima, Wong, Paillet, Borsali, & Pecora, 2003; Dong et al., 1998; Elazzouzi-Hafraoui et al., 2008; Oksman, Mathew, Bondeson, & Kvien, 2006; Roohani et al., 2008).

In general, the aspect ratio depends on the source and whiskers preparation conditions. High aspect ratio cellulose whiskers give a good reinforcing effect, resulting in mechanical improvements at low loads. Moreover, remaining lignin can improve nanowhiskers' hydrophobicity and therefore make them compatible with many non-polar polymers such as polyethylene and polypropylene.

3.2. FTIR characterization

Fig. 4 shows the FTIR spectra and Table 2 shows the peak assignments of coconut husk fibers with and without bleaching treatment.

Table 2 shows that treatments 1B and 4B removed both lignin and hemicellulose as can be seen from lignin (L) and hemicellulose (HC) peaks when the difference between bleached samples (1B and 4B) and untreated (U) raw coconut fibers is computed. For instance, when spectrum 1B is subtracted from untreated coconut fibers (U), the peaks in the difference spectrum (U-1B) are due to lignin and hemicellulose, meaning that these are the major components removed after the first bleaching treatment (1B).

Moreover, when the absorption peaks at 1720, 1647, 1607, 1510, 1426, 1376, 1266, 1165 and 1040 cm^{-1} are normalized with respect to the cellulose peak at 897 cm^{-1} (Fig. 5), assuming that a negligible amount of cellulose is removed during the bleaching process, one can see that lignin content decreased with bleaching and that most of it was removed in the first step (1B) as can be seen from the absorbance ratios.

In order to compare the effect of hydrolysis time and bleaching on the removal of lignin and cellulose, absorbance ratios of lignin (1510 cm^{-1}) to cellulose (897 cm^{-1}) as a function of bleaching and hydrolysis time were calculated from FTIR spectra taken for nanowhiskers extracted for 120, 150 and 180 min (spectra not shown). These results are summarized in Fig. 6.

In sample bleached for four times (4B) cellulose crystals are more exposed to acid attack since more lignin was removed. Therefore, amorphous regions are "dissolved" by acid attack and the peak ratio of lignin to cellulose increases due to the decrease in cellulose content which leads to a decrease in the absorption peak at 897 cm^{-1} (C_1—H deformation) of glucose rings (Socrates, 2004). On the other hand, treatment 1B, which has more lignin, makes the acid attack on the amorphous regions more difficult due to the lignin layer covering part of the microfibril surface. However, when this barrier is overcome by acid diffusion into the amorphous regions, part of this lignin layer covering the fibers is removed and lost during the further purification (dialysis) step. As a consequence, the lignin-to-cellulose absorption ratio decreases slightly with increasing extraction time. However, the difference between 120 and 180 min is more accentuated for 4B than for 1B as can be seen in Fig. 6. In other words, Fig. 6 shows that the subsequent acid hydrolysis steps removed hemicellulose in 4B at a faster rate than the initially lower remaining lignin, while in 1B the hemicellulose was removed at a slower rate than the initially higher remaining lignin.

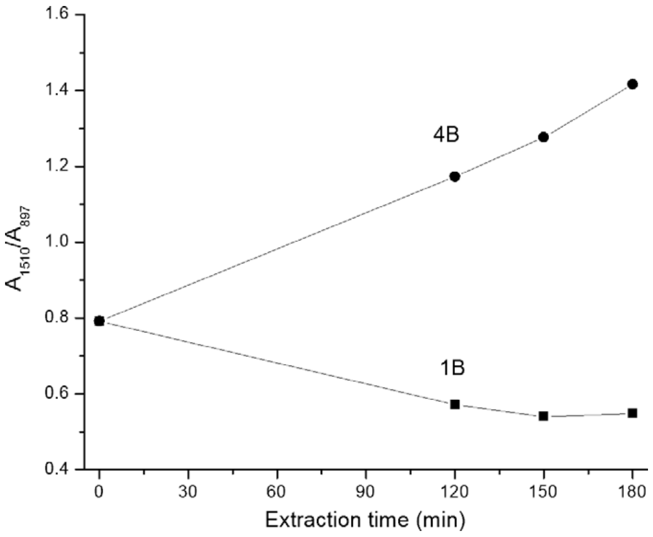


Fig. 6. Absorbance ratio of lignin (1510 cm^{-1}) to cellulose (897 cm^{-1}) as a function of bleaching and extraction time.

3.3. X-ray diffraction

X-ray diffraction patterns of cellulose nanowhiskers compared with treated and untreated coconut fibers, commercial cellulose and Kraft lignin are presented in Fig. 7. As expected, untreated coconut fibers present a large amorphous portion due to their high lignin content (37% lignin), as previously mentioned. This can be corroborated by the lignin and cellulose patterns in Fig. 7(a). Treated and untreated coconut fibers exhibited three main reflection peaks at $2\theta = 15.6°$, 22.7° and 34.6° relative to the cellulose crystalline structure. As a result of bleaching treatment that removed the lignin fraction of the fibers, narrower and more intense crystalline peaks were observed for fibers bleached one and four times. The effect of preparation conditions on the crystallinity of nanowhiskers is shown in Fig. 7(b and c). As can be seen, different conditions resulted in different degrees of crystallinity. Significant increases in relative intensity of the peaks at $2\theta = 16.5°$ and 22.7° were observed giving rise to a pattern typical of cellulose I patterns (Marchessault & Sundararajan, 1993). Similar results were obtained by Li et al. (2009).

The crystallinity, measured by the integration of amorphous and crystalline areas of each sample, is given in Table 3. It can be seen that both bleaching and preparation conditions affected the degree of crystallinity of cellulose nanowhiskers. For non-hydrolyzed samples, there is an increase by about 20% in crystallinity with bleaching and almost no differences between samples bleached once or four times. However, for hydrolyzed samples, hydrolysis time influenced the degree of crystallinity. Samples hydrolyzed for 120 min had the highest crystallinity, whereas it slightly decreased with increasing time. This might have occurred because prolonged acid treatment not only removed the amorphous portion of cellulose fibers but also partly destroyed the crystalline ones. These results were also supported by the FTIR analyses.

3.4. Thermogravimetric analysis

Thermogravimetric analyses of the microfibers shown in Fig. 1(a) before and after bleaching are depicted in Fig. 8. This figure shows that by bleaching the onset of thermal decomposition shifts to higher temperature due to removal of hemicellulose and partial removal of lignin. The first weight loss up to 120 °C is due to water evaporation. Lignin removal is reflected in the amount of residue in the range between 350 and 500 °C, Fig. 8(b), which decreases with increasing number of bleaching steps, and hemicellulose removal can be observed by the disappearance of the shoul-

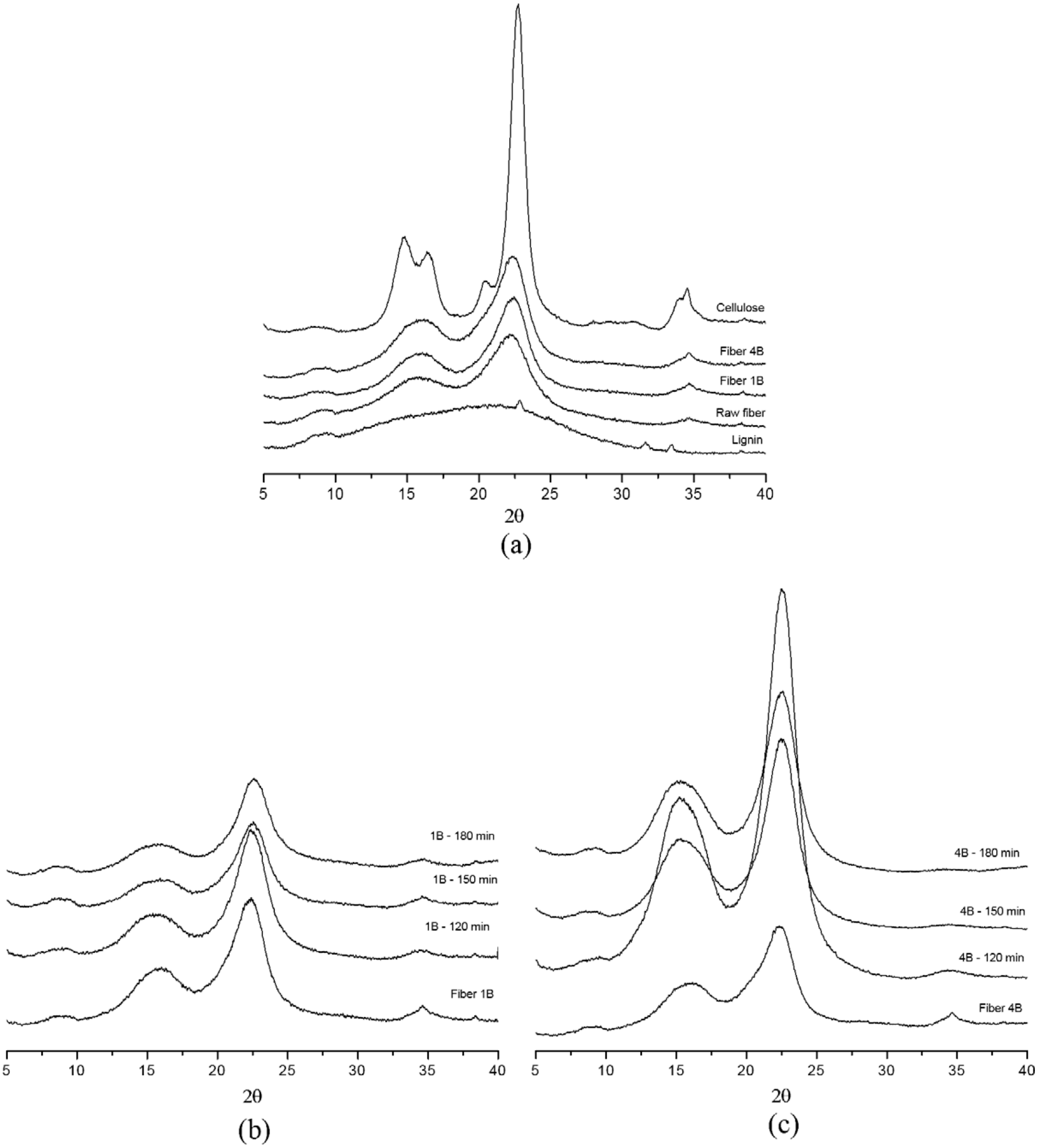


Fig. 7. X-ray diffraction patterns of: (a) lignin, cellulose, untreated and treated fibers, (b) treated fiber (1B), (1B – 120 min; 1B – 150 min and 1B – 180 min); (c) treated fiber (4B), (4B – 120 min; 4B – 150 min and 4B – 180 min).

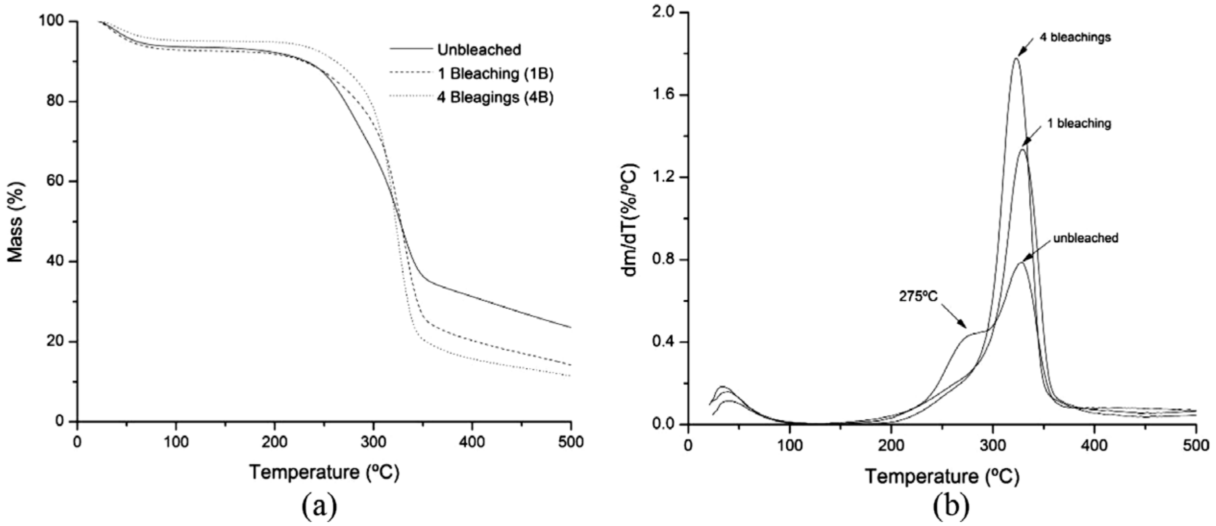
Table 3
Crystallinity degree (%) of coconut fibers compared with bleached fibers (1B and 4B), cellulose nanowhiskers 1B (120, 150 and 180 min) and cellulose nanowhiskers 4B (120, 150 and 180 min).

	Hydrolysis time (min)			
	Non-hydrolyzed	120	150	180
Untreated	38.9 ± 0.3	–	–	–
1 Bleaching	52.6 ± 0.9	65.9 ± 0.2	62.2 ± 0.5	62.5 ± 0.4
4 Bleachings	50.9 ± 0.5	65.6 ± 0.7	64.3 ± 0.6	64.1 ± 0.4

der at 275 °C of DTG curves in Fig. 8(b). These results are therefore in agreement with the FTIR analyses.

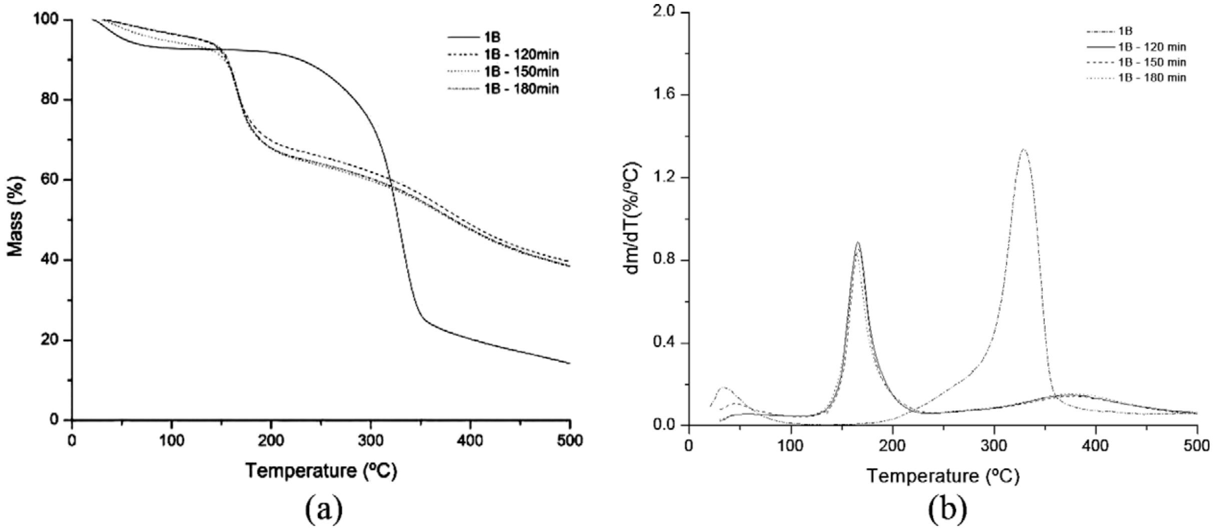
Thermal behavior of bleached fibers (1B and 4B) before and after hydrolysis for 120, 150 and 180 min is shown in Figs. 9 and 10.

Fig. 9 shows that there are no major differences between the thermal behavior of nanowhiskers obtained from the different hydrolysis times when these nanowhiskers were obtained from coconut fibers bleached only once (1B). This occurs because the hydrolysis times used did not impart any major morphological changes since nanowhiskers are somewhat inaccessible to acid attack because of the presence of residual lignin which coats nanowhiskers' surface. It is interesting to note that for fibers submitted to only one bleaching step, thermal decomposition of nanowhiskers starts at ca. 120 °C versus 200 °C for non-hydrolyzed fibers. This shift by 80 °C towards higher temperatures is due to the presence of remaining lignin and also is because hydrolyzed nanowhiskers were tested without neutralizing the sulfate groups on their surface. However, neutralization with NaOH can improve the thermal stability of the nanowhiskers, as reported in the



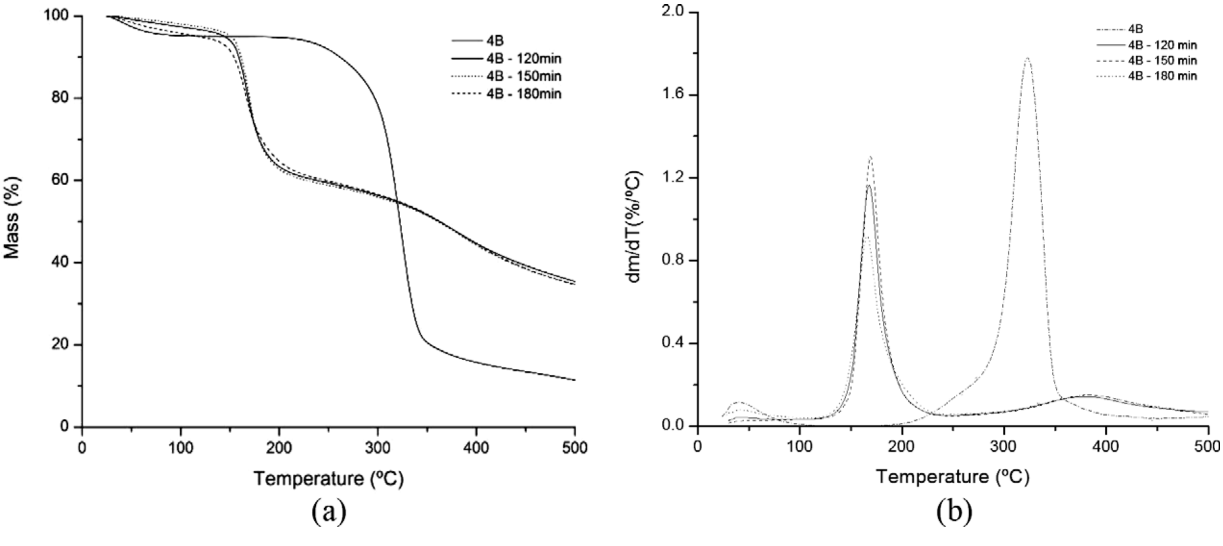
(a) (b)

Fig. 8. TG (a) and DTG (b) graphs of unbleached and bleached coconut fibers.



(a) (b)

Fig. 9. Effect of hydrolysis time (120, 150 and 180 min) on the thermal behavior of nanowhiskers extracted compared to fibers submitted only to one bleaching step (1B). (a) TG and (b) DTG curves.



(a) (b)

Fig. 10. Effect of hydrolysis time (120, 150 and 180 min) on the thermal behavior of nanowhiskers extracted compared to fibers only submitted to four bleaching steps (4B). (a) TG and (b) DTG curves.

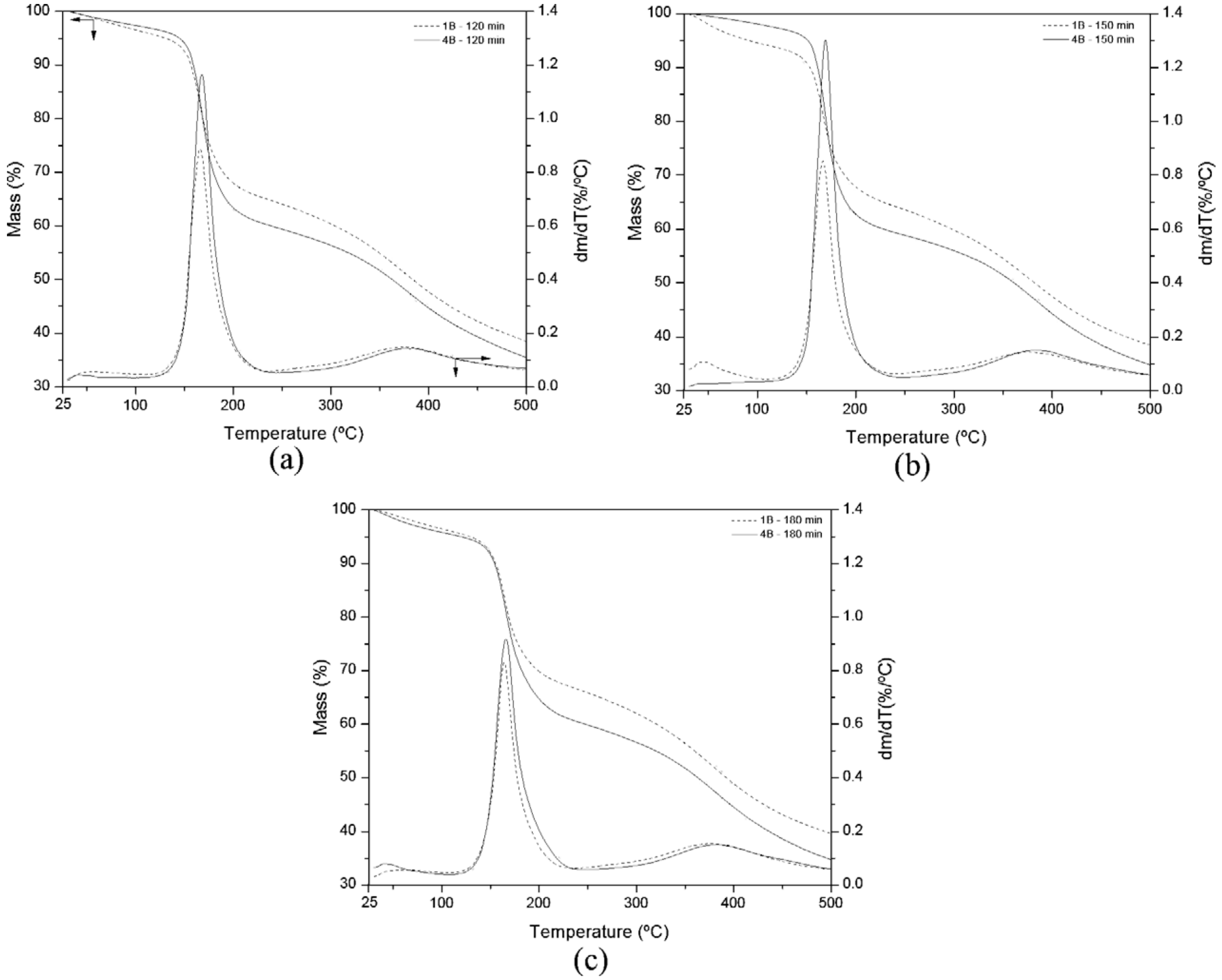


Fig. 11. TG and DTG graphs of the effect of bleaching steps on thermal behavior of coconut fibers hydrolyzed for (a) 120; (b) 150 and (c) 180 min.

literature (Medeiros et al., 2008b; Yang, Yan, Chen, Dong, & Zheng, 2007).

Results for fibers bleached four times followed by acid hydrolysis (4B) (Fig. 10) show similar behavior to 1B. Some minor differences, when comparing the effect of hydrolysis time on nanowhiskers thermal stability, can be observed mainly for 180 min hydrolyzed nanowhiskers that are the least thermally stable. This is attributed to the longest hydrolysis time that not only "dissolved" the amorphous cellulose molecules but also hydrolyzed the crystalline ones to some extent; as a result, the thermal behavior of these nanowhiskers is slightly poorer. Moreover, this is corroborated by fiber measurements, which show a slight decrease in fiber length and aspect ratio as the hydrolysis time increased, as shown in the TEM section.

The effect of bleaching steps on the thermal behavior of coconut fibers hydrolyzed for 120, 150 and 180 min is shown in Fig. 11. It can be seen from the DTG peaks that, for the same hydrolysis time, nanowhiskers from fibers subjected to one bleaching step (1B) are slightly more stable than from four bleaching steps (4B). Although the onset of decomposition temperature is approximately the same in all cases, the amount of material decomposed (proportional to the area under DTG peaks) is higher for nanowhiskers containing less lignin, i.e., treatment 4B. Moreover, TG graphs in the region between 200 and 500 °C show that treatment 1B has a higher amount of residue than 4B. These results are in agreement with the ones for non-hydrolyzed coconut fibers of Fig. 8; therefore pointing out that the residual lignin improves the thermal performance of the nanowhiskers. The literature confirms that lignin decomposition extends over the whole temperature range, starting below 200 °C and persisting above 700 °C (Yang et al., 2007).

4. Conclusions

Cellulose nanowhiskers were prepared by acid hydrolysis from coconut fiber. The effects of preparation conditions, such as bleaching and hydrolysis time, on the thermal and morphological behaviors of nanowhiskers were investigated. Higher residual lignin content (one bleaching step, 1B) was found to induce a higher thermal stability. A possible correlation between preparation conditions and particle size was not observed. The less strong treatment (1B) was considered more appropriate for nanowhisker extraction. This study also shows that cellulose nanowhiskers can be successfully prepared from coconut fibers by acid hydrolysis, stimulating the use of coconut husk fibers as a novel renewable source for production of cellulose nanowhiskers which possess great potential as reinforcing agents in nanocomposites. Moreover, the residual lignin, whose content is controlled by the bleaching step, can act as a compatibilizer to hydrophobic polymer matrices.

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