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Chemical, morphology and thermal evaluation of cellulose microfibers obtained from *Hibiscus sabdariffa*

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ABSTRACT

Cellulose is the most abundant biomass material in nature and finds a range of application. Cellulose microfibers were extracted from *Hibiscus sabdariffa* fibers by steam explosion technique. Structural and surface analysis of the microfibers showed a reduction in diameter and changes in surface morphology from that of the raw fibers. The chemical composition of fibers were analyzed according to the TAPPI standards and showed increase in α-cellulose content and decrease in lignin and hemicelluloses for the microfibers. This has been further confirmed by SEM, XRD and FTIR results. Thermal characterization showed enhanced thermal stability of celluloses microfibers compared to raw fibers.

1. Introduction

Fiber reinforced polymer composites are of tremendous importance both in the industrial field and in the area of fundamental research. Natural fibers are pervasive throughout the world in most of the plants, grasses, seeds, stalks or any kind of woody vegetation. According to the Food and Agricultural Organization (FAO), each year farmers harvest around 35 million tons of natural fibers from a wide range of plants and animals. A major amount of these materials are converted into useful products while the remaining posses a huge disposal problem. These fibers are also referred as cellulosic fibers, related to the main chemical component cellulose. Functional hydroxyl groups in cellulose enable chemical modifications for further applications. The advantage of using biopolymer based fibers is: less energy used lower pollution level during production, lower cost, biodegradability, abundant availability, renewable, etc.

The cell wall of wood fibers consists of repeated crystalline structure resulting from the aggregation of cellulose chains. The microfibers are surrounded by an amorphous matrix of hemicelluloses and lignin. The removal of the hemicelluloses and lignin gives rise to a new class of fibers, cellulose microfibers, with enhanced performance. They are characterized by good modulus, lateral dimension, thermal stability, etc. Micro fibrillated celluloses were first isolated by Turbak, Snyder, and Sandberg (1983). The preparation of cellulose nano/micro fibers from natural fibers such as coir fiber (Rosa et al., 2010), banana fiber (Deepa et al., 2011), bagasse (Teixeira et al., 2009), wheat straw (Kaushik & Singh, 2011), jute (Wang, Huang, & Yafei, 2009), hemp (Wang, Sain, & Oksman, 2007), soybean (Wang & Sain, 2007) have been studied. Selective degradation of fibers results in the formation of micro/nanofibers and their properties depends on their origin, processing techniques adopted, etc.

Several processes are used to extract highly-purified micro fibrils from various sources. They are generally based on successive chemical and mechanical treatments. Chemical treatments with alkaline solutions at different concentrations were used to isolate microfibrils from sugar beet (Dufresne, Cavaille, & Vignon, 1997), potato tuber cell (Dufresne, Dupeyre, & Vignon, 2000), soya bean (Wang & Sain, 2007), lemon and maize (Rondeau-Mouro et al., 2003), and mechanical methods (Herrick et al., 1983).

The microcrystalline celluloses were isolated from bagasse and rice straw by hydrolysis (Ambuj & Dhake, 2008). The characteristic of the obtained microcrystalline cellulose have been compared with Indian standards and commercial microcrystalline cellulose. The result shows that the lignocelluloses waste materials could be converted into valuable microcrystalline celluloses. The isolation and characterization of celluloses micro fibers from bagasse were carried out in three distinct steps: conventional pulping, mechanical separation and acid hydrolysis (Bhattacharya, Louis Germinario, & William Winter, 2008). The resulted celluloses micro fibers were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and

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solid state NMR technique. SEM and AFM indicated that the particle size varied between 200 nm to few microns. Elanthikkal, Gopalakrishnapanicker, Varghese, and Guthrie (2010) studied the extraction of cellulose microfiber from banana fibers and the effect of reaction time and acid concentration on the properties of the resultant fibers. As the concentration of acid increased a more stable aqueous suspension of microfibers was obtained and showed much less fiber diameter. The effect of four types of alkaline treatment on structural and morphological features of celluloses micro fibril obtained from banana rachis were investigated (Zuluaga et al., 2009). Four different alkaline treatments with peroxide alkaline, peroxide alkaline–hydrochloric acid or 5 wt% potassium hydroxide were used for isolation of cellulose micro fibrils from vascular bundles of banana rachis. Isolated celluloses micro fibrils were characterized using TEM, FT-IR and solid ^{13}CNMR. Potassium hydroxide showed better treatment performance compared to other alkaline treatment. The same author also worked on the isolation of cellulose micro fibrils from banana rachis, using a combination of chemical and mechanical treatments (Zuluaga, Putaux, Restrepo, Mondragon, & Ganan, 2007). The chemical treatment involved treatment of bleached banana rachis residues with a mixture of 80% acetic acid solution and 70% nitric acid solution at 120 °C for 15 min. The washed and purified cellulose was sonicated for 15 min. In the mechanical process, a bleached residue was suspended in water and homogenized. It has been noted that, acid treated products resulted in aggregation of cellulose microcrystallines whereas individualized micro fibrils were obtained by homogenization. Cellulose nanospheres were synthesis from cotton fibers by using mixed acid treatment (6:1:3 = water:HCl:H_2SO_4) (Zhang, Elder, Pu, & Ragauskas, 2007). The product mixture consisted of two different particle size species, averaging approximately 500 nm and 70–200 nm. The study revealed that cellulose nanoparticles of smaller sizes could be obtained by a further acidic sonication of the initially sonicated cellulose fibers. The authors pointed out that there was a linear relationship between the size of the cellulose nanoparticles and the treatment time. Another observation was that the initial cellulose sample was cellulose I, whereas the obtained cellulose spherical particles were of cellulose II polymorphic character.

Steam explosion is an excellent alternative for the conventional methods such as CMP (chemical mechanical pulps) and chemical thermo mechanical process. The principles of steam explosion technique are the steam under pressure with increased temperature penetrates through the space between the fibers, thus the middle lamella and the fiber adherent substance becomes soft and water soluble. Marchessault, Morehead, and Koch (1961) described steam explosion process as an auto hydrolysis and the function of the process based on biomass has been described by them as (i) the cleavage of glycosidic bond, β-ether linkage and lignin–carbohydrate complex bond and (ii) some chemical modification in lignin and carbohydrate. The steam explosion process was first introduced by Mason in 1927 to defibrillate wood fiber for board production. Steam explosion is a high yield pulping process based on vapor phase at temperature in the range 80–210 °C.

The aim of the present work is to extract celluloses microfibers (CMF) from *Hibiscus sabdariffa* fibers by steam explosion technique. *H. sabdariffa* is an annual dicotyledonous herbaceous shrub. They have broad leaves and become soft on boiling and the fibers from them are generally used for making ropes. Its long thread like fibers which is soaked and washed with water till it becomes soft and has high mechanical properties. The structural and morphology of the fibers were studied by SEM, optical microscopy, FTIR, and XRD. The chemical compositions of the CMF were analyzed as per TAPPI standards.

2. Experimental

2.1. Materials

H. sabdariffa fiber was collected from local farming community. The chemicals used such as NaOH, acetic acid, oxalic acid (SD fine), sodium hypochlorite (Rankem), potassium permanganate (Qualgen), and ferrous ammonium sulfate (RFCL limited) were of reagent grade.

2.2. Preparation of steam exploded H. sabdariffa fibers

H. sabdariffa fibers were cut into uniform size of approximately 5 cm. The fibers were treated with 2% NaOH in an autoclave with a pressure of 15 lb and at a temperature of 120 °C for a period of 1 h. Pressure was then released immediately. The fibers were removed from the autoclave and continuously washed with water until the solution obtains neutral pH. The fibers were then dried in a hot air oven at 70 °C for 2 h. The pH of the fibers was observed to be around 8.2.

2.3. Preparation of bleached H. sabdariffa fiber

The steam exploded fibers were bleached using a mixture of NaOH and acetic acid and followed by a mixture of 1:3 volume of sodium hypochlorite solution. Each bleaching took 1 h and the process was repeated six times. After bleaching, the fibers were thoroughly washed in distilled water until the smell of the bleaching agent was removed.

2.4. Preparation of acid hydrolyzed H. sabdariffa fiber

The steam exploded bleached fibers were treated with oxalic acid for 3 h in an autoclave after attaining a pressure of 20 lb. The pressure was released immediately. The autoclave was again reset to reach a pressure of 20 lb and the fibers were kept under that pressure for 15 min. The fibers were taken out and then washed until the solution obtains neutral pH.

2.5. Mechanical treatment of the processed H. sabdariffa fibers

The acid hydrolyzed fibers were suspended in water and kept stirring with a mechanical stirrer of type IKA RW 20 Digital Dual at 8000 rpm for 4 h. The pH of the suspension was observed to be around 6.1. The suspension was dried in a room temperature. The final yield is observed to be 38.6%.

3. Characterization of the micro fibers

3.1. Determination of chemical composition of fibers

Chemical compositions of fibers (α-celluloses, hemicelluloses and holocelluloses) were estimated according to the following TAPPI procedures: α-celluloses – T203cm-99, and holocelluloses – Tappi 249-75. The difference between the values of holocelluloses and α-cellulose gives the hemicelluloses content of the fibers. The moisture content of the fibers was estimated by T264om-88 procedure. 5 g of sample was mixed with 7.5% NaOH regent and stirred at 25 °C for 1 h. At the end of 60-min period, the pulp suspension was filtered. The chemical composition was determined using the filtrate. 25 ml of the prepared filtrate and 10 ml of 0.5 N potassiumdichromate were taken and 50 ml of concentrated sulfuric acid was added into it under stirring. 50 ml of water added to the mixture, followed by 2 drops of ferroin indicator and than titrated against 0.1 N ferrous ammonium sulfate solution to a purple color. 12.5 ml of 17.5% NaOH and 12.5 ml of water were used as blank.

The α-celluloses content was estimated using the following equation:

$$\alpha\text{-celluloses}\,(\%) = \frac{(6.85 \times (V_2 - V_1) \times N \times 20) \times 100}{A \times W} \quad (1)$$

where V_1 and V_2 are the titre volume of filtrate and blank, N is normality of ferrous ammonium sulfate solution, A is the volume of pulp filtrate, and W is the oven-dry weight of specimen.

2 g of the sample was weighed and kept in hot air oven at 150 °C for 2 h. The ash residue and the remaining holocellulose has been separated and weighed. From this, the holocellulose content were evaluated as follows:

$$\text{Holo celluloses}\,(\%) = \frac{A - B}{C} \times 100 \quad (2)$$

where A and B are the oven-dry weight of fibers and of ash in A, and C is an initial weight of the specimen.

For the estimation of lignin, 0.75 ml of 0.1 M sodium hydroxide was added to 15 mg of the sample and kept under stirring in hot water bath. After 1 h the sample was removed and washed first with distilled water followed by 10% acetic acid. The samples were dried in a hot air oven. 10 mg of this sample was soaked in 0.2 ml of 72% sulfuric acid for 2 h and than added 10 ml of distilled water. The sample was filtered, washed and dried under high vacuum.

$$\text{Lignin content}\,(\%) = \frac{C - D}{C} \times 100 \quad (3)$$

where C and D are the initial and final weight of fibers.

3.2. Moisture content determination

The weighed amount of sample was kept in air oven for 2 h at 105 ± 3 °C followed by cooling in a desiccators, replaced the stopper and opened the stopper momentarily to equalize the air pressure and weigh. Bottle was returned to the oven for 1 h; repeat the cooling and weighing as above for successive hourly periods until constant weight (B) was reached, that is, until successive weighing do not changed by more than 0.002 g. The moisture content was calculated as follows:

$$\text{Moisture content}\,(\%) = \frac{A - B}{A} \times 100 \quad (4)$$

4. Morphology

4.1. Scanning electron microscope (SEM) examination

The SEM photographs of gongura fiber surfaces of untreated and treated fibers were taken using a scanning electron microscope (SEM) model ZEISS EVO. The samples were sputter coated with gold particles and then photographed and different magnifications.

4.2. Optical microscopy

The optical photographs were taken using a Carl zeiss microscope with clemex software version 4.0. The samples were mounted on a clean glass slide and photographed at 10× and 5× magnification.

4.3. Fourier transform infrared (FTIR) spectroscopy

FT-IR analysis of raw as well as chemically treated *H. sabdariffa* fibers were done in order to obtain composition of the fibers before and after treatment. fibers were ground and mixed with KBr (sample/KBr ratio, 1/99) to prepare pastilles. FT-IR spectra were recorded in a spectral range of 450–4000 cm^{-1} with resolution of 2 cm^{-1}, taking four scans for each sample. The pellets were analyzed using JASCO 400 Infrared spectrometer.

4.4. X-ray diffraction

X-ray diffraction (XRD) profiles of *H. sabdariffa* fibers before and after chemical process were collected in order to examine the crystallinity of the samples with chemical treatment. The samples were taken in powdered form and analyzed using a Bruker D8 Advance X-Ray Diffractometer, using Cu Kα (1.5406 Å), Ni filtered radiation with 40 kV voltage and 40 mA intensity. The radiation has been absorbed in the range of $2\theta = 10\text{–}80^\circ$ in the speed of 2°/min. Crystallinity of cellulose was calculated from the diffraction intensity data. The normal diffraction planes of the celluloses are namely 1 0 1, 1 0 1, 0 2 1, 0 0 2, and 0 4 0 and will be present at 14.8°, 16.7°, 20.7° and 22.5° at 2θ angle. The crystallinity index was obtained using the Eq. (5) (Segal, Creely, Martin, & Conrad, 1959)

$$\text{Crystallinity index} = \frac{I_{0\,0\,2} - I_{\text{amorph}}}{I_{0\,0\,2}} \times 100 \quad (5)$$

where $I_{0\,0\,2}$ is the maximum intensity of the (0 0 2) lattice diffraction and I_{amorph} is the intensity diffraction at 18° 2θ degrees. The calculation of the X-ray crystallinity order index was also performed using Eq. (5). The crystallinity index was calculated from the fraction of the ratio of the (0 0 2) to the sum of (1 0 1), (0 2 1) and (0 0 2) refraction areas. The crystallinity order index was obtained using the Eq. (6)

$$\text{Crystallinity order index} = \frac{A_{0\,0\,2}}{A_{1\,0\,1} + A_{1\,0\,1} + A_{0\,0\,2}} \quad (6)$$

The above equation was used for calculating amorphous fraction in intensity and area to calculate the crystallinity index.

$$t_{h\;kl} = \frac{K\lambda}{b_{hkl}\cos\theta} \quad (7)$$

where t is the thickness of the crystalline, λ is the X-ray wavelength, θ is the Bragg angle of the reflection, b_{hkl} is the pure integral of width of the reflection at half maximum height, and K is the Scherrer constant that falls in the range of 0.87–1.0 (Bodor, 1991). The crystallite size of cellulose fibers was determined by using the diffraction pattern obtained from 0 0 2 lattice plane.

4.5. Thermal characterization

Thermo gravimetric analysis of treated *H. sabdariffa* fiber was carried out in a temperature interval of 25–400 °C under nitrogen atmosphere with a flow rate of 20 ml/min using A Perkin Elmer thermo gravimetric analyzer Pyrisi TGA. A constant heating rate of 20 °C/min was maintained.

5. Results and discussion

5.1. Chemical composition of fibers

The chemical compositions of the fibers are shown in Table 1. The treated fiber showed lower percentage of hemicelluloses, lignin and higher percentage of α-cellulose when compared with untreated fibers. When the raw fiber was subjected to steam explosion process, the 1–4 glycosidic linkages between the hemicelluloses and the lignin gets hydrolyzed, leading to the depolymerization of lignin and hydrolysis of hemicelluloses. The process dissolves the hemicelluloses and lignin and paved the way for the formation of water soluble sugar and phenolic content. High pressure steaming followed by rapid decompression is called steam explosion. The steam explosion process includes saturating the dry material with steam at elevated pressure and temperature followed by sudden release of pressure, during which the flash evaporation of water exerts a thermo mechanical force causing the material to

Table 1
Chemical composition of raw and treated *Hibiscus sabdariffa*.

Materials	Celluloses (%)	Hemicelluloses (%)	Holocelluloses (%)	Lignin (%)	Moisture content (%)
Raw fibers	63.5	17.5	46	12	2
Treated fibers	81.5	4	77	1.5	9

rupture. Steam explosion in alkaline medium results in the hydrolysis of hemicelluloses within the fiber, and the resulting sugars can be subsequently washed out in water, leaving a residue of cellulose and lignin. It also leads to the cleavage of hemicelluloses–lignin bonds. The reaction results in an increased water solubilisation of hemicelluloses and in an increased solubility of lignin in alkaline solvent, leaving the cellulose as a solid residue with a reduced degree of polymerization. Yamashiki et al. (1990) proposed an explanation for the solubility of steam exploded celluloses in NaOH solution, suggesting that during the steam explosion there is a partial break down of the intramolecular hydrogen bond at the C-3 and C-6 position of the glucopyranose unit and result in significant variation in the network and strength of the hydrogen of the celluloses hydroxyls. However the complete removal of these components does not take place during steam explosion, it only results in changes in the arrangements of macro molecular chain.

Bleaching process helps to remove the majority of lignin content of the fibers was carried out using sodium hypochlorite. This results in the further solubilisation of lignin and hemicelluloses. Also it results in the formation of pits on the surface which in turn increases the surface area of the fibers. The bleaching treatment was performed to break down phenolic compounds or molecules having chromophoric groups present in lignin and to remove the by-products of such breakdown, to whiten the pulp. During bleaching, the lignin was oxidized and became soluble in the alkaline medium, also steam explosion at this stage resulted in the removal of other additives and impurities from the fiber external and internal surface of the fiber. It has been reported that cementing materials like lignin and hemicelluloses gets dissolved predominantly during the bleaching process. In order to decrease the diameter of the fibers further treated the resulting fibers with acids. The impacts of the acid treatment of natural fibers were investigated previously also (Araki, Wada, & Kuga, 2001; Dong, Revol, & Gray, 1998; Viet, Beck-Candanedo, & Gray, 2007). Xiao, Sun, and Run (2001) proposed that during steam explosion, the hydrolyses of glycosidic linkages in hemicelluloses and the ether linkages in lignin are catalysed by acetic acid formed at high temperature from acetyl groups present in hemicelluloses (auto hydrolysis). At the end of the process, the steam was suddenly released providing additional mechanical defibrillation. The cellulose is de-polymerised and de-fibrillation. The hydrolysis with acid results in the complete dispersion of the microfibers due to hydrolysis.

The moisture content of the treated fibers is more than that of the raw fibers. It is an important parameter used to determine the properties and end users of the fibers. During the alkali treatment process, some alkali labile linkages (ether and ester linkages) between lignin monomers or between lignin and polysaccharide may be broken. In addition, the steam explosion and bleaching treatments acted to remove some loose substance from the fiber surface, leaving a hard structure that was difficult to dissolve in the caustic solution. Therefore, the percentage of celluloses content increases. As the percentage of the celluloses content increases the moisture absorption rate also increases. This is because the chemical structure of cellulose contains three hydroxyl groups, which in the macromolecular celluloses structure forms hydrogen bonds. When the fibers were exposed to alkaline medium, swelling of the fibers as well as development of strongly hydrophilic ionic groups on the fiber surface were induced, which also promote the absorption of moisture. Chemical treatment results in the removal of surface materials opening up the fiber with more scooped individual cells (Ajayi, Bello, & Yusuf, 2000). The removal of surface impurities exposes the hydroxyl groups (Eromosele, Ajayi, Njaprim, & Modibbo, 1999). The presence of residual alkali remaining in the microfibers after treatment also can cause the moisture absorption.

5.2. *Morphology and structural analysis*

Fig. 1 shows the FTIR spectrum of raw and treated *H. sabdariffa* fibers in step wise. The peak at 1729 $\mathrm{cm^{-1}}$ in the raw fibers is due to either the acetal and uronic ester groups of the hemicelluloses or the ester linkage of the carboxylic group of the ferulic and p-coumaric acid of lignin and hemicelluloses, (Cherian et al., 2008; Sun, Xu, Sun, Fowler, & Baird, 2005; Gronli, Varhegyi, & Blasi, 2002). The change in intensity of the peak at 1729 $\mathrm{cm^{-1}}$ is more evident from stages II to III indicating that the removal of non cellulosic part is mostly in the bleaching stage. The aromatic peak C=C stretch from aromatic ring of lignin gives two peaks at 1504 $\mathrm{cm^{-1}}$ and 1428 $\mathrm{cm^{-1}}$ observed in the untreated fibers. The peak at 2917 $\mathrm{cm^{-1}}$ is due the aliphatic C—H stretching vibration which has shown some changes in absorbance after treatment, due to the changes in chemical composition during removal of lignin from the fibers. The hydrophilic tendency of raw fibers and chemically treated *H. sabdariffa* is reflected in the broad absorption band in the 3700–3100 $\mathrm{cm^{-1}}$ region which is related to the —OH groups present in the main component. The peak at 3288 $\mathrm{cm^{-1}}$ in the spectra of treated fibers shows the stretching vibration of

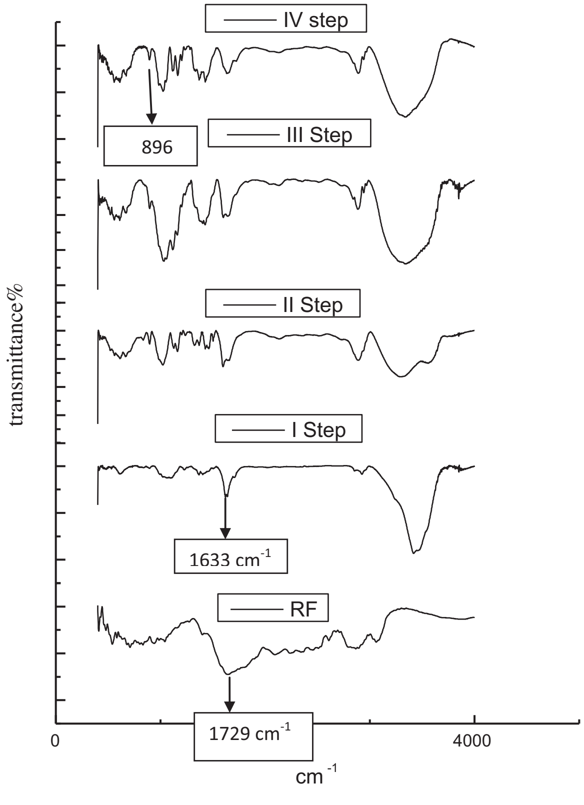

Fig. 1. FT-IR spectrum of raw fiber and celluloses microfibers under different reaction condition.

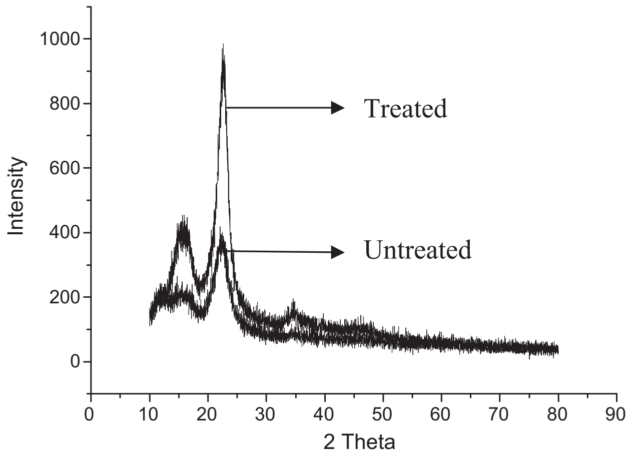

Fig. 2. XRD pattern of treated and untreated fibers.

hydrogen bonding of the hydroxyl groups. In the FTIR spectrum of raw fibers and after stage I, the absorbance at 3700–3100 cm^{-1} of —OH stretching were not clearly evidenced, due to interfering contributions from a variety of stretching modes in the amorphous regions (Liang & Marchessault, 1959). The band at 1633 cm^{-1} is due to the carboxylate group and also due to the bending mode of the absorbed water in the treated fibers (Sun et al., 2005). The band at 1504 cm^{-1} has almost disappeared and also the intensity of the 1428 cm^{-1} has been decreased after the treatment. It indicates the removal of lignin from the fibers. The band at 1372 cm^{-1} due to the asymmetric C—H deformation. The sharp peak at 1245 cm^{-1} has sharply decreased after chemical treatment indicating the removal of hemicelluloses. The band region between 1202 cm^{-1} to 1024 cm^{-1} represents the C—O stretch band and deformation bands in cellulose, lignin and residual hemicelluloses (Sun et al., 2005). The increase in the intensity of the peak at 896 cm^{-1} indicates the typical structure of celluloses (due to β-glycosidic 1–4 linkage of glucose ring in celluloses) (Ganan, Cruz, Garbizu, Arbelaiz, & Mondragon, 2004).

XRD pattern of the treated and untreated samples have been shown in Fig. 2. XRD analyses of the treated and untreated samples have been done in order to determine the structural and chemical change of the treated fibers. Cellulosic fibers consist of three components namely lignin, hemicelluloses, and α-celluloses. Cellulose shows crystalline nature while lignin is amorphous in nature. As a result the crystallinity of the fibers should increase after treatment. The celluloses fibers are surrounded by non-celluloses polysaccharides such as hemicelluloses and lignin matrix. The increase in the overall order of the hydrolysed fibers can be attributed to the removal of the hemicelluloses and lignin during the chemical treatment. The diffractograms, probably representing typical cellulose diffractograms, shows a peak at $2\theta = 22°$ and a shoulder in the region $2\theta = 14–17°$ (Bondsen, Mathew, & Oksman, 2006), which shows the presence of celluloses. The treated fibers shows strong crystalline nature due to its higher diffraction intensity at $2\theta = 22°$ (Bondsen et al., 2006). The celluloses micro fibers obtained from the *H. sabdariffa* fibers showed the diffraction intensity at 22.5° and a shoulder in the region $2\theta = 14–17°$ and also exhibited peaks at some lower intensity such as 14.2°, 17.05° and 34.4°. The broad peaks of the raw fibers are due to the amorphous nature of the lignin where as α-celluloses are crystalline in nature. The diffraction intensity peak at $2\theta = 22.5°$ corresponding to the 0 0 2 lattice plane. The higher peak

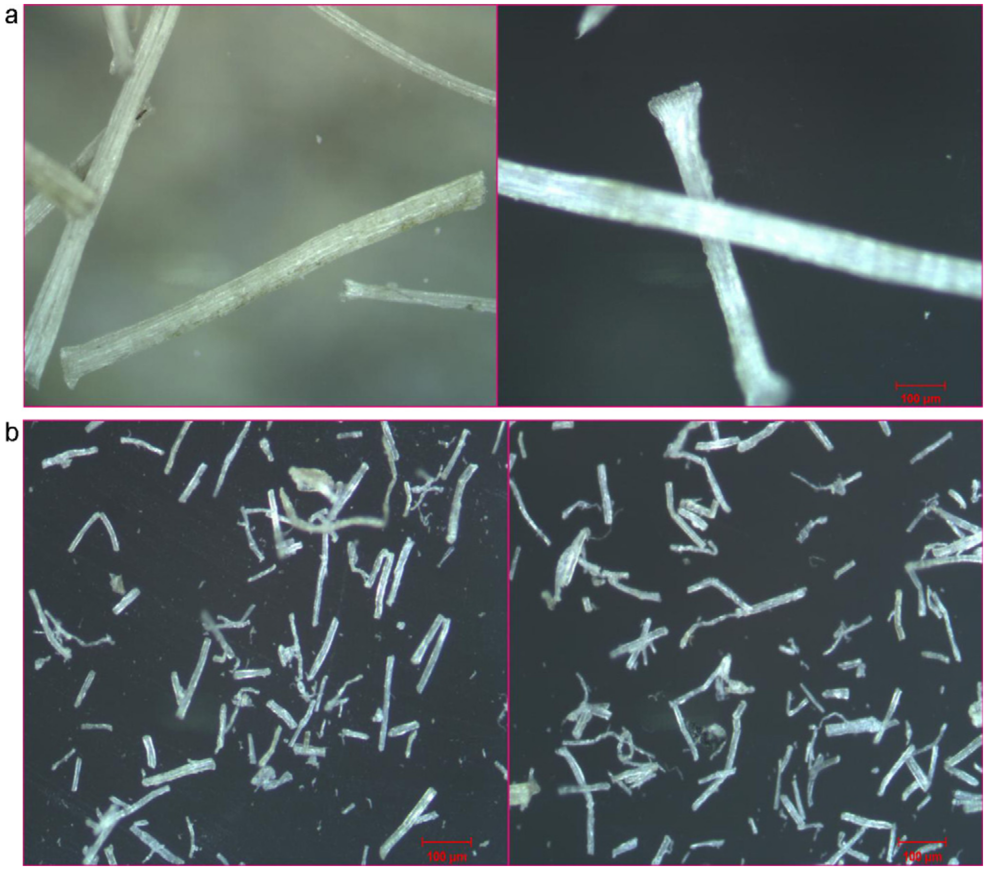

Fig. 3. (a) Optical images of untreated fibers at 5× and 10× magnifications and (b) optical images of treated fibers at 5× and 10× magnifications.

Table 2
Degradation temperature of raw and treated fibers.

Fiber	Degradation temperature (°C)	% of degradation	Ash content at 400 °C
Raw fiber	275	69	31
Treated fiber	300	78	22

intensity of the treated fibers from Fig. 2 indicates the complete removal of non-cellulose, the non-cellulose has been removed due to the acid hydrolysis and also due to the dissolution of the lignin during steam explosion. It has been indicated through the results that the hydrolysis takes place in the amorphous region; it also indicates the crystalline regions are chemically stable. To calculate crystallinity order index width separation of each X-ray diffraction was proceeded for every particular plane. The crystallinity of the obtained microfibers has been increased to 78.95% and the crystallinity order index has been increased to 81.05%. The crystallinity of the celluloses is obtained as the hemicelluloses and lignin have been identified during high temperature steam explosion, it has been proved that the chemical and mechanical treatment improves the α-celluloses and thus there is decrease in the fiber diameter. The additional peaks observed in the treated fibers may be due to the rearrangement of fibrils in the interfibrillar regions giving rise to new crystalline regions. Only the amorphous regions and crystal surfaces in the cellulose structure, that is, the cementing materials, can react with alkali and be removed. Thus, the interfibrillar regions are likely to be less dense and less rigid and thereby make the fibrils more capable of rearranging by themselves (Gassan & Bledzki, 1999).

Optical images of untreated and treated fibers at 5× and 10× magnification are shown in Fig. 3a and b. The image showed excellent difference in both diameter and length of the celluloses micro fibers from the raw fibers. The diameter and length of the fibers were reduced drastically with chemical treatment. This is further supported by SEM photographs shown in Fig. 5a and b. The raw fibers showed a diameter of 90 μm while the treated fibers showed an average diameter of 10.04 μm.

5.3. Thermal characterization of the microfibers

Thermal analysis of *H. sabdariffa* fibers have been done to compare the thermal stability of the treated fibers with the raw fibers. The TGA of the treated and the untreated fibers are shown in Table 2. The TGA graphs of treated and untreated are shown in Fig. 4. The initial weight loss of the celluloses was been started from 50 to 150 °C, this due to the evaporation of the moisture. The temperature range between 150 and 250 °C shows the depolymerization of non-celluloses such as hemicelluloses. It also reveals the breakage of the glycosidic bonds. And the temperature between 300 and 350 °C indicates the degradation of the α-celluloses. A greater crystalline structure required a higher degradation temperature (Ouajai & Shanks, 2005). However both non-cellulosic components and the crystalline order of celluloses played an important role in thermal degradation of the fibers. It reveals that the structure and the crystallinity of the cellulose are related to the degradation of the sample. These indicates that the crystalline sample have higher thermal stability. This corresponds to the vaporization and removal of bound water in the celluloses samples. The cleavage of the glycosidic linkages of cellulose, leading to the formation of H_2O, CO_2, alkanes and other hydrocarbon derivatives, occurs in the temperature range of 230–370 °C. After 380 °C, the residual decomposition products maintain a slow degradation profile (Sakhawy & Hassan, 2007). The degradation of natural fiber takes place in two stages, mainly the degradation of amorphous phase i.e., lignin, hemicelluloses, etc. And that of crystalline phase i.e. of cellulose. The lignin part is responsible for the char formation of the fiber. Thus the raw fiber shows higher ash content as it contains more lignin content whereas the treated fiber shows lesser ash content, indicating the removal of lignin.

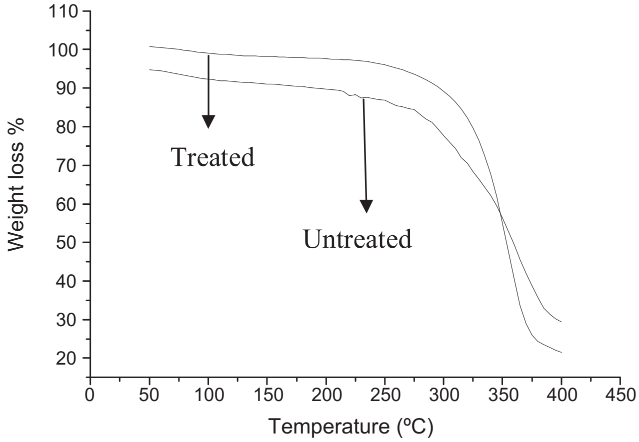

Fig. 4. TGA curves of untreated and treated fibers.

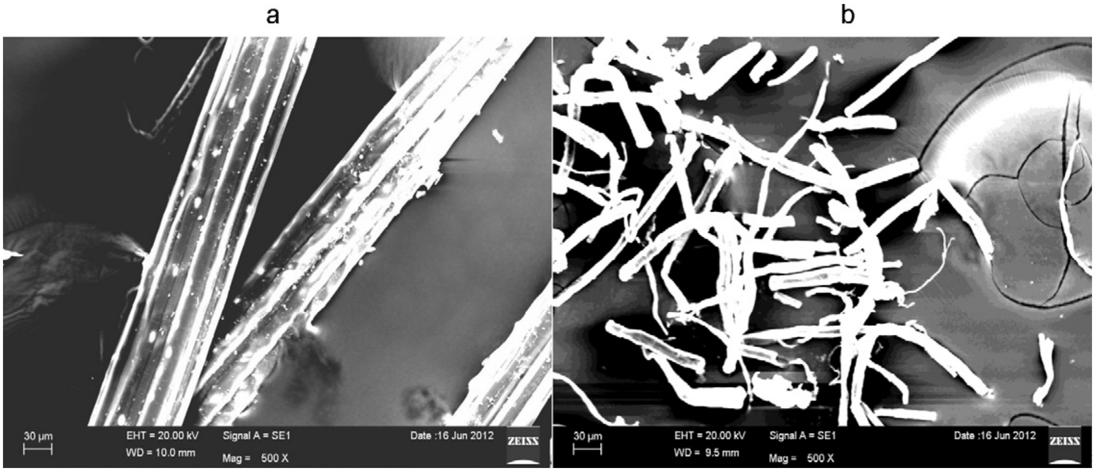

Fig. 5. (a) SEM images of untreated fibers and (b) SEM images of treated fibers.

6. Conclusion

H. sabdariffa fibers have been treated by steam explosion techniques and analyzed by SEM, FTIR, XRD, optical microscopy and chemical composition. The chemical composition confirmed that the treatment result in higher percentage of celluloses and lower percentage of lignin. The hydrolysis of the hemicelluloses and lignin was confirmed by FTIR and XRD. Optical and SEM images showed a drastic reduction in fiber diameter and length with the raw fiber showing an aspect ratio of 57.7 and the treated fibers showing aspect ratio of 19.8. Thermal analysis shows that the thermal stability of the treated fibers has been improved.

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