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Characteristics of Natural Cellulose Fibres Extracted from Sri Lankan Rice Straw Varieties

A. Ratnakumar[1], A.M.P.B. Samarasekara[1*], D.A.S. Amarasinghe[1] and L. Karunanayake[2],

[1]*Department of Materials Science and Engineering, Faculty of Engineering, University of Moratuwa, Moratuwa, Sri Lanka*

[2]*Department of Polymer Science, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka*

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Ratnakumar, A.
https://orcid.org/0000-0001-7489-2732

ABSTRACT

In the recent years, natural fibres have gained greater attention to replace synthetic fibres in producing environmentally friendly green products. These are currently considered as one of the most promising areas of scientific and technological development due to strong global demand for creating a resource circulating society. Rice is one of the largest crops in the world. Sri Lanka being an agricultural country holds twentieth position in the worldwide rice production with 2.4 and 3.9 million metric tons in the years 2017 and 2018 respectively. However, a large amount of rice straw is generated per annum as a by-product of rice production in the country. Even though rice straw is utilized in various ways, there is a possibility for a value addition by extracting its constituents such as cellulose fibres from this underutilized waste material. In this work, cellulose fibres were extracted from locally available rice straw varieties via a series of chemical treatments. Technically modified variety *BG352* and traditional variety *Murunkan* were used for this purpose. The material obtained after chemical treatment was carefully characterized and its chemical composition was determined. Fourier transform Infrared (FTIR) spectroscopy and X-ray diffraction (XRD) analyses showed the progressive and complete removal of non-cellulosic constituents from the rice straw. Morphological investigation was performed using scanning electron microscopy (SEM). Thermal stability of the fibres was investigated using thermogravimetric analysis (TGA). The results showed around 26 and 33 percent cellulose fibres were extracted from rice straw varieties *BG352* and *Murunkan* respectively.

*Corresponding author : banduamp@gmail.com

INTRODUCTION

Natural fibres are renewable sources and can be rehabilitated by nature and human ingenuity. These natural fibres play a key role in the emerging green economy. Cellulose, a linear biopolymer is present naturally in all plants. It is a massive source for environmentally friendly and biocompatible products (Fan *et al.*, 2013). Rice straw is considered as an agricultural crop residue which is rich in lignocellulosic materials. Cellulose is the principal constituent of lignocelluloses which has a long chain polysaccharide structure made of β (1,4) -linked glucose units. The chemical formula of the organic proportions of rice straw is $C_6H_{9.63}O_{4.57}N_{0.11}S_{0.02}$ which is very close to the chemical formula of cellulose monomer ($C_6H_{10}O_5$) (Reddy and Yang, 2006).

Paddy is cultivated as a wetland crop in almost all parts of the country, except at very high altitudes. There are two cultivation seasons in Sri Lanka namely, *Yala* and *Maha* which are synonymous with two monsoons. *Yala* season is effective during "South-east monsoon" from May to end of August whereas *Maha* season falls during "North-east monsoon" from September to March in the following year.

The total production and land extent under paddy cultivation during *Yala* and *Maha* season in the years 2017 and 2018 are shown in Figure 1 (Department of Census and Statistics of Sri Lanka, 2017/2018). Rice straw is a by-product from the paddy cultivation and identified as a residue of agricultural production that is generated in equal or greater quantities than the rice itself. It is projected that the demand for rice will increase at 1.1% per year. In order to meet this demand, the rice production should grow at the rate of 2.9% per year. As a result, a significant amount of rice straw will be generated per annum in the country. However, rice straw is considered to be an agricultural waste in developing countries as it cannot be converted into valuable by-products. As we tend to reduce the adverse impact on the environment, the development of effective technologies for utilization of rice straw is both important and significant.

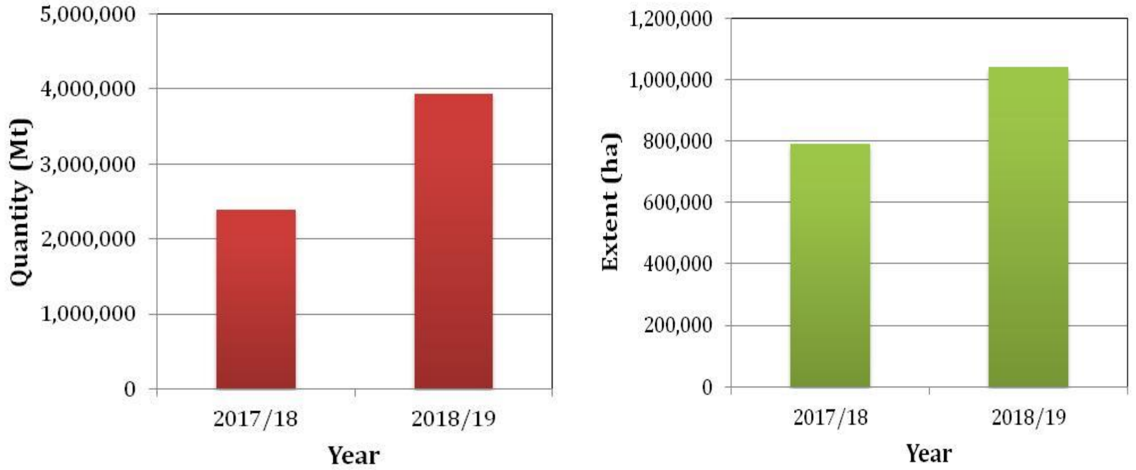

Figure 1. Paddy cultivation in Sri Lanka (a) production quantity and (b) land extent in the years 2017 and 2018.

Rice straw contains cellulose (22 - 47%), hemicellolose (19 - 27%), lignin (5 - 24%), resin, gum, protein, and mineral compounds. However, effective separation of cellulose fibres from rice straw is difficult due to their pristine crystalline structure and the complex structure of lignin and hemicellulose. Therefore, various pretreatments of rice straw have been developed to split up the structure of cellulose and increase its exposure (Poletto *et al.*, 2013).

In this study, cellulose fibres were extracted from locally available technically modified rice straw variety *BG352* and traditional rice straw variety *Murunkan via* a series of chemical treatment methods. The technique adopted includes removal of wax and oil, removal of lignin and removal of hemicellulose and silica from the mentioned rice straw varieties. A comprehensive analysis was performed on untreated and treated rice straw samples to investigate their structural, morphological and thermal properties by using Fourier transform infrared spectroscopy (FTIR), X-ray diffractometry (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Extracting cellulose fibres from rice straw would not only mean an environmentally friendly alternative to synthetic fibres currently in use but will also add value to the rice straw and benefit the farmers economically.

MATERIALS AND METHODS

Processing of Rice Straw

Sri Lankan straw from rice varieties *BG352* and *Murunkan* were used in this study. Technically modified rice straw variety *BG352* was collected after the 2018 *Yala* seasonal harvest from Rice Research and Development Institute (RRDI), Bathalagoda and traditional rice straw variety *Murunkan* was collected after the 2018/2019 *Maha* seasonal harvest from Provincial Department of Agriculture, Jaffna. Stems of the obtained rice straw were initially cut into 3 to 4 cm length pieces, then thoroughly washed and dried at 60 ˚C for 15 h. Dried rice straw was milled to pass through a 60 mesh aperture size screen.

Cellulose extraction

Rice straw powder was subjected to a series of chemical extraction and purification processes. Initially, to remove wax and oil, 10 g of rice straw powder was extracted with 2:1, v/v toluene/ethanol mixture (450 mL) at 400 ˚C for 15 h in a Soxhlet apparatus. Then lignin was removed from dewaxed rice straw powder in 3:10, v/v H_2O_2/CH_3COOH solution at 70 ˚C for 3 h in a thermostatically controlled water bath using H_2SO_4 as the catalyst. Finally, the de-lignified rice straw powder was leached with 110 mL of 5% KOH for 24 h at room temperature then for 2 h at 90 ˚C. After the series of chemical treatments, the samples were vacuum filtered and washed with copious amount of water, purified using Barnstead™ Smart2Pure™ Water Purification System (Thermo Fisher Scientific, Waltham, MA) until filtrate reached neutral p^H. Finally, oven dried, chemically purified cellulose was collected and stored in desiccators for investigation and characterization (Samarasekara *et al.,* 2015; Nanayakkara *et al.,* 2017a; Nanayakkara *et al.,* 2017b). Three replications were carried out for each compositional analysis, and the average is reported here.

Measurements and Characterization

Structural, morphological and thermal properties of rice straw and cellulose fibres were studied. FTIR spectra were used to examine the structure of cellulose fibres which were extracted from rice straw after a series of chemical treatments. A Bruker ALPHA spectrometer (Bruker Corporation, Billerica, MA) was used to characterize the spectra of each sample. The untreated and treated rice straw was mixed with KBr powder (1:100, w/w), and the mixture was compressed into plates for FTIR analysis. FTIR spectra of samples were obtained in the range of 4000 - 600 cm^{-1} in transmittance mode. To achieve the acceptable signal to noise ratio, 24 scans were co-added while the spectra resolution was maintained at 4 cm^{-1}. Structural analysis of the samples was carried out using BRUKER D8 ADVANCE ECO X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å) at 40 kV and 25 mA. Samples were scanned and recorded the intensity in 2θ ranged from 5˚ to 40˚ (step size = 0.02˚, scanning rate = 2 seconds/step). Data refinement and phase analysis were carried out using ICDD database. Scanning electron microscopy analysis (SEM) (EVO 18, Carl Zeiss AG, Germany) was performed to determine the structural changes, morphological structure and surface characteristics of the samples. Gold sputter coated samples were examined with an accelerating voltage of 15 kV. Thermal stability of each sample was determined using TGA SDT Q600 simultaneous thermal analyzer (TA instruments, Delaware, USA). Experiments were performed with a heating rate of 10

˚C/min from ambient temperature to 800 ˚C on rice straw and cellulose under nitrogen environment.

RESULTS AND DISCUSSION

Chemical composition

After the series of chemical treatments rice straw variety *BG352* yielded 25.35 ± 0.91 percent cellulose and *Murunkan* yielded 33.68 ± 0.68 percent cellulose. Figure 2 depicts the amount of cellulose, hemicellulose, lignin, wax and ash present in rice straw varieties *BG352* and *Murunkan*. The results show that amount of cellulose fibres present in both the rice straw varieties ranges between 25 - 34 % which is similar to the previously reported studies (Chen *et al.*, 2011; Nuruddin *et al.*, 2011; Boufi, 2017). However, the observed difference may be due to the difference in rice varieties and soil condition in different locations.

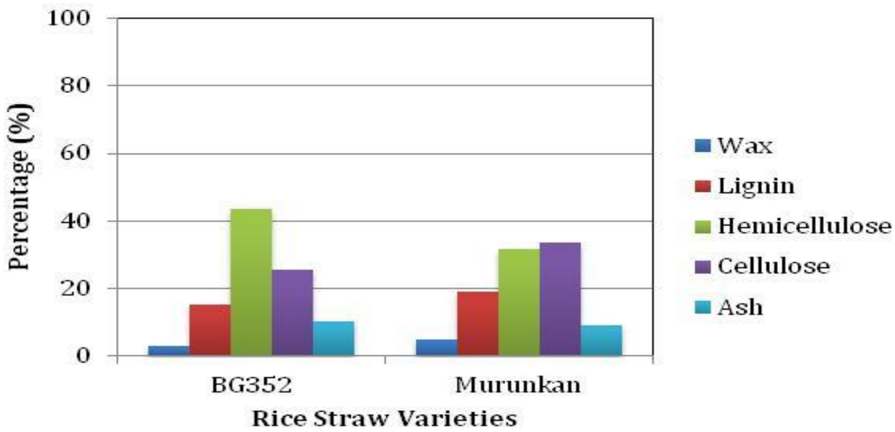

Figure 2. Chemical composition of rice straw varieties *BG352* and *Murunkan.*

Characterization of Untreated and Treated Rice Straw

Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectrum of rice straw during the extraction process is shown in Figure 3. After the successful extraction from chemical treatments, the end-product was confirmed as cellulose.

The sequential and complete removal of lignin (1516 cm^{-1}, aromatic skeletal vibrations) in de-lignification and leaching of hemicellulose (1729 cm^{-1}, carbonyl stretching) and silica (796 cm^{-1}, Si-O-Si stretching) in the third step can also be clearly observed. The dominant peaks between 1200 and 900 cm^{-1} are related to C—O stretching bonds. Enhanced peak intensity around 960 cm^{-1} after chemical treatment implies that a typical structure of cellulose became more dominant compared to the raw materials (Lim *et al.,* 2010).

Figure 4 shows the FTIR spectrum of cellulose fibres extracted from BG352 and Murunkan rice straw varieties. In Figure 4, a strong broad band can be observed in the region of 3700 - 3000 cm^{-1} which is assigned to different -OH stretching modes and another band in the region of 3000-2800 cm^{-1} is ascribed to the stretching of asymmetric and symmetric methyl and methylene cellulose groups (Kargbo *et al.,* 2010). The band at around 3445 cm^{-1} related to -OH stretching mode is prominent for *BG352* than for *Murunkan*. This probably due to a large number of hydroxyl groups in *BG352* which may be associated with an increase in the number of hydrogen bonds formed.

X-Ray Diffraction (XRD) Analysis

XRD analysis was performed on the untreated and treated rice straw and cellulose fibres to investigate the effect of chemical treatments on the crystalline structure of fibres.

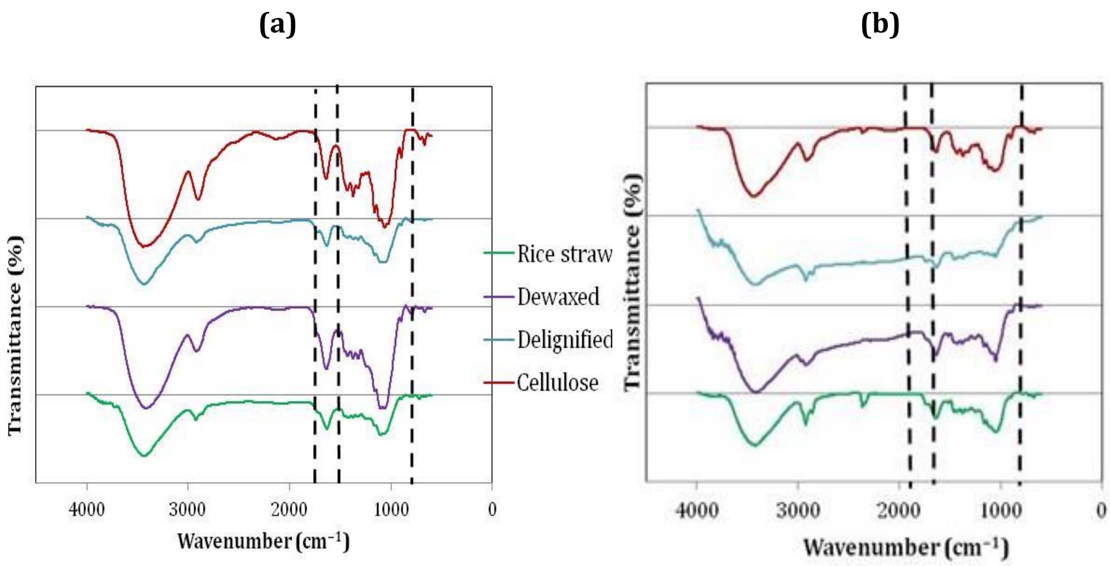

Figure 3. FTIR spectra of rice straw (a) *BG352* (b) *Murunkan* during chemical extraction process

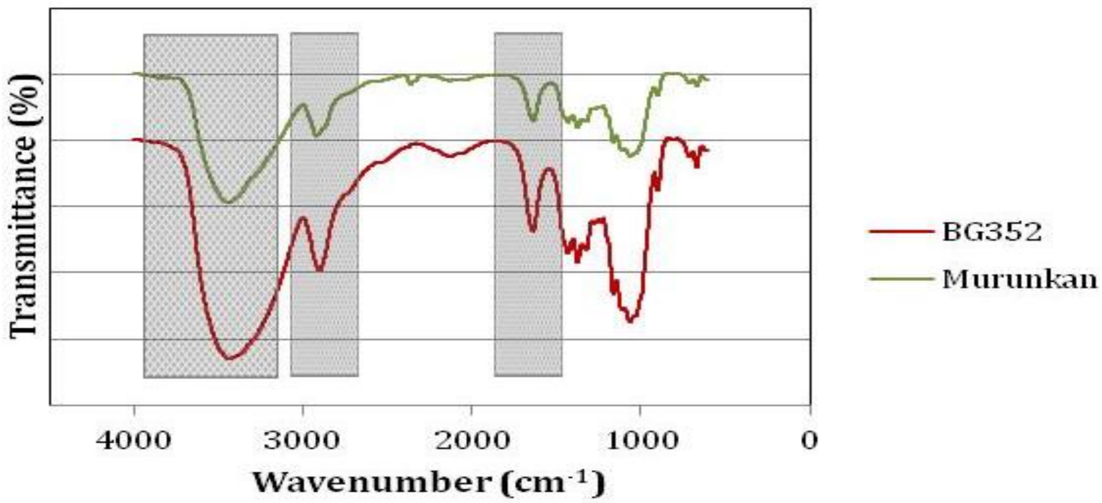

Figure 4. FTIR spectra of cellulose fibres extracted from *BG352* and *Murunkan*

The peak around 22.2° attribute to the typical crystal lattice of I_β which indicates that both rice straw and cellulose exhibit the diffuse characteristics pattern of an amorphous phase. Shoulder peak at 16.4° and weak peak at 34.7° in Figure 5 indicates the removal of lignin and hemicellulose from rice straw (Raj *et al.,* 2015; Taylor *et al.,* 2015.; Zheng *et al.,* 2017; Morone *et al.,* 2018).

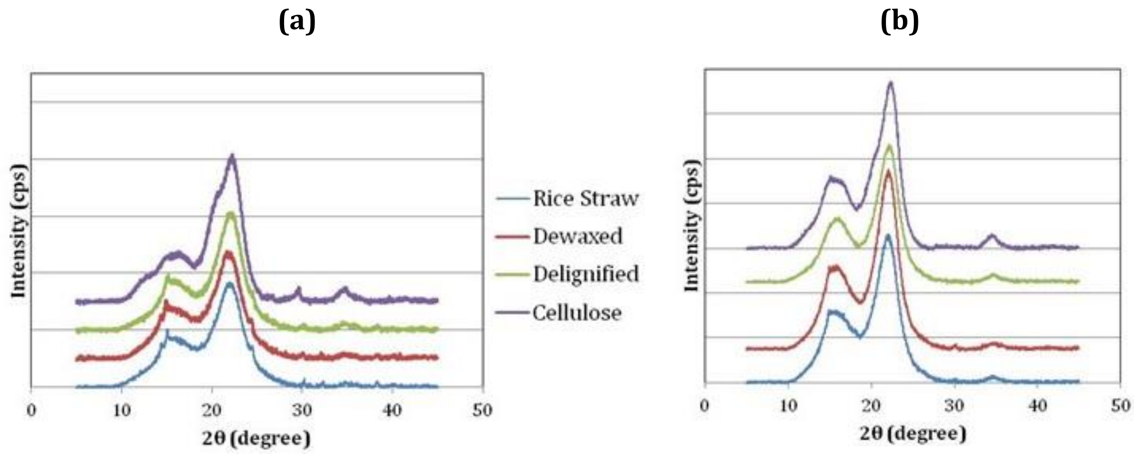

Figure 5. X-ray diffraction patterns of rice straw (a) *BG352* (b) *Murunkan* during chemical extraction process

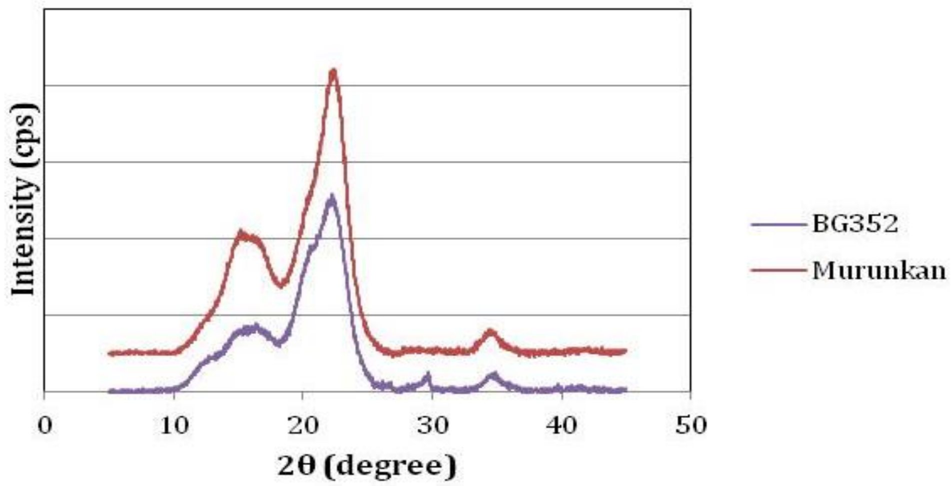

Figure 6. X-ray diffraction pattern of cellulose fibres extracted from BG352 and Murunkan

The series of chemical treatments on rice straw has a great effect on the crystallization of the cellulosic fibres. The sharper diffraction peak around 22.2˚ observed in Figure 6 indicates higher degree of crystallinity in the extracted cellulose fibres. *Murunkan* exhibits sharper peak than *BG352*. Higher crystallinity observed in the cellulose fibres is associated with higher tensile strength of the fibres.

Scanning Electron Microscopy (SEM) Analysis

Figure 7 and 8 presents the wide-angle SEM micrographs of the untreated and treated rice straw fibres of *BG352* and *Murunkan* respectively.

After the removal of lignin, the shape of the phytoliths was revealed. Some of them seemed to be dumbbell shape (Figure. 7(c) and 8(c)). Apparently, the shape of phytoliths is not homogeneous within the delignified sample (some appear as a cross shape).

The morphologies of untreated and treated rice straw are observed as greatly different. For untreated rice straw, some parts of dense lignin, hemicelluloses, and ashes surround fibres. However, the surface of treated fibres looks smoother, which is attributed to the removal of amorphous lignin and hemicelluloses therein. The surface morphology of both the rice straw varieties were significantly varied during the processing. However, both rice straw varieties (Figure 7 and 8) presents the same type of morphological structures.

Thermogravimetric Analysis (TGA)

The thermal degradation of cellulose is known to be due to a pyrolytic fragmentation that leads to aromatized entities and finally to a highly cross linked carbon skeleton (Nanayakkara *et al.,* 2018; Samarasekara *et al.,* 2018). Figure 9 shows the thermal degradation behaviour of both the rice straw varieties during the extraction process.

(a) (b)

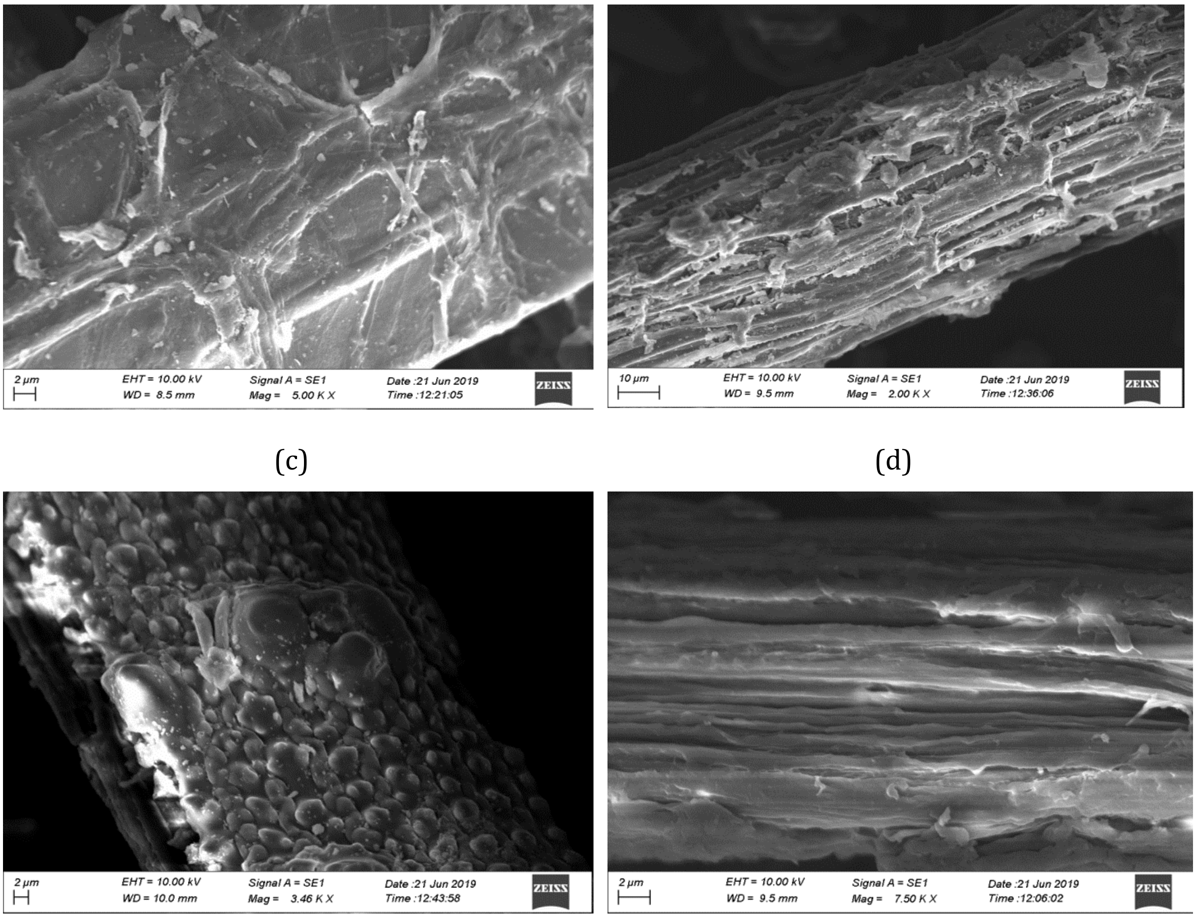

Figure 7. Wide angle SEM micrographs of (a) cleaned, (b) dewaxed, (c) delignified and (d) cellulose fibres derived from rice straw variety *BG352*

Around 100 °C, a small weight loss is observed. This may be due to the low molecular weight components in the fibres and the evaporation of remained humidity. Another main event in TG curves attributed to hemicelluloses which occurred around 260 °C and cellulose pyrolysis, which occurred around 310 °C.

Figure 10 shows the thermal degradation behaviour of cellulose fibres extracted from both the rice straw varieties. The resistant increase in cellulose observed is due to the removal of almost all hemicelluloses from rice straw. Further, a significant difference between the contents of the residues remaining after pyrolysis is also observed which indicates that the thermal stability of cellulose is visibly improved. Cellulose fibres extracted from both the rice straw varieties showed similar thermal degradation behaviour.

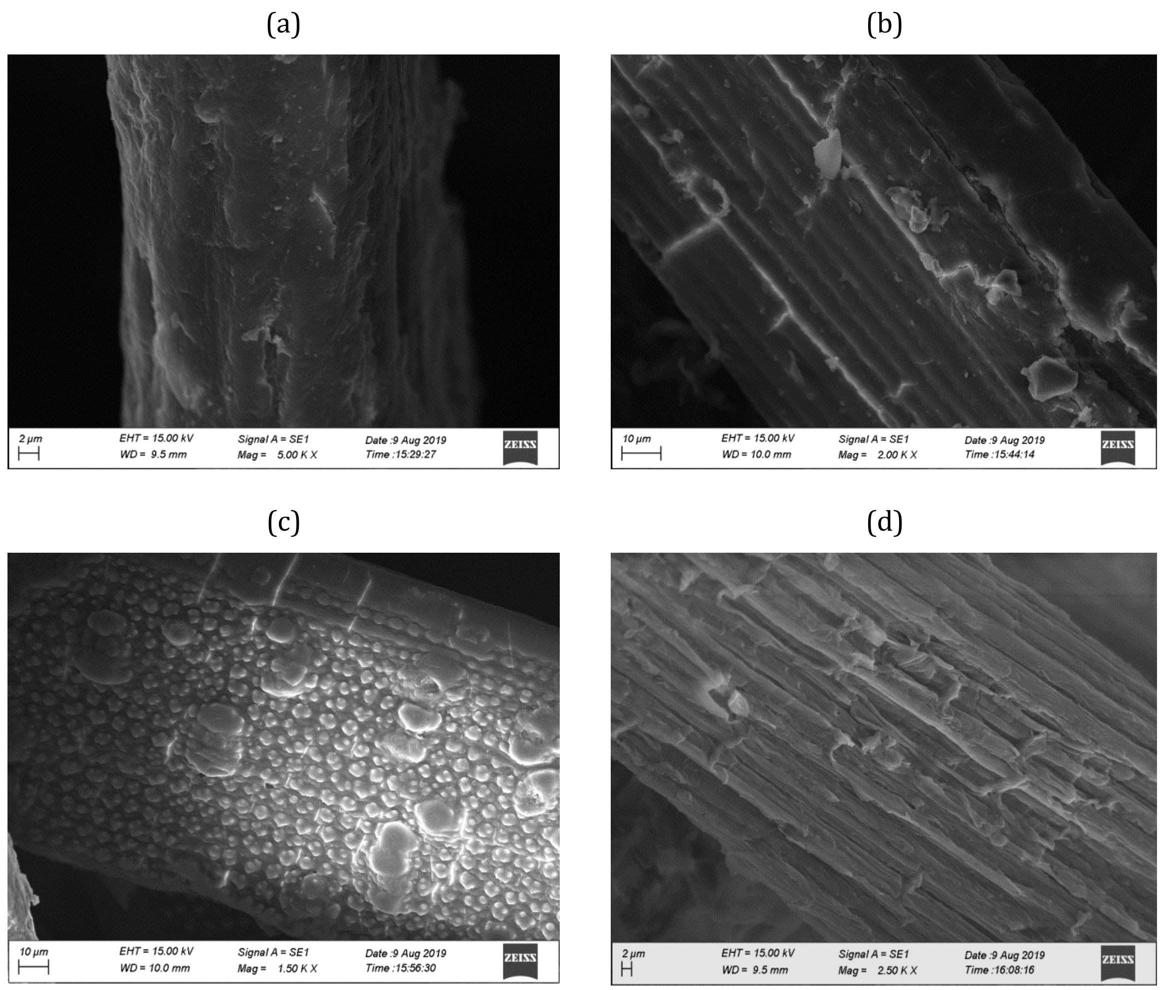

Figure 8. Wide angle SEM micrographs of (a) cleaned, (b) dewaxed, (c) delignified and (d) cellulose fibres derived from rice straw variety *Murunkan*

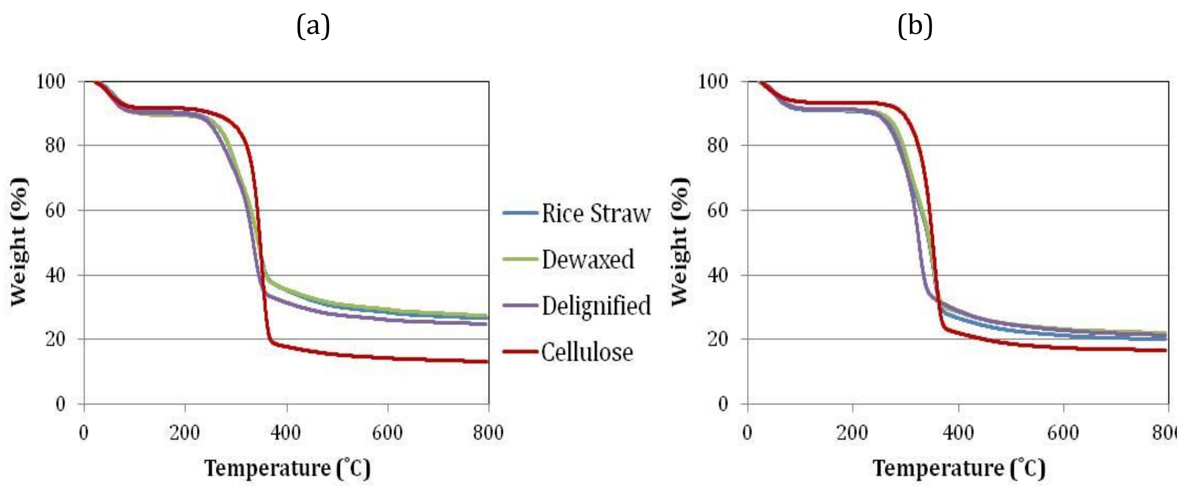

Figure 9. TG curves of rice straw (a) *BG352* (b) *Murunkan* during chemical extraction process

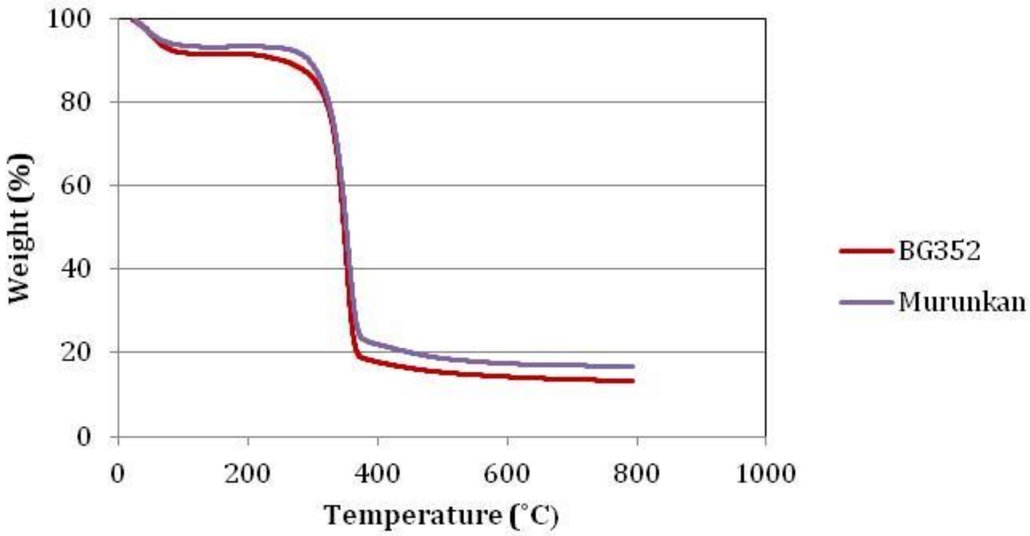

Figure 10. TG curves of cellulose fibres extracted from *BG352* and *Murunkan*

CONCLUSIONS

Cellulose fibres were successfully extracted *via* a three-step chemical extraction process from locally available technically modified rice straw variety *BG352* and traditional rice straw variety *Murunkan.* FTIR analysis of rice straw, the images obtained through scanning electron microscope (SEM), and X-ray diffraction (XRD) analysis showed the progressive removal of lignin, hemicellulose and silica during the chemical treatments and confirms the final product as cellulose. The study reveals that higher amount of cellulose fibres were extracted from *Murunkan (*33.68 ± 0.68 percent) than *BG352* (25.35 ± 0.91 percent). Thermal analysis demonstrated that the thermal properties of the chemically extracted cellulose fibres were enhanced. However, cellulose fibres extracted from both the rice straw varieties exhibited similar thermal degradation behaviour. It can be concluded that the extracted cellulose fibres from both the rice straw varieties illustrate better thermal, structural and chemical properties which can be employed in various industrial applications.

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