Characterisation and Comparison of Pith and Cortex of Napier Grass Stem

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Abstract. In the previous study, only pith part had been attracted to be investigated by researcher eventhough cortex had a high percentage content in the Napier grass stems (NG). Hence, further studied can help to achieve the aim of maximizing the use of NG stems by using cortex and pith in manufacturing biopolymers. For this purpose, the thermal, chemical, morphological characterization of cortex and pith of NG stems had been explore. The results of TGA, FTIR, microscope, and SEM had shown the difference in the cortex and pith of NG stems. Although their peak absorption value appear to be different, the group involved in pith still present in the cortex. The cortex showed a high decomposed percentage which was 93.79 % compared to the pith with 92.55 %. The micrographs images display the presence of hemicellulose, lignin, impurities, and wax on the surface of cortex and pith. Overall, the results of the cortex showed that it had the potential to be used the same as the pith for the production of biopolymers in the future.

1. Introduction

The increasing concern on environmental awareness has risen the interest in using natural fibres as an alternative reinforcement material for biopolymer production. The use of natural fibres is of great benefit as it is environmentally friendly, stable, sustainable, biodegradable, renewable and excellent mechanical properties [1]. Nevertheless, most of natural fibres are costly and in short supply due to scarcity of natural resources such as woods and cotton and require long growth cycle. Therefore, these have led to another further recent in recent years to discover the plant fibre from the fruit waste such as pineapple [2], oil palm [3] and durian rind [1]. Other than that, Napier grass stems (NG) also one of a good choice as it is classified in second generation source of renewable energy [4]. Hence, plant fibre has been considered as an excellent alternative feedstock [4]. The large amounts of Napier grass production in each year was sufficient to support the production of an annual dry matter per year [4]. The Napier grass stems is divided into two main part which are cortex and pith. the bark of napier grass which also known as cortex represents 84% of Napier grass dry weight. While the remaining pith which is inner part contributes 16% of Napier stems dry weight [5]. However, only pith part had been attracted to be investigated by researcher even though cortex had a high percentage content in the Napier grass stems [6, 7].

In previous papers, Pérez-boada et al. illustrate the utilize of Ultraflo in isolated hydrolysis of the pith and cortex components of the NG stem [4]. Prinsen et al. have carried out a thorough analytical study for the lipophilic fraction composition of the cortex and pith of NG stems [8]. Therefore, no previous studies have been published for characterization of the thermal, chemical composition and morphological of cortex and pith of NG stems. In this paper, the thermal, chemical composition, and morphological characterization of the cortex and pith of Napier grass stems were reported. To the best of our understanding, this is the first time characterization of the thermal, chemical composition and morphological of cortex and pith of NG stems had been done. This can contributed for maximizing the use of NG stems in manufacturing application. Therefore, this study should provide the research community with new information. In addition, the cortex and pith of Napier grass stems were subjected using
thermo-gravimetric analysis (TGA), Fourier transforms infrared spectroscopy (FTIR), microscope and scanning electron microscope (SEM).

2. Methodology

2.1 Material Preparation
The Napier grass stems (NG) was acquired from local farm in northern peninsular Malaysia near Bukit Kayu Hitam, Kedah, Malaysia. The leaves were then cleared out from the stems. Then, the NG stem was washed several times before it was crushed. Next, the NG stem was cut 4-6 cm and submerged in water for 2 months. The soaked NG stems were washed several times. After that, the total weight of each NG stems was measured and the ratio of the cortex to pith of PP stem was 21:4 [5]. The cortex and pith of NG stem were shown in Figure 1. The separated process from the NG stems had been done. The separated cortex and pith of NG stem were dried under the sun for 2 days. To prepare the separated cortex and pith of NG stem into powder form, the dried cortex and pith of NG stem were grounded and sieved.

![Figure 1. The cortex and pith of NG stem.](image1.png)

2.2 Sample Characterization
The thermal stability behaviour for the cortex and pith of NG stem had been evaluated with the aid of TGA device. To ensure constant temperature, 6–8 mg of the cortex and pith of NG stem powder were weight and put in an alumina crucible. Then, the flow rate of flowing nitrogen (N₂) atmosphere, heating rate and temperature range of cortex and pith of NG stem were set as 10 mL/min, 10 °C /min and 37-600 °C, respectively. The FTIR spectroscopy were conducted in 32 scans per sample and 4 cm⁻¹ spectral resolution. The low digital microscope had been used to evaluate the surface and the diameter size of the samples using magnification of 25× and 45×. The surface morphologies of the cortex and pith of NG stem were examined using SEM. The scanning images were obtained by using an acceleration voltage of 5 kV and magnification of 50×. Prior to coating the samples with the platinum, the samples were mounted on an aluminium stub.

3. Results and Discussion

3.1 Thermo-gravimetric analysis (TGA)
The thermo-gravimetric analysis (TGA) curves for the cortex and pith of NG stem were presented in Figure 2. The TGA curves illustrated a decrease in the moisture content following the burning of the cortex and pith of NG stem. The thermo-gravimetric analysis (TGA) for the cortex and pith of NG stem were shown in Table 1.
Table 1. Thermo-gravimetric analysis (TGA) for the cortex and pith of NG stem

| Materials | Degradation of weight loss (%) | Finale residue (%) |
|-----------|---------------------------------|-------------------|
| Cortex    | 1.58 12.27 1.48 4.73           | 6.21              |
| Pith      | 1.54 11.07 1.35 6.1            | 7.45              |

Figure 2. TGA curves for the cortex and pith of NG stem.

Figure 2 shows the weight change for TGA curves of the cortex and pith of NG stem. Prior to low temperature less than 138 °C, small initial weight loss can be observed. This has been corresponding to the loose of moisture bounding for all the samples [9]. Based on Table 1, it shows the degradation of weight loss for moisture content, hemicellulose, cellulose, and lignin. The degradation of weight loss for the cortex and pith of NG stems were approximately 1.58 and 1.54 %, respectively which attributed to decomposition of moisture content. The physical properties and dimensions of material fibre can be influenced by the moisture content of material fibre [10]. Therefore, low moisture content is more preferable as the filler in polymers due to its low tendency to hold the water molecules [11]. In addition, it can also be observed that the degradation of weight loss for cortex and pith of NG stems were approximately 12.27 and 11.07 %, respectively which attributed to decomposition of hemicellulose, cellulose, and lignin. This indicates that the cortex had decomposed high percentages of cellulose, hemicellulose and lignin compare to pith of NG stems. The percentage of the residue remaining were 6.21 and 7.45 % for the cortex and pith of NG stems, respectively. This indicates that the cortex and pith of NG stems had decomposed by approximately 93.79 and 92.55 %, respectively.

Overall, the thermal properties of the reinforcing bio-renewable composite material are important to their proposed use in industrial [12]. The results shows that high percentages of degradation for cortex compare to the pith. Therefore, thermal properties studies can determine either it is desirable for the sample as reinforcing material in bio-renewable composite material.

3.2 Fourier transforms infrared spectroscopy (FTIR)

The FTIR spectra of the cortex and pith of NG stem were presented in Figure 3. The FTIR studies was performed to identify the functional group of spectra bands that existed. The main peaks for each sample are concluded in Table 2.
Table 2. Peak absorption of samples at different stages for the cortex and pith.

| Band position (cm⁻¹) | Pith          | Cortex         | Involved group                                                                 |
|----------------------|---------------|----------------|--------------------------------------------------------------------------------|
| 3329, 3273           | 3331, 3282    | O-H vibration of inter and intramolecular H-bonds [13] |
| 2891                 | 2898          | C-H groups vibration of aliphatic saturated C=H [14] |
| 1636                 | 1642          | water absorption, stretching O-H groups [15]          |
| 1316                 | 1319          | CH₂ wagging vibration [1]                             |
| 1162                 | 1162          | C₃ carbon vibrations, C-O antisymmetric bridge stretching of cellulose [16] |
| 1099                 | 1114          | C₃ carbon vibrations, anti-symmetric bridge stretching of C-O-C groups [1]       |
| 1052, 996            | 1057, 1015    | C-O-C pyranose ring skeletal vibration of cellulose [14] |
| 905                  | 902           | C-H rocking cellulose vibrations [14]                  |

Figure 3 shows the spectra of the cortex of NG stem are bands at approximately 3329, 3273, 2891, 1636, 1316, 1162, 1099, 1052, 996 and 905 cm⁻¹ within its spectra. While the spectra of the pith of NG stem shows the bands at 3331, 3282, 2898, 1642, 1319, 1162, 1114, 1057, 1015 and 902 cm⁻¹ within its spectra. From Figure 3, although the drying process was carried out prior to the FTIR analysis, the samples could not ensure completely dried as cellulose water interactions were still present in the cortex and pith of NG stems [14]. This also due to there are three main constituents in any plant which is cellulose, hemicellulose and lignin. The highest percentage among them are cellulose and continues with hemicellulose and lignin [2]. Other than that, the peaks were present in the cortex shows more prominent compare to the pith. It had been showed that the cortex had peak at high intensity than the pith of NG stem [1]. Therefore, the FTIR studies proved that there are different composition in the cortex and pith. However, this showed that the group involved in the pith also presence in the cortex but at different peak absorption values. Hence, further studied can help to achieve the aim for maximizing the use of NG stems by used cortex and pith in manufacturing biopolymers.

Figure 3. FTIR for the cortex and pith of NG stem.

3.3 Low digital of microscope
It is seen that the biological composition of the cortex and pith of NG stem difference remarkably as shown in Figure 4. In other words, the size of diameter of the cortex and pith of NG stem difference remarkably. In general, the diameter size of the pith was larger than the cortex of NG stems. Usually, the size of the added filler was an essential factor which affecting the strength, durability, and stability
of biocomposite materials [17]. This is because Zaini et al. stated the results of the combination between larger sized of oil palm wood flour filled composites and polypropylene causes a higher modulus and tensile strength [18]. The microscopic examination on six random section for diameter size of sample were taken in the images. This showed that the pith of NG stem had larger average diameter size with 170.06 μm compared to the cortex of NG stems with 163.105 μm. Other than that, the diameter distributed of the pith were evenly consistent compared to the cortex of NG stems.

![Figure 4](image)

**Figure 4.** Low digital microscope of the cortex and pith of NG stems.

Therefore, the filler size can be contributed to the positive impact in the production of biopolymer.

### 3.4 Scanning electron microscope (SEM)

The scanning electron microscope (SEM) micrographs of surface morphology for the cortex and pith of NG stem were shown in Figure 5. It was important to study the differences of surface morphology for the cortex and pith of NG stems. These micrographs showed that the surface were covered with a lot of impurities and wax due to the white layer in the images [19]. It also can be observed the presence of hemicellulose and lignin on the surface [9].

![Figure 5](image)

**Figure 5.** SEM for (a) the cortex of NG stem and (b) the pith of NG stem.

The rougher surface of the cortex and pith can be seen clearly as shown in Figure 5. The cortex showed distribution of long and short length samples were balanced through 50x magnification compared to the pith of NG stems. While the pith showed distribution of long more than short length samples. Usually, a good interfacial bonding among the filler and matrix was expected in reinforced materials of the composite. Therefore, a rough surface was required in this good interfacial bonding.
[19]. However, this needs to be ensured that it was not more than preferred roughness surface. This can caused the decreases in the tensile strength of the composites [19].

Further research using sodium hydroxide could lead to different result of FTIR, TGA and smoother the surface morphology for the cortex and pith [10]. This is because, the alkali treatment process can remove the lignin and hemicellulose indirectly smoother the surface [3]. Therefore, this result had agreed with results of FTIR, TGA, and XRD due to the present of wax, impurities, lignin and hemicellulose.

4. Conclusions
The thermal, chemical composition and morphology of the cortex and pith of NG stems were analysed. There were different compositions in the cortex and pith of NG stem. The result also shows that the group involved in the pith also presence in the cortex but at different peak absorption values. The residue remaining for the cortex was 6.21% which shows it had decomposed 93.79 % of moisture content, cellulose, hemicellulose, and lignin. The results had agreed with FTIR, TGA, and microscope results due to the presence of wax, impurities, lignin and hemicellulose on the surface as shown in the micrographs images. Overall, further studied in the cortex and pith of NG stems can help to achieve the aim of maximizing the use of NG stems in manufacturing biopolymers.

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References
[1] Penjumras P, Rahman R B A, Talib R A and Abdan K 2014 Agric. Agric. Sci. Procedia. 2 237
[2] Mansor A M, Shiu Lim J, Ani F N, Hashim H and Shin Ho W 2019 Chem. Eng. Trans. 72, 79
[3] Rasila S, Rasli A M, Ahmad I, Lazim A M and Hamzah A 2017 Malaysian J. Anal. Sci. 21 1065
[4] Pérez-boada M, Prieto A, Prinsen P, Forquin-gomez M, Carlos J, Gutiérrez A, Martinez A T and Faulds C B 2014 Bioresour. Technol. 167 469–475
[5] Del Río J C, Prinsen P, Rencoret J, Nieto L, Jiménez-Barbero J, Raphael J, Martinez A T and Gutiérrez A 2012 Stems. J. Agric. Food Chem. 60 3619–34
[6] Revati R, Abdul Majid M S, Ridzuan M J M, Normahira M, Mohd Nasir N F, Rahman Y M N and Gibson A G 2017 Mater. Sci. Eng. C 75 752–759
[7] Indira Devi M P, Nallamuthu N, Rajini N, Varada Rajulu A, Hari Ram N, and Siengchin S 2018 Int. J. Biol. Macromol. 118 99–106
[8] Prinsen P, Gutiérrez A and del Río J C 2012 Stems. J. Agric. Food Chem. 60 6408–17
[9] Yue Y, Han J, Han G, Aita G M and Wu Q 2015 Crops Prod. 76 355–363
[10] Ridzuan M J M, Abdul Majid M S, Khasri A, Basaruddin K S and Gibson A G 2019 Compos. Part B Eng. 160 84–93
[11] Murali Mohan Rao K, Mohana Rao K and Ratna Prasad A V 2010 Mater. Des. 31 508–513
[12] Reddy K A, Maheswari C U, Dhammini M S, Mothudi B M, Kommula V P, Zhang J, Zhang J and Rajulu A V 2018 Carbohydr. Polym. 188 85–91
[13] Ilyas R A, Sapuan S M and Ishak M R 2018 Carbohydr. Polym. 181 1038–51
[14] Xiang L Y, P Mohammed M A and Samsu Baharuddin A 2016 Carbohydr. Polym. 148 11–20
[15] Choi M, Kang Y R, Lim I S and Chang Y H 2018 J. Exp. Nutr. Food Sci. 23 166–170
[16] Juliana Spiridon, Teaca C A and Bodirlău R 2011 BioResources. 6 400–413
[17] Španić N, Jambreković V, Šernek M and Medved S 2019 Int. J. Polym. Sci. 17
[18] Zaini M J, Fuad M Y A, Ismail Z, Mansor M S and Mustafah J 1996 Polym. Int. 40 51–55
[19] Ridzuan M J M, Abdul Majid M S, Afendi M, Aqmariah Kanafiah S N, Zahri J M and Gibson A G 2016 Mater. Des. 89 839–847