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Modification of Bioplastic from Napier Grass (*Pennisetum purpureum*) Cellulose with Various Plasticiser

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ABSTRACT: *Pennisetum purpureum*, or Napier grass, is a perennial monocot C4 grass belonging to the Poaceae family. Napier grasses have the potential to serve as feedstock to produce bioplastics. Cellulose was extracted from Napier grass using dimethyl sulfoxide (DMSO). The dark solution obtained after dissolution indicated the presence of lignin in Napier grass, while the extracted green residue represented the cellulose content. The extracted cellulose from Napier grass was incorporated into various bioplastic samples with varying compositions, mixed with plasticizers. Gelatin and starch were also added to the extracted cellulose from Napier grass for comparison in bioplastic production. The characterization of the bioplastics involved Fourier Transform Infrared (FTIR) Spectroscopy, tensile strength testing, and assessment of biodegradable properties. The FTIR spectra revealed intermolecular interactions in the bioplastics involving C-O-H, O-H, C-H aliphatic, and C=O groups. Tensile tests were conducted on bioplastics made from both gelatin and starch, highlighting properties such as elongation at break, stress at break, and peak strength. The bioplastic made from gelatin exhibited significantly greater elongation at break compared to the starch-based bioplastics in this experiment.

Keywords: Napier grass; starch; gelatin; dimethyl sulfoxide; bioplastic

1. Introduction

Plastics play a crucial role in various aspects of human life, and their widespread use is deeply ingrained in daily routines. Replacing plastics with alternative materials poses a challenge due to their integral role in human lifestyles. Improper disposal of plastic materials can lead to soil nutrient depletion, adversely affecting soil fertility and impacting agricultural sectors [1]. Additionally, the accumulation of plastics in the environment poses health risks to humans, causing immune and enzyme disorders, hormonal disruptions, infertility, and potentially leading to carcinogenic diseases such as cancer [2].

The adverse effects of continuous plastic use extend beyond human health, impacting other living organisms and disrupting environmental sustainability. To address these concerns, environmentally friendly plastics can be categorized into three types: bioplastics, biodegradable plastics, and eco/recycled plastics. Bioplastics, derived from natural raw materials, and biodegradable plastics, designed to break down more rapidly, offer alternatives to conventional plastics. Eco/recycled plastics involve the recycling of plastic materials rather than relying on petrochemicals [3].

Efforts to replace plastics with alternative materials are underway due to the environmental problems associated with plastic use. This has led to a global increase in bioplastic production. Bioplastics, can be categorized into bio-based non-biodegradable plastics, bio-based and biodegradable plastics, and bio-degradable fossil resource plastics, play a vital role in conserving fossil resources and reducing carbon dioxide emissions, contributing to sustainable development [4-6].

According to European Bioplastics and the nova-Institute data, global bioplastics production capacity is expected to rise from 2.11 million tonnes in 2018 to approximately 2.62 million tonnes in 2023. Bioplastics are becoming integral to everyday life, finding applications in food services, packaging, agriculture, and various consumer goods. Despite the development of different biodegradable plastics, physical limitations persist [7].

Bioplastics derived from plant sources, such as Napier grass, are promoted as environmentally friendly alternatives. Napier grass, also known as elephant grass, is a perennial tropical forage with high cellulose content, making it a promising renewable resource for bioplastic production. The cellulose composition of Napier grass, ranging from 40-50%, and its biodegradability make it a subject of extensive research. Extracting cellulose from Napier grass, often using ionic liquids like Dimethyl Sulfoxide (DMSO), is a common method, breaking down lignin walls from raw material samples [7].

The benefits of using agricultural resources and biomass feedstock for bioplastics lie in their eco-efficiency and sustainability. With its high cellulose content and water resistance, Napier grass holds potential as

a bioplastic source. However, the use of appropriate plasticizers and careful consideration of properties such as biodegradability and tensile strength are essential before introducing these bioplastics to the market [8, 9].

The development of bioplastics from various renewable sources, including Napier grass, underscores the importance of environmentally conscious research. While Napier grass exhibits properties conducive to high-quality bioplastics, it is crucial to formulate them correctly using non-toxic materials like starch and gelatin to ensure they remain environmentally friendly.

2. Experimental

2.1 Materials

The Napier grass (*pennisetum purpurem*) was harvested from the Agro Park of Universiti Malaysia Kelantan, Jeli Campus which was used to produce bioplastics. Starch from cassava was used in making bioplastics. The formulation and composition of the bioplastics were made of gelatins to compare the features of bioplastics. The bioplastics from starch and gelatin were characterised and synthesized accordingly to the formulations.

2.1.1 Chemical and Reagent

The extraction of the cellulose from the Napier grass was done by using the ionic liquid called Dimethyl Sulfoxide (DMSO) from Sigma-Aldrich [14] and glycerol.

2.2 Methods

2.2.1 Collection of Napier grass

The fresh Napier grass was collected from Agro Park of University Malaysia Kelantan Jeli Campus. Napier's grass was harvested depending on its length and formed into clumps. About 1 kg of the grass was washed and dried in room temperature for a whole night.

2.2.2 Processing the Napier grass

The grasses were cut into 2.5 cm and dried in oven at 70°C for 5 hours. After that, the dried grasses were grounded into smaller sizes. The ball milling machine was used to make the dried grasses into powder form.

2.2.3 Extraction of cellulose from Napier grass

Dimethyl sulfoxide (DMSO) was used to extract cellulose from milled Napier grasses. 10 g of milled Napier grasses was mixed with 190 g of DMSO in a beaker. The mixture was mixed homogeneously on a hot plate at 50°C. The mixtures were stirred about 1 hour and 30 minutes. After the dissolution, vacuum pump was used to filtrate the cellulose-rich extract.

After the mixture was heated a few hours at 50°C, the colour of the mixture became darker, and the viscosity increased, indicating the dissolution of the milled Napier grasses. This process was followed by filtration which produced dark green colour of solution, indicating the Napier grass's lignin. The rate of dissolution of the Napier grasses increased at the temperature of 50°C. There were no changes in colour of the solution after few minutes of observation. The colour of the solution remained in dark green while, the light green colour of the residue on the filter paper was the extracted cellulose. The total cellulose extraction (%) can be calculated based on the mass extraction of Napier grass divided by the total mass of Napier grass sample after dissolution in DMSO (Equation 1).

$$\text{Total cellulose extraction (\%)} = \frac{\text{Mass of extraction}}{\text{Mass of sample}} \times 100 \% \quad (1)$$

2.3 Preparation of bioplastics

2.3.1 Starch-based bioplastic (bioplastics from starch)

The preparations of bioplastics were done using different amounts of the extracted cellulose and starch. Four samples were prepared using different amount of concentrations of starch and cellulose while an equal amount of glycerol added to each of the samples. Sample control of bioplastics was prepared without adding starch. The samples were prepared at 70 °C for 2 hours by using magnetic stirrer.

2.3.2 Gelatin-based bioplastics

Bioplastics was made by using gelatin as the substitute for starch. Three samples were made with different amounts of cellulose and gelatin while constant amount of glycerol was used to every samples. The samples were prepared at 70°C for 2 hours by using magnetic stirrer. **Table 1** shows different composition of bioplastic (g) prepared.

Table 1: The formulation of bioplastics of different samples

Sample	Composition of bioplastics (g)
S1	2 g starch, 2 g cellulose, 1 g glycerol
S2	1 g starch, 3 g cellulose, 1 g glycerol
S3	3 g starch, 1 g cellulose, 1 g glycerol
S4	4 g cellulose, 1 g glycerol
S5	1 g cellulose, 3 g gelatin, 1 g glycerol
S6	2 g cellulose, 2 g gelatin, 1 g glycerol
S7	3 g cellulose, 1 g gelatin, 1 g glycerol
S8	4 g cellulose, 1 g glycerol

2.3.4 Drying of bioplastics

The samples were left for drying under room temperature. Each sample were monitored daily to observe the condition of bioplastics. The bioplastics were left to dry for 14 days.

2.4 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The examination transmits infrared radiation ranging from 10,000 cm^{-1} to 100 cm^{-1} across the sample. Then, the absorbed radiation will convert into vibrational energy by the sample molecule. The detector or spectrum usually from 4000 cm^{-1} to 400 cm^{-1} will act as a resulting spectrum which showing the sample's molecular fingerprint.

2.5 Tensile testing

The tensile testing was performed on one of the sample from the bioplastic which was made from starch and another one from the bioplastic which was made from gelatine. The comparison on elongation at break (mm), stress at break (N/mm^2) and stress at peak (N/mm^2) was done for bioplastics made up of starch and gelatin.

2.6 Biodegradable testing

The biodegradable test was done to a sample from the bioplastic which was made from starch and another one from the bioplastic which was made from gelatine. Both types of bioplastics put in soil. The locations of planted bioplastics were labelled accordingly. After first five days of the biodegradable test, the bioplastics were weighed and recorded. Then, the observation was continued on the 10th day and 15th day of planting.

3. Results and Discussion

3.1 Dissolution of Napier grass in DMSO

The colour of the mixture became darker, and the viscosity was increased distinctively, which indicated the dissolution in the milled Napier grasses occurred. This process was followed by filtration which produced dark green colour of solution. This solution recommended the lignin of the Napier grass as shown in **Fig. 1** [14].

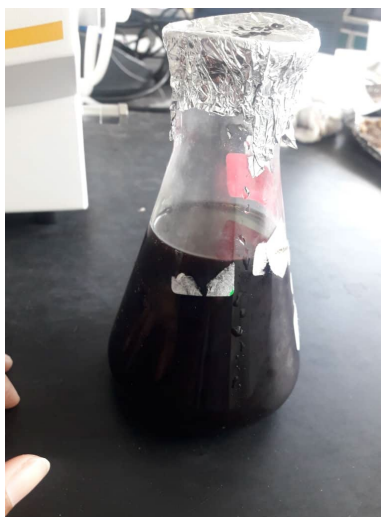


Figure 1: The filtrated lignin from the cellulose of Napier grass

The rate of dissolution of the Napier grasses increased at the temperature of 50 °C. This can be seen by the most milled Napier grasses started to disappear and the solution turned darker. There was no change in colour of the solution after few minutes of observation. The colour of the solution remained green.

The light green colour of residue on the filter paper was the cellulose-rich extract, as shown in **Fig. 2**. 12.5 g of cellulose of Napier grass was extracted from 50 g of total mass of the sample. The Napier grass exhibited a 25% extraction yield, indicating that the cellulose content was successfully extracted. This aligns with a prior study that reported a cellulose content of 25.208% in Napier grass [10].

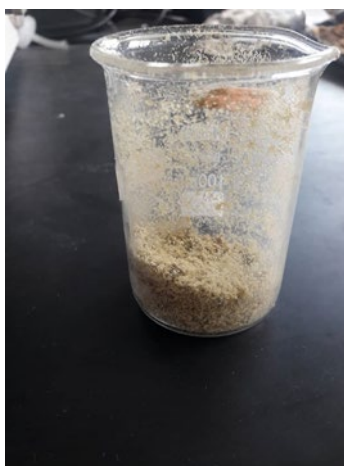


Figure 2: The extracted cellulose from Napier grass

3.2 Detection of cellulose content from the extracted samples of Napier Grass by using FTIR

The FTIR analysis was done to the extracted cellulose from the dissolved Napier grass with the DMSO solution. **Fig. 3** shows the reading of the wavelength of the particles of the extracted cellulose from the Napier grass.

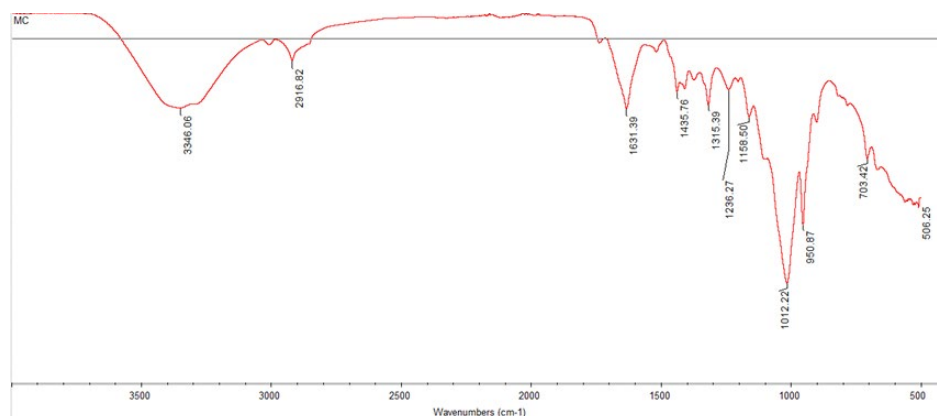


Figure 3: FTIR spectra of the extracted cellulose from the Napier grass

The FTIR analysis was implemented to the cellulose extract of the Napier grass from the reading of the wavelength of the peaks, there was a reading of peak at 3346.06 cm^{-1} , which indicated the stretching vibrations of O-H bonds of water molecules that absorbed by the sample. Then, the peak appeared at 1631.39 showed that the conjugation of the C=O with two aromatic rings. The broad peak was detected at the wavelength of 1012.22 cm^{-1} . This peak indicated the presence of C-O bonds of stretching vibration of primary alcohols. The peaks that were found in the analysis of FTIR for cellulose extract of Napier grass after the dissolution in DMSO proved that the lignin was removed because there was no broad peak which indicated the presence of lignin. There were no peaks around 1514 cm^{-1} which shows the presence of the aromatic skeletal vibration of C=C of lignin. A study of infrared spectroscopy of surface of thermally modified teak juvenile wood listed the wavelength for the cellulose, hemicellulose, and lignin. **Table 2** shows the summary of FTIR spectroscopy band assignments of unmodified and thermally modified teak heartwood and sapwood [11].

Table 2: The reading of FTIR spectroscopy [11].

Wavenumber (cm^{-1})	Band Assignment	Polymer
≈ 3470	O-H stretching	Polymers
$\approx 2900, \approx 2943$	CH- sp^3 stretching	Polymers
≈ 1725	C=O stretching of carbonyl, carboxyl and acetyl group and xylans	Oils, cellulose, hemicellulose
≈ 1640	Conjugation of C=O with two aromatic rings	Quinones
≈ 1514	Aromatic skeletal vibration (C=C) of lignin	Lignin
≈ 1474	C-H deformation in lignin and carbohydrates, CH_2 symmetric angular deformation	Lignin, oils and waxes
≈ 1342	C- H_2 deformation vibration, CH_3 symmetric deformation	Cellulose and hemicellulose, oils
≈ 1245	C-C, C-O and C=O stretching,	Lignin, oil
≈ 1175	C-O-C stretching, C-O stretching	Cellulose, hemicellulose, oil
≈ 1074	C-O stretching of secondary alcohol	Cellulose, hemicellulose, lignin
≈ 1000	C-O stretching of primary alcohol	Cellulose and hemicellulose

The FTIR analysis was also done to four different samples of starch-based bioplastics. The four different samples S1, S2, S3 and S4 consisted of the various compositions of starch and cellulose content in bioplastics. Fig. 4 shows the reading of peaks of wavelength.

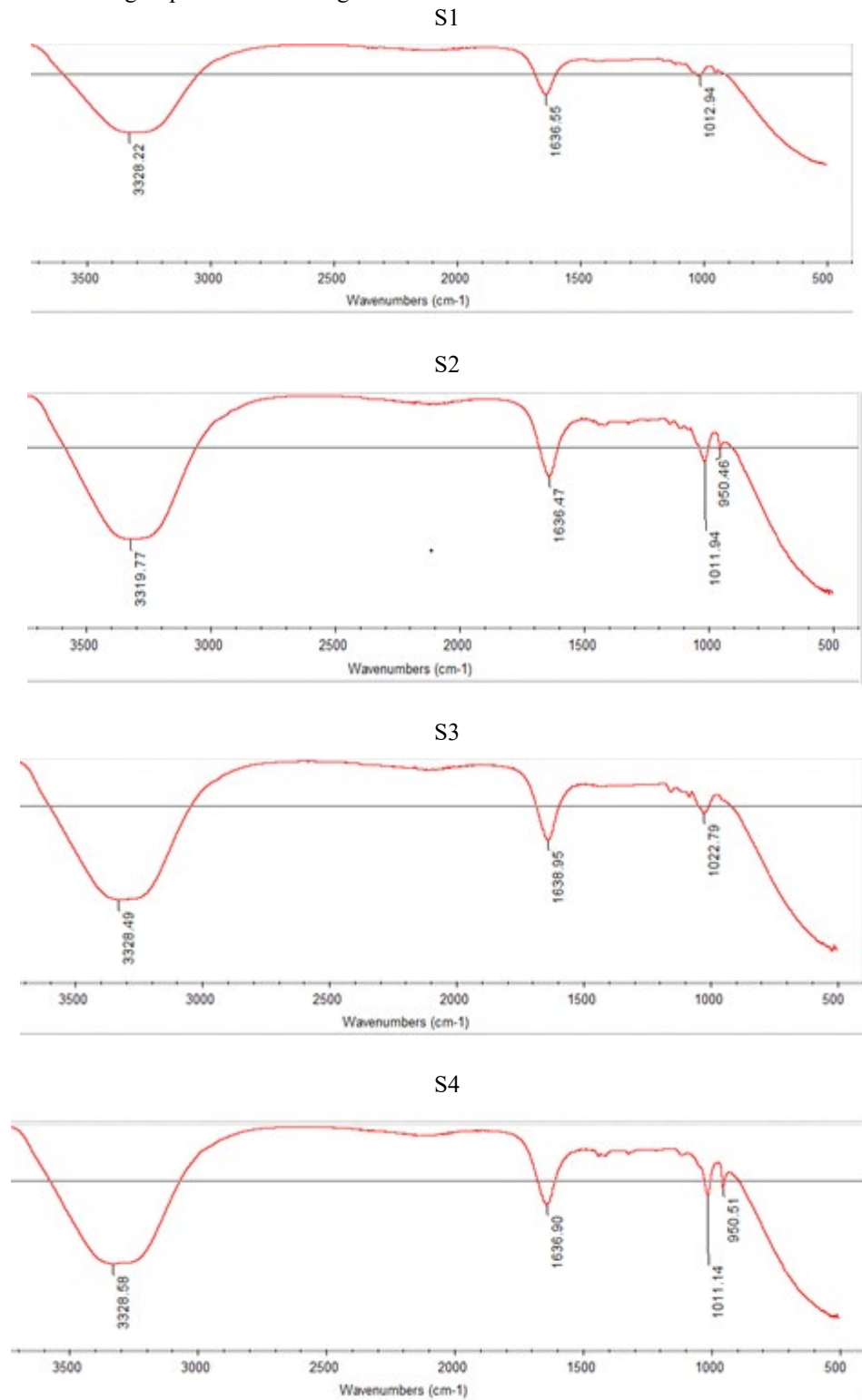
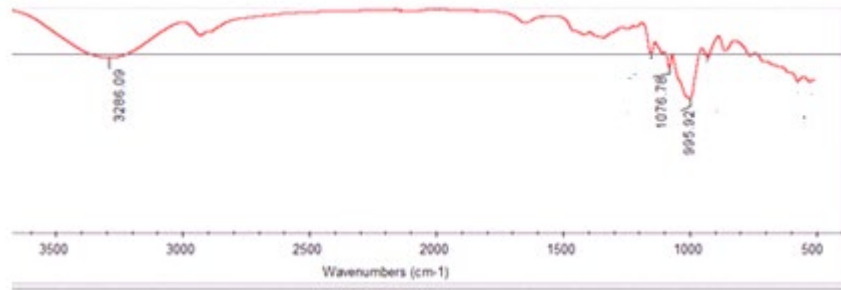


Figure 4: Reading of FTIR of four different type of samples S1, S2, S3 and S4

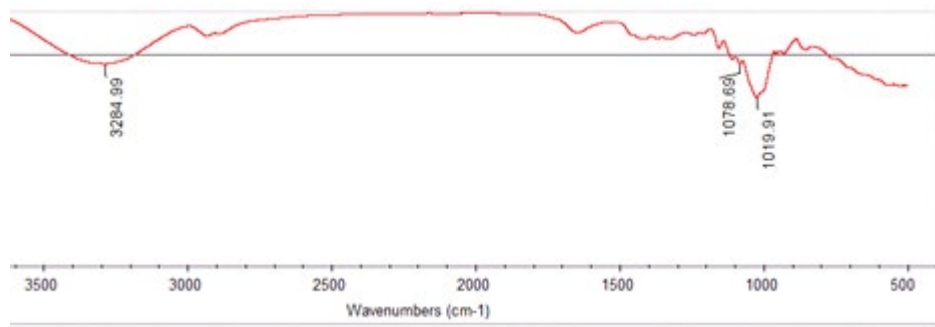
The bioplastic of sample S1, which consisted of 2g of starch, 2g of cellulose and 1g of glycerol showed the reading of the peak at 3328.22 cm⁻¹, 1636.55 cm⁻¹, and 1012.04 cm⁻¹. These peaks revealed that the bioplastic

consists of the functional group of O-H bond, C=C bond and C-O-H bond. The bioplastic of sample S3 which had the composition of 3g of starch, 1g of cellulose and 1g of glycerol showed the wavelength of 3328.49 cm^{-1} , 1638.95 cm^{-1} , and 1022.79 cm^{-1} . This sample recorded the same functional group as Sample S1.

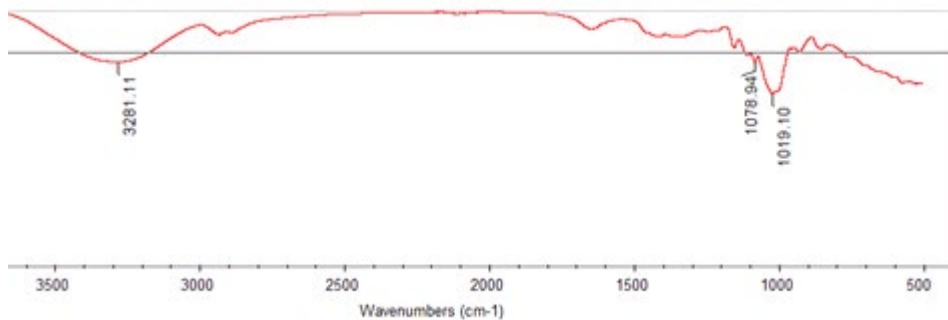
S5



S6



S7



S8

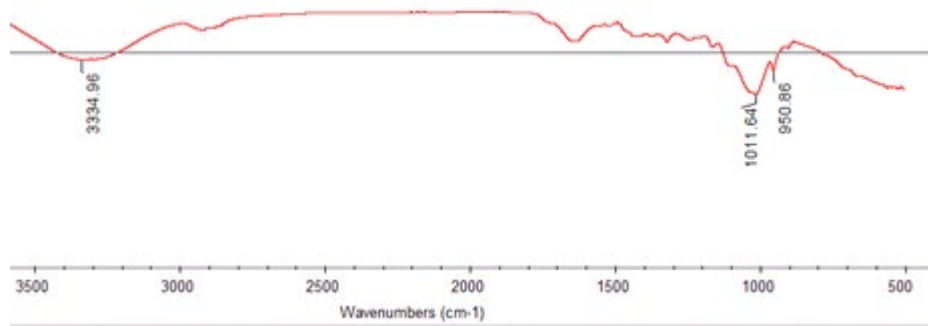


Figure 5: Reading of IR of four type of samples S5, S6, S7 and S8

Sample S2 which was made of 1 g of starch, 3 g of cellulose, and 1 g of glycerol shows the peak reading of 3319.77 cm^{-1} , 1636.47 cm^{-1} , 1011.94 cm^{-1} , and 950.46 cm^{-1} . This bioplastic also consisted of O-H bond, C=C and C-O-H. But the peak reading of 950.46 cm^{-1} was detected. This wavelength revealed the C-O stretching of primary alcohols and the presence of cellulose compounds. Sample S4 which was made up of 4 g of cellulose and 1 g of glycerol also showed the peak reading of C-O stretching of primary alcohols with wavelength of 950.51 cm^{-1} . Other reading of 3328.58 cm^{-1} , 1636.50 cm^{-1} , and 1011.14 cm^{-1} showed the presence of O-H bond, C=C and C-O-H. Both sample S2 and S4 recorded the high composition of cellulose, where the C-O bond detected clearly.

The FTIR reading also was observed to the bioplastics which were made from gelatin. **Fig. 5** shows the reading of the peaks of the FTIR analysis of bioplastics. The sample S5 which consists of 1g of cellulose, 3g of gelatin and 1g of glycerol showed wavelength reading of 3286.02 cm^{-1} , 1076.78 cm^{-1} , and 995.02 cm^{-1} . For the bioplastic of sample S6 which had the composition of 2g of cellulose extract, 2g of gelatin and 1g of glycerol shows the peak reading of 3284.99 cm^{-1} , 1078.69 cm^{-1} , and 1019.91 cm^{-1} . Sample S7 showed the reading of 3281.11 cm^{-1} , 1078.94 cm^{-1} , and 1019.10 cm^{-1} . For sample S8 the peak reading recorded as 3334.96 cm^{-1} , 1011.64 cm^{-1} and 950.86 cm^{-1} . These revealed the presence of O-H stretching, C-O stretching of secondary alcohol and C-O stretching of primary alcohol.

3.3 Tensile testing

The tensile testing was performed to each sample from starch-based bioplastics and gelatin-based bioplastics. The chosen bioplastics tend to carry on with the tensile testing. This was because the proportion of the cellulose of the Napier grass influences the strength of the bioplastics. Among the four samples from the starch-based bioplastic, S3 sample was chosen for the tensile testing based on the strength to withstand the elongation and stress. From another four samples of gelatin-based bioplastics, one sample was also selected to be compared to the tensile analysis.

Bioplastics with the component of 1g of cellulose, 3g of starch and 1g of glycerol chosen for the tensile testing among the samples of bioplastics with. Bioplastics with the component of the 1g of cellulose, 3g of gelatin and 1g of glycerol was chosen. The elongation at break, stress at peak and stress at break of both bioplastic were analysed. **Fig. 6** and **Fig. 7** shows bioplastics of samples S3 and S5.

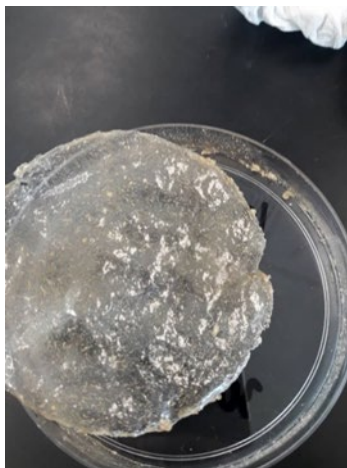


Figure 6: Bioplastic of S3



Figure 7: Bioplastic of S5

The tensile testing ASTM PWG50 was implemented to both samples at the speed of 3.000mm/min with the pretension of 2.000N. The samples were tested for its elongation at break (mm), stress at the peak at peak (N/mm^2) and stress at break (N/mm^2). **Table 3** shows the result of tensile testing for sample S3 and sample S5.

Table 3: The result of tensile testing for sample S3 and sample S5

Sample	Length of sample(mm)	Pretention,N	Elogation at break (mm)	Stress at peak(N/mm^2)	Stress at break (N/mm^2)
S3	50.00	2.000	7.845	1.594	-0.469
S5	50.00	2.000	19.893	0.426	-0.463

The elongation at break of sample S3 recorded as 7.845 mm whereas for sample S5 recorded as 19.893 mm. Sample S5 which contained gelatin supported the plastic specimen to resist changes of shape without cracking to occur for longer duration compared to the sample that made up of starch. Then for the testing of stress at peak of bioplastic for sample S3 was 1.594 N/mm^2 whereas for sample S5 recorded as 0.426 N/mm^2 . The results for stress at breaking test for sample S1 and S5 were -0.469 N/mm^2 and -0.463 N/mm^2 . The sample with gelatin showed high elongation at break value compared to the sample of bioplastic with starch. In this study, gelatin promoted the increase in the number of superficial protein chains that improved in the intermolecular interactions. The thickness of the bioplastic which was made from gelatin became one of the factors for the long elongation value [12]. The value of stress at break showed the negative value because of the presence of glycerol as plasticiser gave less tensile strength to the bioplastics. The bioplastic made from plasticiser of glycerol showed lower tensile strength compared to other plasticisers like sorbitol [13].

3.4 Biodegradability of bioplastics

The biodegradable test was conducted to one of the samples from the starch-based bioplastic and another one from gelatin-based bioplastic. The bioplastic for the biodegradable test was done based on the texture of the bioplastic. Bioplastics with the component of 1g of cellulose, 3g of starch and 1g of glycerol was chosen among the samples of the starch-based bioplastic whereas. Bioplastics with the element of the 1g of cellulose, 3g of gelatine and 1g of glycerol was selected among the gelatin-based bioplastics.

Both types of bioplastics was put in soil on the same day. The locations of planted bioplastics were labelled. After five days of the biodegradable test, the bioplastics were weighed and recorded. **Table 4** shows the result of biodegradation with differences in weight of bioplastic of sample S3 and sample S5.

Table 4: result of biodegradation with differences in weight of bioplastic

Type of bioplastic	Initial weight(g)	5days(g)	10days(g)	15days(g)
Sample S3	0.550	0.337	-	-
Sample S5	0.640	0.421	0.103g	-

The 10th day of biodegradation was observed and recorded. The sample S3 was completely degraded while sample S5 did not degrade in the soil. On the 15th day, the bioplastic of sample S5 also degraded completely. Based on the result the weight of the bioplastic reduces day by day. But the sample S3 which had the composition of starch degraded much faster compared to the sample S5. Bioplastics made from starch as polymer promoted the decomposition process faster since it gives off CO₂ as they decompose [14].

4. Conclusions

In summary, Napier grass's characteristics have facilitated bioplastic production. The inclusion of an appropriate plasticizer in the correct proportion has proven instrumental in generating high-quality bioplastics. The cellulose derived from Napier grass, acting as reinforcement, has contributed to enhancing the mechanical strength of bioplastics. The FTIR spectra has revealed that the intermolecular interaction in bioplastics involves C-O-H, O-H, C-H aliphatic, and C=O groups. Tensile testing conducted on bioplastics made from starch and gelatin indicates that the gelatin-based bioplastic exhibits a substantial elongation at break property compared to starch-based bioplastics. Furthermore, the starch-made bioplastic demonstrates faster biodegradability than its gelatin-made counterpart. Consequently, Napier grass facilitates the development of bioplastics with edible characteristics through appropriate proportions and formulations of starch and gelatin, both of which are environmentally non-toxic.

Acknowledgements

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Conflict of Interest

The authors declare that they have no conflict of interest.

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