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Effects of weight ratio of novel *Calotropis Procera* seed fiber on PLA polymer composite

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The current study presents a new bio-composite of PLA reinforced with *Calotropis Procera* seed fiber. The effect of *Calotropis Procera* seed fiber on the mechanical behaviour of polylactic acid (PLA) polymer was investigated. The composite was prepared by varying the percent weight of *Calotropis Procera* seeds with PLA as the matrix and then the impact, tensile and microstructural properties were evaluated using Charpy impact test, ultimate tensile machine and scanning electron microscope (SEM), respectively. Also, the thermal behaviour of *Calotropis Procera* seed fiber was investigated using a differential scanning calorimeter (DSC). The results showed that the impact strength decreases with the increase in fiber content from 17 kJ/m^2 for the pure PLA to 11.198 kJ/m^2 at 20%. There was no significant change in the impact strength for more than 20% fiber content. Tensile strength was found to decrease with the increase in fiber content from 54.2 MPa for pure PLA to an average strength of 47 MPa at 30% fiber in the composite. Tensile modulus, however, was found to increase with fiber content from 2.14 GPa for pure PLA to 2.45 GPa at 30% wt. fiber in the composite. The obtained result suggests that the *Calotropis Procera* seed fiber has a potential to be used as a reinforcement in polymer composites. Furthermore, this fiber could assist in cost reduction of PLA and thus increase the application of PLA.

Keywords: *Calotropis Procera*; composites; PLA; DSC; mechanical properties; microstructure

INTRODUCTION

Composites are heterogeneous materials which are derived from two or more constituents with different properties to obtain a material with better properties than those of the individual components [1]. Composites have been in use in a wide range of applications mainly in the fields such as biomedicine, aerospace, automotive and emerging consumer and construction industries, and others [2]. Their adoption in various fields has been attributed to their high strength-to-weight ratio, ease in manufacturability, good corrosion resistance, etc. [3]. However, most of the commercial composite materials, which are extensively used, are fabricated from synthetic materials [4]. Environmental issues associated with the disposal of these materials, cost and diminishing fossil fuels together with the new regulations has forced most industries to adopt the use and continuous search for eco-friendly materials to substitute the fossil fuel-based polymeric materials [5]. Natural fiber-reinforced polymer composites have been found to be neutral to the environment, resistant to chemical corrosion, offering good electrical resistance and acoustic insulation [6]. These composites find applications in the design and manufacturing of automotive interiors such as dashboard parts, cabin linings, door panels and center console among others [7]. Natural fibers possess good and desirable properties such as low density, abundancy, biodegradability, eco-friendliness, low carbon emissions and non-toxicity when compared to the synthetic fibers (Kevlar, glass and carbon) [8] and are most commonly used for the production of paper or packaging materials [9] [10]. These properties elevate lignocellulosic fibers as a potential substitute to the synthetic fibers.

In the search for sustainable fibers for polymer reinforcement, *Calotropis Procera* is identified, it is a member of the plant family, *Asclepiadaceae* and grows at an altitude of up to 1300 m with a mean annual rainfall of between 300-400 mm, in a preferably alkaline sandy soil [11]. It is a native plant in Kenya and other tropical countries amongst Afghanistan, Algeria, Burkina Faso and others. The latex and leaves of *Calotropis Procera* trees have antiviral, antifungal, and insecticidal functions [12]. Ushar seed fibers, which are composed of strong white and silky fibers with the length of 2–3.5 cm, and diameter between 28-33 μm, have been used as a stuffing material for mattresses and pillows, as well as a weaving into a strong cloth and a substitute for cotton wool for surgical uses [13]. *Calotropis Procera* grows well in drylands and is being domesticated in Kenya for textile uses [14]. Rhim *et al*. [15] found out that *Calotropis Procera* seed fiber

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contained 45.07% α-cellulose, 35.07% hemicellulose, 11.57% lignin, and 8.57% extractives which are comparable to those of wood and higher than those of some non-wood/vegetable fibers like kenaf, coir, rice straw, corn stalks and wheat straw, although the composition is said to depend on the geography of growth. *Calotropis Procera* seed fiber has not or insignificantly been investigated as a possible reinforcement or filler in bio-composite production [16].

In an attempt to evaluate its applicability as a natural fiber for bio-composites, this study seeks to evaluate the physical and thermal properties of *Calotropis Procera* fruit fiber, as sufficient information could not be found in the literature. Then, a composite was fabricated from seed fiber as a reinforcement at percentage weight ratios of 5%, 10%, 20% and 30% of the total fiber mass and PLA matrix combined. The resulting composites were characterized for mechanical and morphological properties. The study is an advancement towards the application of *Calotropis Procera* seed fiber as a natural fiber for reinforcing polymer and bioplastics - PLA for advanced applications.

EXPERIMENTAL

In this study, polylactic acid (PLA), which was used as the matrix, was delivered from Nature Works with the trade name Nature Works® Biopolymer 2003D and exhibited the following properties: residual monomer of 0.27%, relative viscosity of 4.04 P.s and color, yellowness index – 33.3. The PLA was oven-dried at 105℃ for 24 hours to reduce the amount of water suspension in the materials. The *Calotropis Procera* seed fiber used as matrix reinforcement in this study was delivered from World Agroforestry Center Nairobi - Kenya. Prior to use, impurities, including seed, were manually picked and the selected clean glossy fibers were dried at 105 ℃ for 3 hours.

The composite sample was prepared by mixing *Calotropis Procera* seed fibers and PLA as the matrix. The formulation of the constituents was aimed at determining the maximum amount of fiber that can be blended with PLA and the effects on its properties. The process consisted of two steps, namely: 1. Mixing the components on a Brabender measuring mixer, and 2. Pressing the mixture on a Servitec laboratory press Polystat 400 S. The raw material PLA was loaded through the top opening into the heated (160℃) mixer bowl where it was melted and homogenized by mixing blades. After the PLA was melted, the fibers were added, progressively from 5, 10, 20 and 30 percent wt of mixture as shown in Table 1. After the whole fiber amount was added, the blends were mixed for another 15 min at 160℃ and then all blends were pressed in a mold 200 × 200 × 4 mm on a laboratory press at a temperature of 160℃.

A scanning electron microscope (SEM) (JEOL JSM-6010 LV, TH Wildau - Germany) was used to analyze and collect microscopy images of the fiber and the fractured surface of the tensile test samples. The samples for microscopy were prepared by spraying with a 50 nm thick gold layer at pressure of 10-2 bar and a current of 50 mA. The machine used during this process was a high vacuum sputter coater (LEICA EM SCD 500, Germany).

The thermal phase transformation of the fiber was estimated using differential scanning calorimetry (DSC) 204 Phoenix, NETZSCH, Germany. The fiber sample weighed accurately in aluminium pan, the weight of the DSC samples was between 5 and 10 mg and heated in, from -100 to 300 ℃ temperature range with heating rate 10 °C/min under nitrogen. DSC curves showing exothermic and endothermic reaction peaks were recorded from the analysis.

The mechanical properties of the fabricated composites were studied through tensile and impact tests. Measurements were performed with a Zwick Z 020 (Zwick GmbH & Co. KG, Ulm, Germany) tensile testing machine according DIN EN ISO 527-1. For the determination of the Young's modulus an initial speed of 1 mm/min was chosen. After 0.25% elongation, the speed was increased to 55 mm/min. The resulting stress-strain curves show values such as the Young's modulus, the yield strength, the breaking strength, as well as the elongation at yield and at break. The ambient air temperature during the tensile test was 23°C. For each sample, five measurements were taken and the average was computed for statistical accuracy. The samples were cut and prepared according to EN ISO 527-1:1995 [17] [18].

Table 1. Sample formulation

	Composite				
Constituents	Sample $_1$	Sample $_2$	Sample $_3$	Sample $_4$	Sample $_5$
PLA (%)	100	95	90	80	70
Calotropis Procera (%)	0	5	10	20	30

Charpy impact test was carried with PSW 4J impact tester according to DIN EN ISO 179 [19], using 10 unnotched samples as standards. In each case a standard deviation of < 15% (weight drop) was used to calculate the Charpy impact strength. The Charpy impact strength of the unnotched specimen a_{cU} expressed in kilojoules per square meter, was calculated for each sample as follows:

$$a_{cU} = \frac{E_c \times 10^3}{h \times b}$$

where: *Ec = corrected stored energy in Joules, h = thickness in mm of the test sample, b = width in mm of the test sample.*

RESULTS AND DISCUSSION

Fig. 1 presents the thermal properties of the fiber. The fiber showed an endothermic reaction between 25°C and approx. 125°C. This peak was associated with the evaporation of moisture absorbed by the fiber. This evaporation occurred at 68°C. Between 125°C - 260°C, there was no endothermic or exothermic reaction, signifying that the fiber was thermally stable between these temperatures. The exothermic peak experienced at 327°C was associated with the degradation of lignin and hemicellulose present in the fiber. Above this temperature, an endothermic peak was observed signifying the degradation of cellulosic matter in the fiber. The behavior observed is comparable to those of other lignocellulosic fibers [20]. Figs. 2(a) and 2(c) show SEM images of *Calotropis Procera* fiber at different magnifications (×150, ×1200 and ×30000), respectively. Fig. 2(a) shows the broken fibers cross-section which was observed to be hollow. An approximate diameter was measured as shown in Fig. 2(c) and found to be about 102 nm. Fig. 2 (b) at a magnification of ×150 shows feather-like appearance crisscrossing one another with some bent and macerated.

Scanning electron microscope images were taken from a broken surface of a tensile test specimen and presented in Figs. 3 and 4. Higher magnification of ×550 was used to study the interface between the matrix and the fiber while low magnification of ×150 was used to study the fiber dispersion in the matrix, as well as the failure modes during the tensile test. Figs. 3(a) and (b) show SEM images of a composite with 5 % fiber content. Fig. 3(a) shows a good interface between the matrix and the fiber. Breakage of the latter, as well as delamination was observed. The dispersion of fibers in the matrix was noted to be uniform as shown in Fig. 3(b). Figs. 3 (c) and 3 (d) show SEM images at 10% fiber weight, voids were observed which could be attributed to vaporization of moisture in the mixture. Uniform fiber distribution in the matrix was noted. The interface was also found to be good, delamination was also noted. The figures also indicate the matrix failure and fiber debonding due to the compressive loading on the specimen. At 20 % as in Figs. 4 (a) and (b), there was uniform fiber dispersion in the matrix with little physical appearance of the matrix; this could lead to poor wetting of the fiber resulting in poor interface between the matrix and fiber and hence to constant deterioration of mechanical properties. Fiber breakage was intense at 20% and could be attributed to the low density of fiber which occupied large volume and hence longer time to load to the mixer.

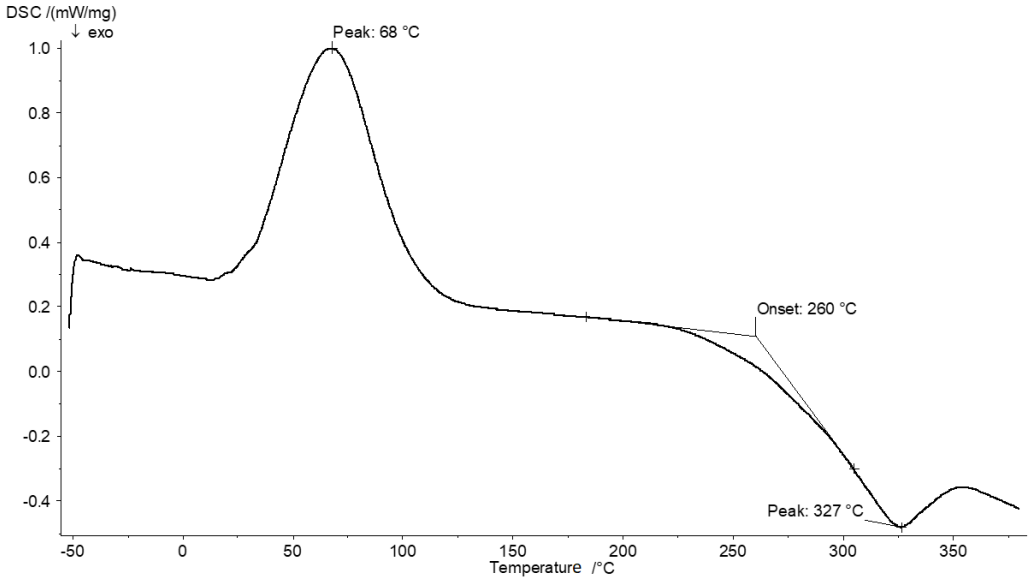

Figure 1. DSC analysis of the *Calotropis Procera* seed fiber

This destruction process of the fiber explains the decrease in the mechanical properties of the composites. SEM images at 30 % as in Figs. 4 (c) and (d) show fiber breakage and uniform fiber distribution in the matrix with no physical appearance of the matrix. Furthermore, they show that the fibers collapsed. This could mean that more than 30% weight could be used. Poor wetting of the fibers was also noted.

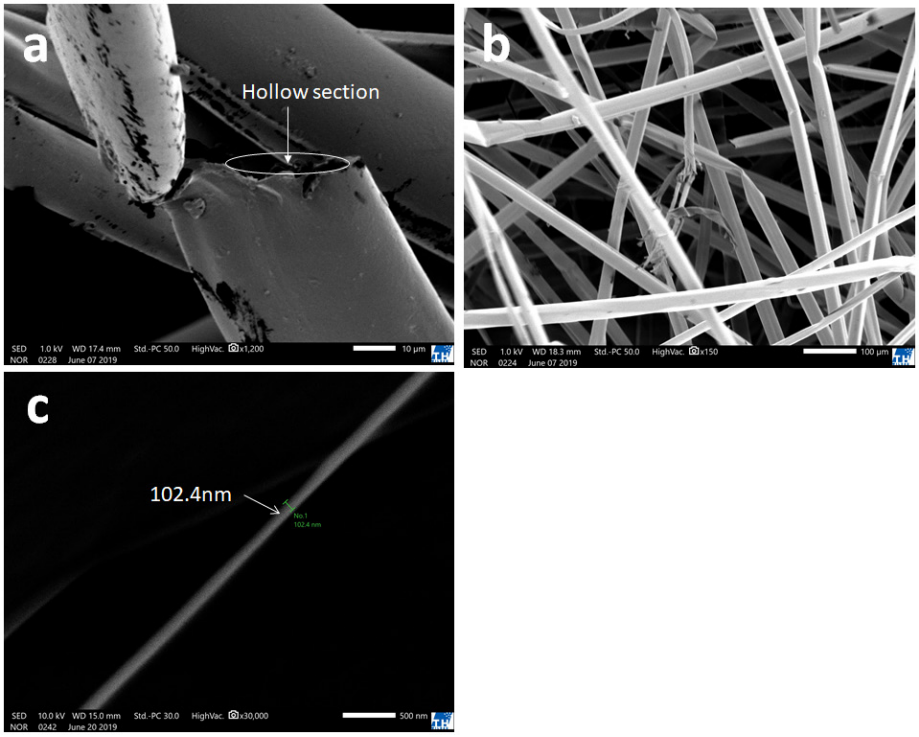

Figure 2. SEM micrographs of *Calotropis Procera* seed fiber at magnification (a)×1200, (b) ×150 and (c) ×30000

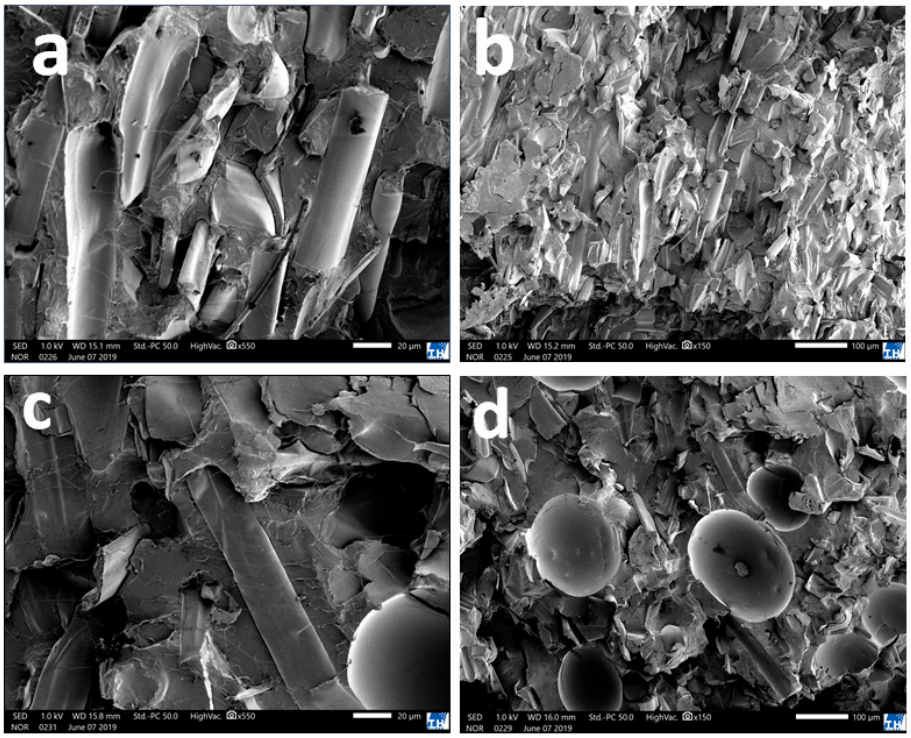

Figure 3. SEM micrographs of PLA reinforced with 5% and 10% *Calotropis Procera* seed fiber at magnifications of ×550 ((a, c) and ×150 (b, d)

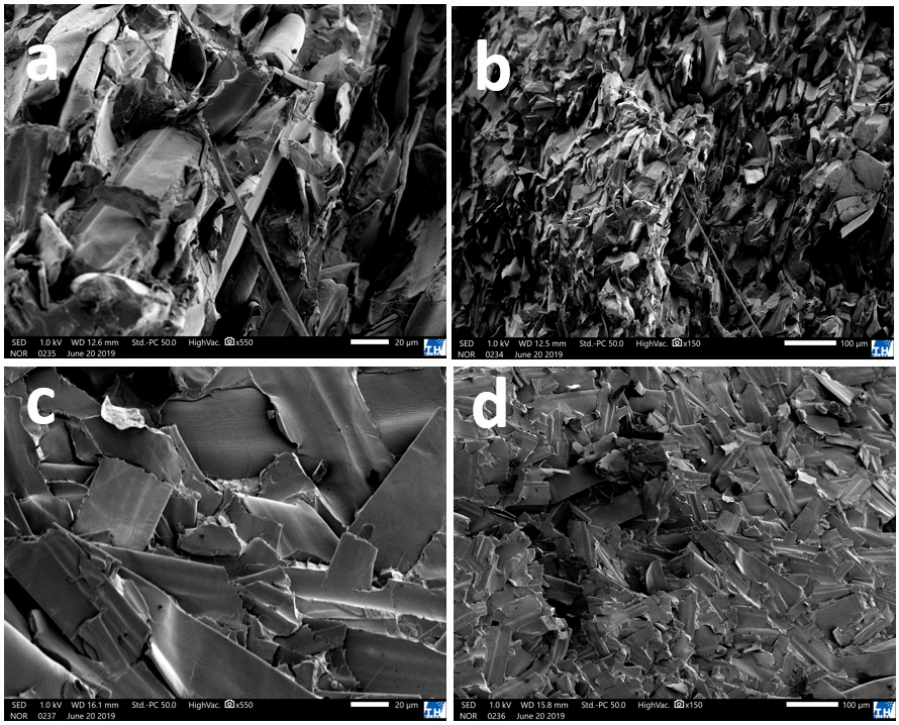

Figure 4. SEM micrographs of PLA reinforced with 20% and 30% *Calotropis Procera* seed fiber at magnifications of ×550(a, c) and ×150 (b, d)

The impact strength of the composite samples tested using 10 unnotched samples showed a reduction in impact strength with fiber loading. The impact strength for PLA reinforced with *Calotropis Procera* fibers at 5% 10% 20% and 30% was 15, 11.7, 11.1 and 11.1 kJ/m^2, respectively, which was found to be less than that of pure PLA at 17 kJ/m^2. The reduction in the strength could be a result of fiber breakage owed to the long time required to load the fiber into the extrusion machine and milling of the fibers as portrayed in the SEM images.

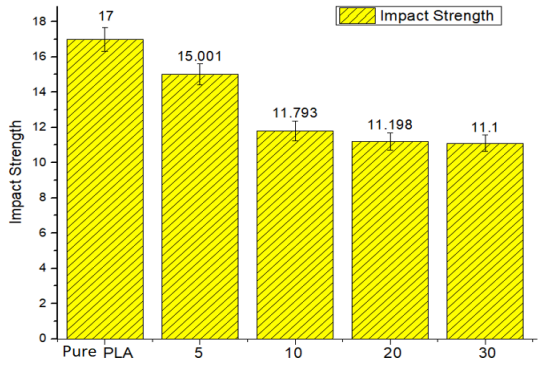

Figure 5. Impact strength of composites for pure PLA, 5%, 10%, 20% and 30% fiber content

The results of the tensile tests conducted on the *Calotropis procera* fiber-reinforced PLA composite are shown in Figure 6. The tensile strength of the composite at 5% is 47.4 MPa which is lower than that of PLA at 54.2 MPa and on further addition of the fiber there is no significant change. From these results, it is clear that there was no significant enhancement of the mechanical properties, however, there was a reduction in the amount of PLA used and this means a reduction in cost of producing PLA composites. The U.S. export price of PLA was 1,910 U.S. dollars per ton in 2018. The reduction of 5 % means a cost reduction of 100 U.S. dollars per ton. The reduction in tensile strength could be due to the short fiber resulting from milling of fibers during loading. The higher the fiber content the longer the time it takes to completely load the fiber in the mixing chamber owing to the large volume per kilogram of the fiber.

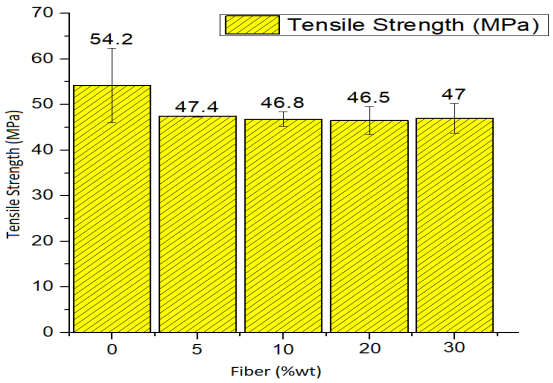

Figure 6. Tensile strength of composites for pure PLA, 5%, 10%, 20% and 30% fiber content

Tensile modulus was used to measure the stiffness of the material. Figure 7 shows an increase in the tensile modulus of the composite on increasing the fiber amount. This means the stiffness of the composite was maximum at 30% fiber loading at 2450 MPa. This is slightly higher than that of pure PLA at 2140 MPa. These results are important for the future choice of application of the composite materials. On the one hand, the tensile strength decreased with increasing the amount of the fiber but the stiffness of the materials increased. There is a vast array of applications for polylactic acid. Some of the most common uses include plastic films, bottles, and biodegradable medical devices (e.g. screws, pins, rods, and plates that are expected to biodegrade within 6-12 months). The use of *Calotropis Procera* as a reinforcement in synthetic polymer composites could reduce the amount of plastics released to the environment. On the other hand, when blended with biopolymers, the degradability is enhanced.

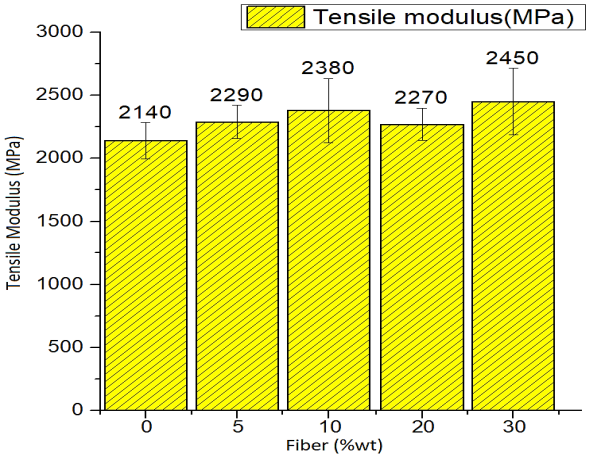

Figure 5. Tensile modulus of the composites for pure PLA, 5%, 10%, 20% and 30% fiber content

CONCLUSION

The physical and thermal properties of the novel *Calotropis Procera* fiber were evaluated. The effects of this fiber as a reinforcement of a PLA matrix were also determined. The result obtained from the SEM analysis revealed that the fiber had hollow cross-section which makes it lighter, with a diameter of approximately 102.4 nm. DSC analysis showed that the fiber was thermally stable between 125°C - 260°C. This temperature allows for easy blending with most thermoplastics without deterioration of properties. Results obtained from tensile test and impact test showed a marked decrease in strength with an increase in fiber loading. This could have been due to the nature of the fiber surface. SEM images revealed a smooth surface, further the non-cellulosic components present in the fiber may have led to deterioration in the properties. Narayana *et al.* [21] reported on surface treatments as a way of enhancing the surface properties of natural fibers. The treatments accelerate the creation of interfibrillar spaces which promote the anchoring mechanism of the matrix to the fiber. Therefore, a further investigation on the effect of surface properties of this fiber on the properties of the composite is recommended.

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