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Characterisation of Miswak (*Salvadora persica*) Fibre-reinforced Polylactic Acid Composites Prepared by Twin Screw Extrusion

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ABSTRACT

Processing of polymer composites employing fibres from sustainable sources as reinforcement has drastically grown in recent years. This research used Miswak fibres (MF) and polylactic acid (PLA) as the main materials for composite processing. Natural fibres typically include a hydroxyl group (-OH), which makes them hydrophilic. In contrast, the hydrophobic nature of polymer matrices causes them to naturally repel water. This problem was resolved by chemically altering the surface of natural fibres using a 2 wt% sodium hydroxide (NaOH) solution. In this paper, the effect of alkaline treatment has been proven by performing chemical analysis, tensile properties, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) to analyse the influence of treated MF content on composite characteristics. The results revealed that biocomposites with modified miswak fibres exhibited better properties than untreated miswak fibres-reinforced polymer biocomposites. Treated MF/PLA composites showed an increase in tensile strength of 52.9% and tensile modulus of 8.16%. From the chemical composition test, lignin composition was reduced from 5.09% to 3.06% and hemicellulose from 28.12 to 10.62% after MF was treated. Meanwhile, thermal properties for both TGA and DSC

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revealed the elimination of hemicellulose and lignin characteristic peaks, improving the thermal stability of the treated MF/PLA composite. Thus, compared to a pristine sample, the resultant composites' higher mechanical strength and thermal stability demonstrated the significance of chemically treated natural fibres. The novelty of this research is the data on miswak fibre treatment, as no research has been found for this selected treated fibre.

Keywords: Alkali treated fibre, extrusion, miswak fibre, polylactic acid, thermal properties

INTRODUCTION

Biodegradable plastic development has recently garnered more attention as a potential replacement for non-biodegradable polymers in most applications. Using biodegradable plastics would reduce pollution and waste disposal concerns while being environmentally friendly. Biodegradable plastics can be created with both natural and synthetic polymers. Natural polymers are produced largely from renewable resources, while synthetic polymers are derived from non-renewable petroleum resources (Shafi et al., 2020a). Many studies have been performed to reduce the cost of production and the negative environmental effects—the prospect of employing entirely natural fibres biodegradable in conjunction with thermoplastic degradable materials. Blending natural fibre with polymer could improve the properties of composite in terms of strength and other performance. However, the limitation on incompatibility between fibre and polymer may be overcome by surface modification, chemical treatment and improved blending processing (Ezeamaku et al., 2022).

Due to the fibres' incompatibility with the polymer matrix, the composites' mechanical properties are poor due to low fibre-matrix interfacial bond strength and poor matrix resin wetting of the fibres. Therefore, surface modification using physical or chemical approaches tends to mitigate these disadvantages (Shafi et al., 2023). Miswak fibre, which belongs to the *Salvadoraceae* family, is a durable, robust, and adaptable fibre used rarely in polymer composites. Miswak is commonly used for a variety of aspects, most notably its antibacterial properties and low production costs. It is also convenient to obtain from the source. Miswak fibre, derived from *S. persica* roots and combined with PLA pallets, may be utilised as fibre reinforcement in natural fibre composites with greater sustainable benefits, such as renewable resources and a smaller carbon footprint. By testing and obtaining their behaviours and properties, there should be a good and efficient mixing quantity of blending weight percentage ratio between them. The idea is that it may be utilised in a specific application, such as a toothbrush handle. Detailed information about miswak fibre collected and obtained from previous studies is shown in Table 1.

Table 1
Characteristics of miswak fibre

Characteristics	Description	Reference
Colour	Brown/light brown/pale yellow	Moawed (2013)
pH	6.3 (1%), 4.5-4.6 (20%) (miswak storage time before preparation affects the pH)	Moawed (2013); Moawed and Abulkibash (2016)
Density (Bulk)	0.54 g/cm^3, 0.67 g/cm^3 (dried at 250°C)	Moawed (2013); Moawed and Abulkibash (2016)
Chemical composition	Cellulose, hemicellulose, lignin	Moawed (2013); Moawed and Abulkibash (2016); Ramadan and Alshamrani, (2016)
Functional groups	Phenolic, carboxylic, alcoholic, and amine groups	Alili et al. (2014); Moawed and Abulkibash (2016); Tahir et al. (2015)
Phytochemicals	Sulphur, fluorides, chloride, vitamin C, silica, tannins, benzyl isothiocyanate, alkaloids, butanediamide, and essential oils	Abhary and Al-Hazmi (2016); Chaurasia et al. (2013); Ahmad and Rajagopal (2014); Amoian et al. (2010)

Polymer-reinforced composites have significantly improved the physical characteristics of polymeric materials. Fillers are commonly used to reinforce polymers in the creation of high-performance plastics. Manufacturers have been filling polymers with particles/fillers (polymer composites) to improve the characteristics of polymer products for many years. PLA is a biodegradable polymer manufactured from lactic acid (or lactide), which may be derived from renewable sources such as corn or sugarcane (Mukherjee & Kao, 2011; Murariu & Dubois, 2016; Nofar et al., 2019). PLA was hailed as one of the most promising biodegradable polymers, with excellent biodegradability and processability. The versatility of PLA material was expected to take the place of several non-biodegradable engineering plastics (Saini et al., 2016; Xu & Song, 2015). However, its uses were limited due to its weak heat stability and mechanical qualities (Sarasini, 2017; Satyanarayana et al., 2009; Wang et al., 2021). Many approaches, such as annealing and adding nucleating agents, have been proven to increase the thermal stability or mechanical characteristics of PLA materials (Ageyeva et al., 2021; Aliotta et al., 2017; Moser et al., 2016; Nagarajan et al., 2015), built composites with fibre or nanoparticles (Raquez et al., 2013; Yu et al., 2010; Yusoff et al., 2016; Zhang et al., 2015), extend chain (Corre et al., 2011; Correia et al., 2022), and introduce crosslinking structures.

Chemical treatment procedures often involve reagent functional groups that can interact with the fibre structures and alter their composition. As a result, the fibres' propensity to absorb moisture diminishes, facilitating better compatibility with the polymer matrix. Fibre

strands that have undergone chemical alteration exhibit changes in their surface topography, crystallographic structure, and removal of surface contaminants. On the other hand, fibres treated with alkali chemicals have rougher surfaces, which improves mechanical interlocking and increases the amount of cellulose exposed on the fibre surface. Chemical and physical treatments improve fibre-matrix compatibility and change the structure and surface of the fibres (Li et al., 2007). The mercerisation method requires soaking fibres in an alkaline solution to treat them. This procedure improves resin-fibre interfacial bonding, reduces fibre diameter, and removes oil and hemicellulose from fibres (Sherwani et al., 2021; Siakeng et al., 2020a). The surface modification of sodium hydroxide (NaOH) causes acetylation of a portion of the hydroxy surface functional groups of fibres, which inhibits moisture absorption in the fibre cell membrane, leading to high fibre wetting capacity via the matrix (Sherwani et al., 2021; Siakeng et al., 2020b). The treatment also promotes mechanical interaction between the fibres and the polymeric by changing the surface abrasion of the miswak fibres. Alkaline solutions have not been used to cure miswak fibre, yet this research attempts.

The blending of PLA and MF is performed using a twin-screw extruder. Since it delivers homogeneous, high-shear compounding, twin-screw extrusion is excellent for melt blending procedures for making thermoplastic composites. Materials mixed in a two-roll mill or a high-speed mixer have strong mechanical properties as a result (Guillaume et al., 2013; Hyvarinen et al., 2020; Kuzmin & Radaikina, 2020; Mikulyonok, 2013; Singh & Singh, 2020). When employing reinforcing agents in polymer composites, natural fillers such as clay, silica, calcium carbonate, hemp fibre, and wood fibre have been shown to produce a variety of advantageous qualities (Arbelaiz et al., 2005; Hristov & Vasileva, 2003; John & Thomas, 2008; Pluta et al., 2006; Sgriccia & Hawley, 2007; Tokoro et al., 2007). Discovery of novel natural fibres, such as miswak fibres, has become a way to address resource limitations and environmental pollution issues by examining the possible use of restricted natural fibre resources for diverse applications (Chaaben et al., 2020; Savaş, 2018). A novel plant fibre, miswak fibre (MF), was combined in a polylactic acid (PLA) matrix using a twin-screw extruder to use the agriculture byproduct fully.

This research examines the influence of MF on the thermal and mechanical characteristics of the PLA matrix. The fibre surface was chemically treated to examine the MF's blending and bonding potential on the polymer matrix. PLA was treated similarly to polypropylene; hence, it should be possible to extrude miswak fibre-reinforced composites. Tensile testing was used to examine the composites' mechanical properties; meanwhile, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to examine thermal characteristics.

MATERIALS AND METHOD

Materials

Miswak chewing sticks manufactured by Al-Khair Premium Natural Products, Karachi, Pakistan, were purchased from the local store Al-Imtinaan Sdn Bhd. Then, the miswak chewing stick was chopped, crushed, ground, and sieved into miswak fibre. Polylactic acid (PLA) thermoplastic polymers in pellets, grade 2003D, were obtained from Polycomposite Sdn. Bhd. in Seremban, Malaysia. They have a specific gravity of 1.24 g/cm, a melting temperature of 145–160°C, and a glass transition temperature of 55–60°C. Evergreen Engineering and Resources, Semenyih, Malaysia, provided the sodium hydroxide (NaOH).

Alkali (NaOH) Treatment

The miswak fibre was then soaked in a 2 wt% NaOH solution at room temperature for 60 min. The fibre-to-solvent ratio was 1:10 (w/v). After pretreatment, the material was washed and rinsed several times with distilled water and dried for 24 hours at 80°C in an oven.

Composite Processing via Extrusion

PLA with treated and untreated MF were maintained at 6–8% moisture content before blending the material in twin screw extrusion. A mixture of PLA and MF was premixed first using the dry mix technique before feeding into the main feeder. The extrusion consists of 10 heating zones, and the temperature was set starting from 160–190°C. The main screw frequency was maintained at 0.44Hz with a die head pressure of 0.10 MPa. The filament will pass through the die and be dried before being cut into small pellets.

Compression Moulding

The composite pellets from the previous phase were placed in a mould with 150 mm x 150 mm x 3 mm dimensions. The compression moulding (hot-press) machine was set at 170°C and underwent preheating for 10 min, fully press heating for 10 min and cooling for 10 min. The material was then cut into shapes in accordance with characterisation testing. Five specimens for every combination were tested for each test and then formed into sheets with dimensions of 150 mm x 150 mm x 3 mm. Details on the composite process are presented in Figure 1.

CHARACTERISATION

Scanning Electron Microscopy (SEM)

The fibre surface was observed using a scanning electron microscope (Hitachi S-3400N) outfitted with an energy-dispersive X-ray at an emission current of 58 μA and an accelerating

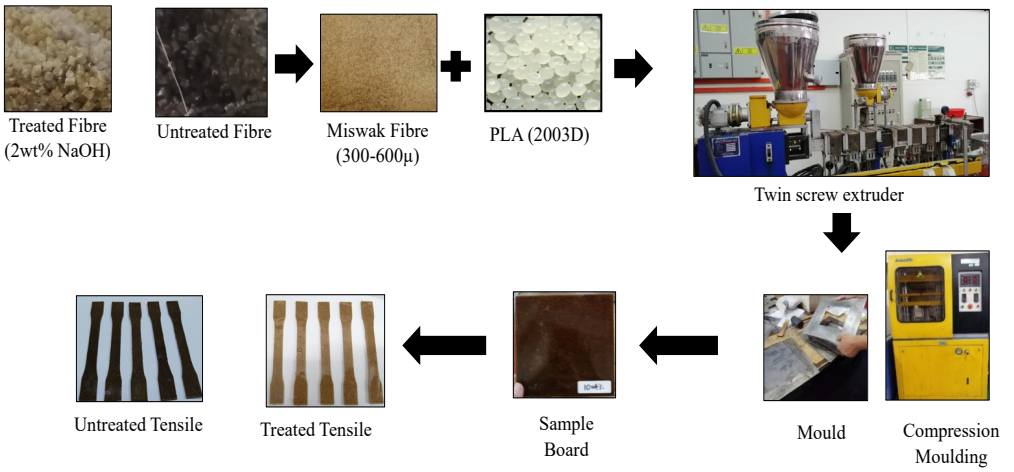

Figure 1: PLA/MF composite fabrication

voltage of 15 kV. The fracture ends of the samples were mounted on an aluminium stub and covered with a thin layer of gold to prevent electrostatic charging during testing.

Tensile Testing

A tensile test was performed on a flat dog-bone-shaped sample that was cut on the plastic mould cutter in the specified length of 150 mm, width of 23 mm and thickness of 3 mm, respectively, as per ASTM D638-14 test standards (ASTMD638-14, 2014). The 5kN Bluehill INSTRON 5566 universal testing machine was used to perform the test. The composites were grasped at a gauge length of 30 mm, and the crosshead speed was adjusted at 5.0 mm/min. A conditioning room was used to hold the five samples, and the test was run at 20.5°C and 48% relative humidity (RH). Each test was run five times for each sample to determine the outcome. The average of these five samples was then computed.

Thermogravimetric Analysis (TGA)

The samples were tested using thermogravimetric analysis (TGA) at a 10°C/min scanning rate on a Mettler Toledo TGA/DSC 1HT Stare System (Switzerland) between 30 and 600°C. TGA is a technique that monitors weight changes as a sample is heated at a consistent rate to evaluate the thermal stability of materials and their fraction of volatile components.

Differential Scanning Calorimetry (DSC)

The thermal transition properties were determined by differential scanning calorimetry using a Mettler Toledo TGA/DSC 1 HT apparatus in accordance with ASTM D3418. The weights of the treated and untreated PLA composite constructions reinforced with miswak fibre ranged from 6 to 8 mg, respectively, and the weight of the miswak fibre structure was

between 6 and 7 mg. They were heated in a nitrogen flow of 50 mL/min between 25 and 200°C at a steady rate of 10°C/min. The sample masses ranged from 5.0 to 7.0 mg in all the tests. Equation 1 is used to calculate the degree of crystallinity:

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \text{ X } 100 \quad (1)$$

where X_c is the degree of crystallinity (%); ΔH_m^a is the melting enthalpy of the sample (J/g); and ΔH_m^{100} is the melting enthalpy of 100% crystalline PLA (J/g), which was considered to be 93.7 J/g (Jia et al., 2017).

Chemical Composition Test

Chemical composition tests were conducted using the TAPPI standard procedure to determine the fibre's extractive, cellulose, hemicellulose, and lignin composition. The extractive test was initially conducted, followed by the holocellulose, cellulose and lignin tests.

The extractive test was conducted using the TAPPI T204 standard (T204). A 2g sample was put in a thimble and placed inside a condenser. Three samples containing thimbles were placed inside the condenser, each for extractive, holocellulose and lignin tests. A160ml ethanol-toluene solution was poured into a round-bottomed flask to extract the solvent from the sample. All round-bottomed flasks and the condenser were placed on the Soxhlet extraction hotplate. The test took about 6 to 8 hours to obtain the extractive solvent. Then, a bottomed flask with the sample was placed in a Rotavapor machine to obtain the extracted solvent. The round-bottomed flask with the sample was then dried in an oven at 105°C, and the sample was periodically weighed until a constant sample weight was achieved.

A holocellulose test was conducted according to standard procedure. A 2 g sample was placed into a 250 mL beaker. A 100 mL of distilled water was poured into the beaker, followed by 1.5 g of $NaClO_2$ and 5 mL of 10% acetic acid. Then, 5 mL of 10% acetic acid was added in 4 repeated pours after every 30 min. Then, 4 repeated pours of 1.5 g of $NaClO_2$ were added every 30 min. The 250 mL beaker was boiled in a water bath at 70°C. Then, 30 min after the last addition of 1.5 g $NaClO_2$, the beaker was cooled in an ice bath for 1 hour. Then, the sample was rinsed with iced distilled water and acetone in a crucible before being placed in a desiccator and weighed.

The cellulose test was conducted using the TAPPI T203 standard (T203). A sample from holocellulose used for this test was then put into a beaker with 75 mL of 17.5% NaOH before adding 15 mL of the same solution and stirred for 1 min. After that, 10 mL of NaOH was poured while stirring for 45 sec before adding 10 mL of NaOH while stirring for 15 sec and let stand for 3 min. After this, 10 mL of NaOH was added 4 times, stirred every 2.5 minutes, and left to stand for 30 minutes. Then, add 100 mL of distilled water while

stirring and allow to stand for 30 min. Later, weigh the empty crucible before filtering the sample into the crucible. Rinse the sample with 25 mL of 8.3% NaOH and 650 mL of distilled water. Then, fill the crucible with 2N acetic acid and let it stand for 5 min before rinsing it with distilled water. After that, the sample was oven-dried at 105°C and weighed.

The Lignin test was conducted using the TAPPI T222 standard (T222). A sample weighing 1 g was put in a conical flask. Distilled water and 15 mL of 72% H_2SO_4 were poured into the conical flask. The solution was boiled for 4 hours with condenser reflux. Then, the sample was filtered in a crucible by rinsing it with hot water. Then, the sample was oven-dried and weighed.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)

Figure 2a shows the SEM micrograph of untreated MF. The figure unequivocally demonstrates that MF's exterior comprised certain nodes, impurities, and wax. In essence, by eliminating wax and non-cellulose components from the outer layer, lignocellulosic fibre surface treatment could increase the fibre's surface wettability.

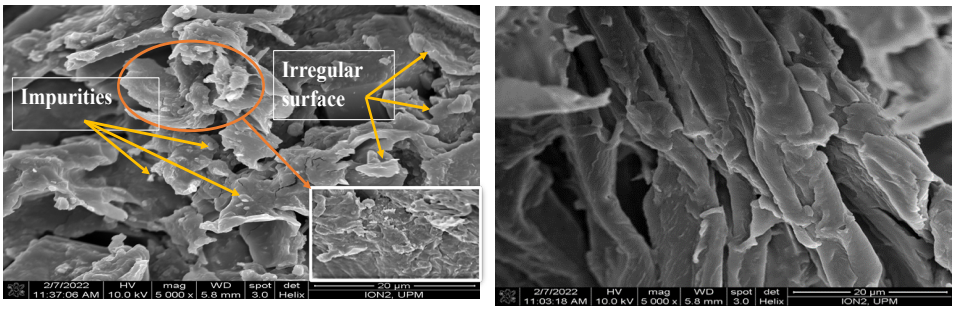

Figure 2. (a) SEM micrograph of untreated MF with 5000x magnifications and (b) SEM of 2% NaOH treated miswak fibre with 5000x magnifications

The composition of miswak fibre before and after alkali treatments is shown in Table 2. From the table, after alkali treatment, the cellulose content was increased, which led to an improvement in the properties of fibre. This treatment eliminated the lignin, wax, and oil that cover a portion of natural fibres, making the surface rougher and resulting in greater fibre interlocking with the polymer matrix. According to the micrographs, there were more residues on the surface of untreated miswak fibre (Figure 2a) than on the surface of treated miswak fibre (Figure 2b). Untreated miswak fibre is projected to have lower thermal stability than treated miswak fibre (Marques et al., 2014). The findings showed that following alkali treatment, cellulose content increased while hemicellulose and lignin content decreased. The mechanical properties may improve as a result of the observed increment in cellulose content.

Table 2
Composition of miswak fibre before and after alkali treatment

Miswak fibre	Cellulose (%)	Hemicellulose (%)	Holo-Cellulose (%)	Lignin (%)	Extractive (%)
Untreated	21.81	28.12	49.93	5.09	20.12
Alkali treated (2% w/v NaOH solution)	51.86	10.62	62.48	3.06	3.89

Tensile Properties

When defining a material, its tensile qualities are essential to be taken into consideration due to their dictate how long the material can endure controlled tension before failing. A tensile test, therefore, can be used to directly evaluate ultimate tensile strength, tensile modulus, and maximum elongation. Untreated MF/PLA composite tensile values were compared to treated MF/PLA composite. Figure 3 shows the mechanical properties of 100% PLA, 70% PLA with 30% untreated MF, and 70% PLA with 30% treated MF. Tensile strength, tensile modulus, and elongation were compared.

The tensile strength of 100% PLA was 52.11 MPa, and the tensile modulus was 2819 MPa. However, after adding 30% untreated MF, the tensile strength decreased to 38.16 MPa, and the tensile modulus decreased to 2742 MPa. It has been observed that adding natural fibre to the polymer matrix reduced the PLA/MF composite's tensile strength. This response provided a strong indication that the stress within the composite was absorbed by the matrix, indicating that the intrinsic fibres were unable to distribute stress evenly with the fibre (Shafi et al., 2020a) due to the load on the fibre mainly depends on the transfer of the matrix through the interface. The different properties of blended elements, which are PLA and MF, may cause the compound to not be fully homogenous during the blending process. The same trends were observed by Shafi et al., 2020a, who studied polybutylene succinate-reinforced empty fruit bunch fibre. However, with an addition of 30% treated MF, the results showed increments in both tensile strengths by 52.96% and tensile modulus by 8.16%. This finding proved the efficiency of the performed alkali treatment, which may influence the compatibility between fibre and polymer in composites. Other than that, the treated fibre can result in high fibre stiffness because of the higher crystallinity of hard cellulose.

Figure 4 depicts the results of elongation at the break of the composite at maximum load. The findings showed that composite with treated MF had the highest elongation rate compared with neat PLA and untreated MF composite. After adding 30% untreated MF, the elongation rate was reduced to 38.2%. On the other hand, the fibre treatment process might also contribute to the flexibility of the composite sample.

This behaviour showed increased fibre-to-PLA matrix bonding, which improved fibre-matrix interaction (Orue et al., 2016). Fibrillation was also brought on by the alkaline

treatment, which divided the composite fibre bundle into smaller fibres and shortened the fibres' diameter and length. The fibre aspect ratio rose as the surface roughness increased, resulting in better fibre-matrix interface adhesion (Das & Chakraborty, 2006; Orue et al., 2016; Yee et al., 2016). Furthermore, the alkali treatment improved fibre-matrix interaction by eliminating lignin and hemicellulose, resulting in larger inclusion. According to Rajesh and Prasad (2014), when compared to untreated jute/PLA and neat PLA, 10% alkali-treated short jute fibre/PLA showed a 7.5% increment in tensile strength because alkali surface treatment improved the compatibility of jute fibre and PLA matrix, resulting in effective transfer between fibre and matrix, as shown in the SEM study.

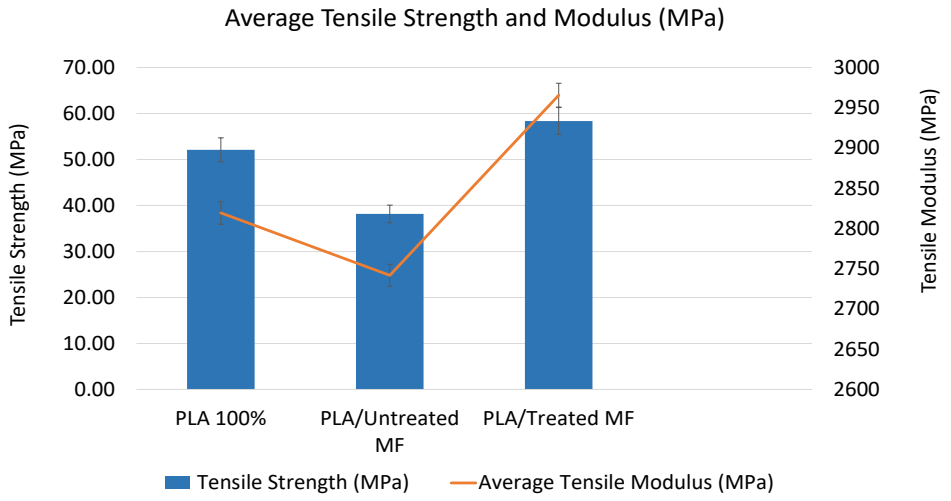

Figure 3. Average tensile strength and modulus

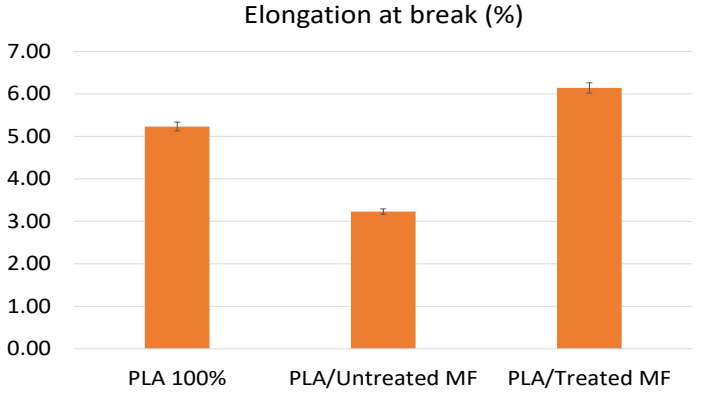

Figure 4. Average elongation at break

Thermogravimetric Analysis (TGA)

(a) Thermal stability of untreated and treated Miswak fibre

Thermal degradation is a crucial factor to consider when using high-temperature production techniques and lignocellulosic materials as reinforcements for polymers. Thermal degradation of lignocellulosic materials begins with moisture loss at temperatures below 100°C, followed by hemicellulose, cellulose, and lignin. Figures 5 and 6 demonstrate the weight loss and heat deterioration of untreated and treated miswak fibres.

The TGA curves for treated and untreated fibre are shown by the thermographs in Figure 5. At 90 to 100°C, weight loss of miswak fibre, both treated and untreated, started, suggesting that the fibre was losing moisture. The untreated fibre's next deterioration temperature, connected to hemicellulose components, was 130 to 195°C, and the third degradation temperature, related to the loss of cellulose components, was in the range of 195 to 280°C. Untreated fibre's final breakdown temperature was 280 to 600°C, denoting lignin components decomposition. The absence of a transition for hemicellulose components in treated fibre indicated that alkaline treatment successfully removed the components, and the next transition occurred in the range of 200 to 600°C for cellulose and lignin components. Untreated fibre lost 8%, 14%, 25%, and 60% of its mass at 88, 166, 261, and 334°C, respectively, whereas treated fibre lost 9% and 65% in that sequence at 94 and 353°C. Miswak fibre hemicellulose was thermally damaged at 166°C, while cellulosic content was degraded at 334°C, as demonstrated in the third stage. The cellulose content of treated miswak fibre was destroyed at 353°C, as shown by a peak in the 200 to 600°C. (Ray et al., 2002) obtained similar results, observing one peak in the weight loss curve of alkali-treated jute fibre. The initial peak did not occur in treated fibres because lignin and hemicelluloses were partially eliminated.

The DTG curves of untreated and treated miswak fibre are illustrated in Figure 6. The untreated fibre DTG curve shows 3 phases of decomposition, and the treated fibre DTG curve shows 2-phase decomposition. The untreated and treated fibre started to degrade at 88.9 and 94.6°C, respectively. This decomposition indicated moisture loss or volatile compounds in miswak fibre. The untreated fibre phase decomposition took place at 166.3°C, indicating degradation of hemicellulose components. The third phase of decomposition of untreated fibre occurred at 261.6°C, related to cellulose components degradation. At 334.2 and 353.7°C, respectively, the last phase of untreated and treated fibre degradation occurred. The results presented evidence that the alkaline treatment of miswak fibre improved the thermal stability of PLA/MF composites. The alkaline reaction removed the impurities, pectin, hemicelluloses, lignin, wax, and oil that covered the fibre surface. This treatment was predicted to improve the composites' thermal properties (Li et al., 2007).

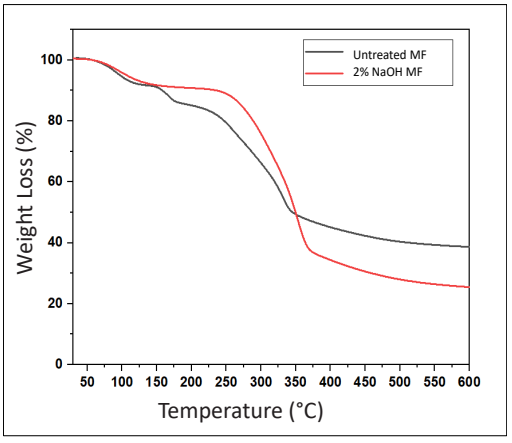

Figure 5. Thermographs of untreated miswak fibre with treated miswak fibre

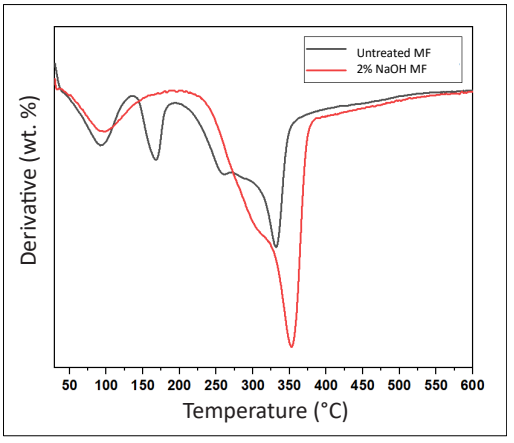

Figure 6. DTG curve of untreated miswak fibre and treated miswak fibre

(b) Thermal stability of untreated and treated MF/PLA composites

Figures 7 and 8 show the thermograms of PLA, untreated fibre/PLA, and treated fibre/PLA, with the results recorded in Table 3. Thermogravimetric curves for PLA, untreated fibre/PLA, and treated fibre/PLA composites are shown in Figure 7. At 367°C, the simple PLA weight loss curve was observed as a single step in the composite material. As demonstrated in Figure 7, the weight loss peak temperature of untreated fibre/PLA shifted to a lower temperature area. The maximum thermal degradation temperatures for untreated and treated miswak fibre were 334.25 and 353.72°C, respectively, substantially lower than the 367°C for plain PLA.

The thermal stability temperature decreased due to the low thermal degradation of the miswak fibre and the trace of moisture introduced by the miswak fibre. The pyrolytic reaction of the PLA matrix was accelerated by moisture in composite materials (Cornelissen et al., 2008). The degradation temperature tended to decrease with the addition of miswak fibre, resulting from miswak fibre's lower thermal degradation temperature. However, the treated fibre/PLA degradation temperature at 355°C was higher than the untreated fibre/PLA degradation temperature at 335°C. The mass loss for untreated fibre/PLA composite was 92% at 335°C, whereas the mass loss for treated fibre/PLA composite was 94% at 355°C in the specified sequence.

The derivative curves for PLA, untreated fibre/PLA, and treated fibre/PLA composites are shown in Figure 8. PLA had a maximum degradation temperature of 367.3°C and a residue concentration of 0.8%. The highest deterioration temperature for treated fibre/PLA was 355.2°C with a 3% residue percentage, whereas the maximum degradation temperature for untreated fibre/PLA was 335.4°C with a 3.7% residue concentration. Clearly, the presence of miswak fibre allowed for a fall in PLA thermal stability due to the miswak

fibre's reduced thermal stability. Increased treated coir fibre content caused a decrease in the thermal stability of PLA/treated coir fibre biocomposites due to coir fibre's reduced thermal stability, according to a study (Sun et al., 2017). However, alkaline treatment improved the thermal stability of treated fibre/PLA composites, with a 5.5% increase in maximum degradation temperature compared to untreated fibre/PLA composites. Moreover, the alkaline treatment resulted in fibrillation, decreased fibre diameter and length, and increased the fibre's aspect ratio. This behaviour improved the adhesion between the fibre and matrix at the interface because the higher surface roughness provided better PLA absorption. All of these factors improved the thermal behaviour of the fibre (Bakri et al., 2017).

Table 3
Thermal degradation temperature of miswak fibre/PLA composites

Samples	Tonset (°C)	Tmax (°C)	Residual (wt%)
PLA	336.3	367.3	0.8
Untreated fibre/PLA	298.5	335.4	3.7
treated fibre/PLA	320.2	355.2	3

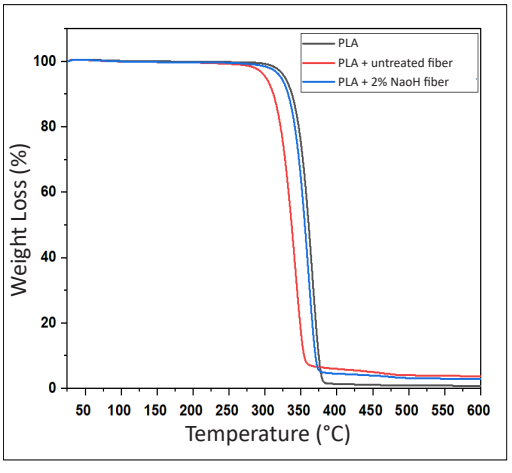

Figure 7. Thermographs of plain PLA, untreated fibre composite and treated fibre composites

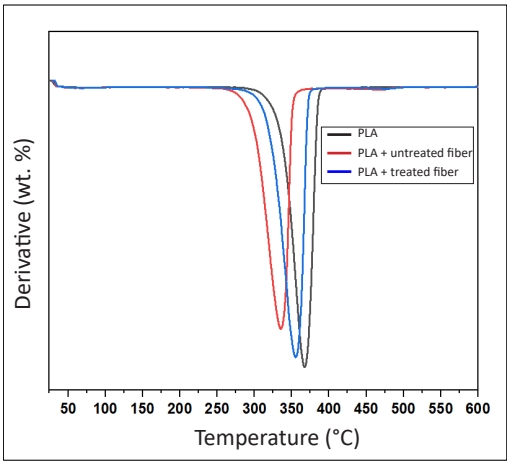

Figure 8. DTG curve of plain PLA, untreated fibre composites and treated fibre composite

Differential Scanning Calorimetry (DSC)

(a) DSC curve of untreated and treated Miswak fibre

Figure 9 shows the DSC curves of untreated and treated miswak fibre. Moisture loss caused a slight endothermic peak in the untreated fibre at temperatures below 100°C. The treated miswak fibre's DSC curve exhibited no exothermic or endothermic changes in the 25 to 200°C range, implying that the fibres were stable across the temperatures. In contrast, the

untreated miswak fibre's DSC curve revealed a strong endothermic peak at 166.70°C. This peak was caused by the breakdown of hemicellulose and cellulose, respectively. After treating bamboo fibre with alkali, Das et al. (2006) observed similar effects. It indicated that the hemicellulose and lignin fibres formed a stable network structure with the cellulose through extensive intermolecular and intramolecular hydrogen bonding, likely resulting in a stable peak between the temperature changes. In contrast, the alkali-treated bamboo exhibited two exothermic peaks, which correlated to alpha-cellulose on the DSC curves of the untreated and treated bamboo fibre samples in the range of 100 to 235°C (Das & Chakraborty, 2006).

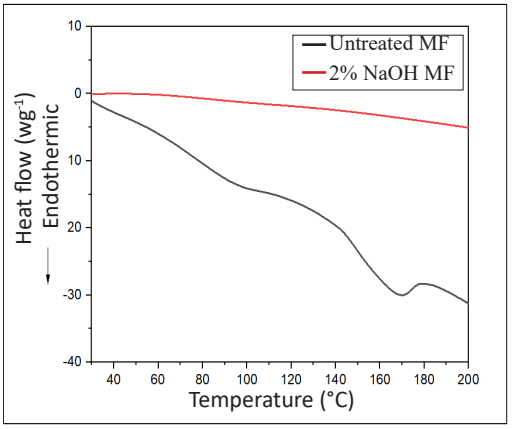

Figure 9. DSC curve of untreated and treated miswak fibre

(b) DSC curve of Miswak fibre/PLA composite

The thermograms in Figure 10 show the findings of the DSC scan listed in Table 4. The scan was performed to see how the untreated and treated miswak fibres affected the thermal performance of the composite. This thermogram was endothermic because the sensor collected the heat absorbed, and it was exothermic because the specimens released the heat. Although the curvature of the thermograms was similar, the heat released from the treated miswak fibre composites was higher compared to the untreated miswak fibre composites. For both composite samples, the initial temperature peak occurred between 50 and 55°C. This peak was endothermic, indicating that the glass transition temperature was used as the starting point for the energy necessary to modify the molecular structure of PLA. The thermal breakdown proceeded until roughly 150°C when it was discovered that both samples were undergoing another endothermic process. This peak showed that the miswak/PLA composites were about to enter the breakdown phase.

Karsli and Aytac (2014) found that the degree of crystallinity and melting of composites made with treated short flax fibres/PLA/PC was greater in all circumstances than composites made with untreated short flax fibres/PLA/PC (Karsli & Aytac, 2014). When miswak fibres were incorporated into the PLA matrix, the crystallisation temperature (Tc) increased, indicating that miswak fibres can function as nucleating agents. Consequently, the process of matrix crystallisation was expedited (Jia et al., 2017). In comparison to plain PLA, there was a little drop in the melting temperature of composites, which might be due to the development of more defecting crystals, as seen by the minor expansion of their

endothermic peaks in the second peak DSC curve and regarding the thermal behaviour of composites, fibre composites that have undergone treatment exhibited a greater degree of crystallisation temperature in comparison to their untreated counterparts.

Table 4
Thermal properties of miswak fibre/PLA composites

Sample	Description	Tc (°C)	Tm (°C)	ΔHm (J/g)	*X*c (%)
PLA	plain PLA	58.2	149.8	2	2.1
untreated fibre/PLA	PLA + untreated miswak fibre	56.9	148.3	6	6.4
treated fibre/PLA	PLA + 2% NaOH treated miswak fibre	57.3	148.6	5	5.3

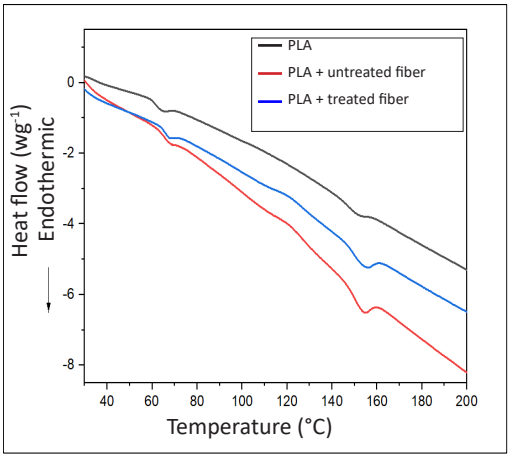

Figure 10. DSC curve of PLA, untreated fibre/PLA composite, and treated fibre/PLA composites

CONCLUSION

The current research examined the thermal stability and melting behaviour of PLA, untreated fibre/PLA, and treated fibre/PLA, in addition to their tensile strength, elongation at failure, and tensile modulus. When compared to neat PLA and untreated fibre/PLA composite, the mechanical strength of the treated fibre/PLA composites demonstrated the highest result for tensile strength, modulus, and elongation at break. The tensile strength of 30% untreated fibre decreased to 38.16 MPa, and the tensile modulus reduced to 2742MPa. However, with 30% treated MF, the tensile strength increases by 52.96% and tensile modulus by 8.16%. According to TGA and DSC data, adding miswak fibre to a composite impacted its thermal stability. Adding treated miswak fibre to this compound decreased residual weight and increased thermal stability. The melting temperature of miswak fibre was increased by alkaline treatment, which affected the melting temperature of the composite. PLA's tensile and thermal characteristics were affected by alkaline treatment. Overall, treating miswak fibre has a significant effect on the tensile characteristics and thermal stability of the PLA matrix. Future studies will examine this material to develop a miswak holder using 3D printer processing.

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