Characterization and Comparative Study on Chemically Treated Luffa Fiber as Reinforcement for Polylactic Acid Bio-composites

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Luffa reinforced polylactic acid (PLA) bio-composites were prepared and examined. The luffa surface was treated using three chemicals, i.e., sodium hydroxide, 3-aminopropyltriethoxysilane, and acetic anhydride, which enhanced luffa compatibility with PLA. Mechanical testing was done on the chemically modified luffa reinforced PLA bio-composites, i.e., tensile, flexural, hardness, and thermal. Infrared spectral functional group and morphological analyses were performed on each sample. The results showed increases in tensile and flexural strength of 7.1% and 6.9% for sodium hydroxide, 5.7% and 1.4% for silane, and 4.3% and 0.4% for acetylation, respectively, especially to the surface-treated samples at 15 wt.% fiber volume, and a decrease in water uptake (%). Fourier transform infrared spectroscopy confirmed that the chemical surface treatments were successful with the removal of lignin and hemicellulose structures, which cause the surface structure of the modified fiber to be rough. Smooth surfaces were observed through SEM images. Thermal stability was enhanced due to improved interfacial bonding between luffa and PLA, eliminating other constituents and impurities. Moreover, the morphological analysis showed improved bonding compatibility between the luffa and PLA matrix.

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INTRODUCTION

Biodegradable composites have been developed to minimize polymer pollution caused by non-biodegradable polymer composites. Therefore, many researchers have begun extensive research on natural fibers and biodegradable polymers to mitigate polymer pollution (Bakri *et al.* 2022). These natural fibers are commonly used due to their wide-ranging advantages, *i.e.*, lightweight, abundant, cheap, renewable, biodegradable, and

decent mechanical properties (Majeed et al. 2013).

Polylactic acid (PLA), also known as polylactide, is produced using microorganisms. It is an aliphatic polyester that can be biodegraded (Sin and Tueen 2019). PLA has been increasingly used to create environmentally friendly composites. The mechanical properties of PLA typically differ between soft and high strength materials, depending on the parameters used (Taib *et al.* 2022). The properties are uniquely influenced by crystallinity, composition mixing, molecular weight, and orientation. PLA has been used to make composites with several natural fibers, *i.e.*, flax, pulp, hemp, and kenaf (Oksman *et al.* 2003; Hu and Lim 2007; Du *et al.* 2014; Georgiopoulos *et al.* 2018). As an example, Masmoudi *et al.* (2016) prepared biodegradable PLA using alfa and luffa cellulose. At the addition level of 10%, this fiber improved the mixture mechanical properties, where both materials were biodegradable, but the plasticized starch exhibited faster biodegradation kinetic compared to PLA/cellulose fibers. According to Tanpichai and Wootthikanokkhan (2016), including nano-fibrillated cellulose into PLA successfully boosted the composites' tensile strength and Young's modulus by 18% and 42%, respectively.

The processing temperatures vary in different processing techniques. Different processing methods affect other properties. The processing temperature for injection molding machines can range from 170 to 180 °C (Hu and Lim 2007). For an extrusion machine, and the processing temperature was between 180 to 190 °C (Serizawa *et al.* 2005). A temperature range of 150 to 170 °C is used to produce PLA composites using compression molding. Pure PLA samples or composites can be made using injection molding, compression molding, and extrusion.

Luffa, which refers to the loofa or sponge gourd, is widely available in China, India, and Japan. Luffa is a cellulose/lignocellulose natural fiber (Tanobe et al. 2005). The cellulose content may be as high as 55 to 70%, with a hemicellulose content of 8 to 22% and lignin from 10 to 23% (Saw 2017; Karthi et al. 2020). Fibrous luffa mat has high mechanical properties, including high strength, stiffness, and energy absorption. Luffa composites have been made with polypropylene, polyester, thermoplastic starch, and epoxy (Saw 2017). Commonly used processing techniques to prepare luffa composites include hand lay-up, compression molding, extrusion (twin/single screw), and injection molding (Kaewtatip and Thongmee 2012; Sakthivel et al. 2014; Lai et al. 2016; Patel and Dhanola 2016; Kakar *et al.* 2018). The highest tensile strength recorded for a luffa-epoxy composite was 192.7 MPa (Krishnudu et al. 2018). The lowest tensile strength of 1.24 MPa was recorded for luffa-thermoplastic starch composites (Kaewtatip and Thongmee 2012). In addition, luffa is used to prepare packing mediums, mats, soundproofing, and to remove heavy metals from wastewater (Snafi et al. 2019). Some luffa composites were created to remove metal ions. According to Rahem et al. (2019), the final torque of PLA and luffa decreased as the luffa content increased, however the interfacial interaction between maleic anhydride groups of the compatibilizer and the hydroxyls of luffa caused the final torque of PLA/PLA-g-MA/LF composite to rise.

Fibre surface treatment is essential for the development of bio-composites using natural fiber. Surface treatments remove hydroxyl groups and waxy impurities that inhibit adherence between the fiber and polymer. These surface treatments are obligatory to enhance the adhesion between luffa and any polymer. Sodium hydroxide is used often to modify the surface of luffa to enhance the interfacial adhesion between luffa and polymer due to the ease of availability and usage (Parida *et al.* 2015; Saw 2017). Moreover, it aids in eliminating the waxy impurities from the surface of luffa, while luffa's mercerization enhances the interlocking between luffa and improves the interfacial adhesion with

polymer (Kaewtatip and Thongmee 2012; Panneerdhass et al. 2014; Ebrahimnezhad-Khaljiri et al. 2020).

This paper provides an analysis of luffa-PLA bio-composites. It compared the effects of sodium hydroxide, silane, and acetylation chemical surface treatments. These chemical surface treatments were performed to enhance the interfacial compatibility of luffa with PLA. The untreated and chemically surface treated luffa-PLA bio-composites were evaluated by mechanical, water uptake (%), and thermal tests, Fourier transform infrared (FTIR) spectroscopy, and morphological properties.

EXPERIMENTAL

Materials

White solid powdered PLA (Product No. 38534, Shenzen Esun Industrial Co., Ltd., Shenzen, China) had the following properties: density, 1.24 g/cc; molecular weight, 60 kg/mol; grade AI – 1001; and melt flow index, 5.9 ± 0.08 g/10 min. The luffa (*L. acutangula*) was acquired from a local supplier. Sodium hydroxide and acetic anhydride were purchased from Thermo Fisher Scientific (Waltham, USA). Silane and 3-amino propyltriethoxysilane (APS) were purchased from Merck Sdn. Bhd. (Sunway, Malaysia). Bis-(3-triethoxysilypropyl) was purchased from GELEST Inc (Morrisville, PA, USA), and acetic acid and sulphuric acid were purchased from LabChem Inc (Zelienople, PA, USA).

Fibre Preparation

Before performing any surface treatment, luffa was cut into pieces with dimensions of 5 mm. The samples were submerged in a 5 % sodium salts solution at 60 °C for 2 h to remove surface impurities. Luffa samples were removed from the solution and washed with distilled water until the sodium salt was removed entirely and the samples were no longer slippery. The samples were dried for three days at room temperature (Gupta *et al. 2012*).

Luffa Chemical Treatment

Sodium hydroxide surface treatment

Dried 5 mm luffa samples were submerged into a mixture of 5 wt.% sodium hydroxide and distilled water solution for 1 h at room temperature. The luffa samples were rinsed thoroughly with distilled water containing a few drops of acetic acid, which helped neutralize the samples. Furthermore, samples of luffa were washed using a continuous flow of distilled water to ensure that sodium hydroxide was eliminated and that the fiber samples did not have a soapy feeling on the surface. Sodium hydroxide surface treated samples were dried for 24 h at room temperature and then in an oven for 12 h at 80 °C (Vilay *et al.* 2008; Gupta *et al.* 2012).

Silane surface treatment

Dried 5 mm luffa samples were submerged into ethanol-water (60:40) solution containing 5 wt% silane for 1 h at room temperature. Bis-(3-triethoxysilypropyl) and APS coupling agents were used. In addition, a few drops of acetic acid were added to maintain the solution at pH 4. Following an hour of submergence time, luffa samples were washed thoroughly using distilled water. Silane surface-treated luffa samples were dried at room temperature for 24 h and then in an oven at 80 °C for 12 h (Kumar *et al.* 2010; Gupta *et al.* 2012).

Acetylation surface treatment

Dried 5 mm luffa samples were submerged in a 1:1 acetic acid and acetic anhydride solution for 1 h at room temperature; 1 mL of concentrated sulphuric acid was added as a catalyst. The samples were vigorously washed in distilled water to remove the chemical solution entirely from the fiber's surface. Cleaned samples were dried at room temperature for 24 h and then in an oven at 80 °C for 12 h (Gupta et al. 2012; Hajiha et al. 2014).



Fig. 1. Shows the samples of luffa preparation



(b)



Fig. 2. Samples of luffa composites (a) Sodium hydroxide-treated, (b) Silane-treated and (c) Acetylated luffa-PLA composites with varying fiber volumes

Bio-composites Preparation

Utilizing the GOTECH hot press compression molding machine (Model No. GT-7014-H100, Guangzhou, China), the samples were prepared. Luffa with 5 wt%, 10 wt%, 15 wt%, and 20 wt% was used to manufacture bio-composites with PLA to forecast the bio-composites overall mechanical properties. The mixing was performed using a dry mixer. For the preparation of flexural, hardness, tensile, and water uptake (%) samples, the ASTM D790-17 (2017), ASTM D2240-15 (2021), ASTM D638-14 (2017), and ASTM D570-98 (2018) standards, respectively, were used. All samples were prepared using the following processing parameters: 165 °C, 6 MPa pressure, 30 min compression time, and 3 h of cooling time. In addition, the mold was preheated to 165 °C. Figure 1 shows the sample of the experiments.

Testing and Characterization

Mechanical testing

The GOTECH Universal Testing Machine (UTM) (Model No. UN-7001-LAC) was utilized to test the flexural and tensile strength of the samples. The tensile and flexural samples were tested according to the ASTM D638-14 (2017) and ASTM D790-17 (2017) standards, respectively. The hardness test was conducted using the SHORE hardness meter (Deutschland, Germany). According to the ASTM D2240-15 (2021) standard, the SHORE hardness was changed to the Rockwell hardness C scale. Five samples were tested, and the average result was recorded for each fiber percentage configuration.

Water absorption

The water absorption tests were performed using ASTM D570-98 (2018). Samples were dried in the oven at 80 °C for 12 h to ensure the moisture was removed entirely. Dry sample weight was recorded, and the samples were submerged in distilled water. Samples were removed after 24 h of submergence and weighed to an accuracy of 0.001 g. Four samples were tested for each type of configuration, and the average uptake percentage (%) for the moisture was calculated using Eq. 1 (Demir *et al.* 2006),

$$Uptake (\%) = \frac{M_t - M_0}{M_0} \times 100$$
(1)

where M_t is the mass of the sample at a particular time, and M_0 is the mass of the sample at t = 0. The samples were immersed in distilled water again. The second reading was taken after a week using a similar approach. The third reading was recorded two weeks after the second reading. A similar system was utilized for the fourth reading. However, the third and fourth reading difference was less than 5 mg. Therefore, it was not recorded because the samples were substantially saturated. This type of approach is known in theory as longterm immersion.

Scanning electron microscopy (SEM)

A Hitachi Analytical Tabletop Microscope-3030 (Tokyo, Japan) was utilized to perform SEM analysis. The ASTM E2015-04 (2014) standard was referred. Initially, the specimens were cut and placed on a metal stub. The accelerating voltage was set at 10 kV. The magnifications of 100x and 200x were utilized to observe the surface of the biocomposites (Oushabi *et al.* 2017; Saw 2017).

Thermal analysis

The thermal analysis was performed using Perkin Elmer simultaneous thermal analyzer (Model No. STA8000, Manila, Philippines). The ASTM E1641-18 (2018) standard was utilized. The study was performed using samples weighing 14 mg, and purified nitrogen gas with a gas flow rate of 20 mg/mL was used. It ensured that the sample only reacted with temperature (Kaewtatip and Thongmee 2012; Saw *et al.* 2013). The temperature increment was set at 20 °C/min, with an initial temperature of 50 °C and final temperature of 700 °C. The obtained result generated from the machine was used to plot thermogravimetry (TGA), derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) graphs. The crystallinity (%) was calculated using Eq. 2 (Takemura *et al.* 2009),

$$\%X_{c} (Crystallinity\%) = \frac{\Delta H_{m}}{(\Delta H_{m}^{0})(w)} \times 100$$
(2)

where ΔH_m is the enthalpy of melting for the sample, ΔH_m^0 is the enthalpy of melting for 100% pure crystalline PLA (93 J/g), and "w" is the mass fraction of PLA in the biocomposites.

Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis was performed for chemical surface treated and untreated luffa samples with a Shimadzu IRAffinity⁻¹ machine (Kyoto, Japan). All scans were taken in the range of 400 to 4000 cm⁻¹. The IR spectrum information from the investigation was used to plot the FTIR plots under the compliance of ASTM E168-16 (2016) and ASTM E1252-98 (2021) standards.

RESULTS AND DISCUSSION

Mechanical Properties

The effect on mechanical properties due to the loading of luffa in PLA is shown in Figs. 3, 4, and 5. The bio-composites mechanical properties were shown at a variable percentage of fiber loading ranging from 5 to 20 wt%. With the help of pure PLA mechanical testing as a control sample, the sample revealed a tensile strength of 2.2 MPa, a flexural strength of 7.6 MPa, and a Rockwell hardness of 59. The tensile and flexural strength almost doubled with the incorporation of 15 wt% untreated luffa in the PLA sample. Whereas, the Rockwell hardness showed the same values of 5 wt% and 15 wt% of fiber loading. However, the Rockwell hardness value was marginally increase in 10 wt% of fiber loading but it further decrease in 20wt% of fiber loading. The strengthening effect of luffa, where the stress was transmitted from PLA to luffa, suggested increased strength. However, the tensile strength of luffa-PLA bio-composites drops drastically due to the fiber matrix agglomeration when the fiber loading reaches 20 wt%. The high luffa content caused a drop in the strength of the biocomposites as a reduction in a binder, which is the PLA. The interface between the polymer and fiber was enhanced for better mechanical properties. Better stress transfer from polymer to fiber was also shown by (Gupta et al. 2012). One way to achieve this was by removing waxy impurities, lignin, and hydroxyl groups from the fiber's surface using chemical surface treatments.



Fig. 3. Tensile strength for pure PLA, untreated and chemically surface treated luffa-PLA biocomposite at different fiber volumes (5 to 20 wt%)



Fig. 4. Flexural strength for pure PLA, untreated and chemically surface treated luffa-PLA biocomposite at different fiber volumes (5 to 20 wt%)



Fig. 5. Rockwell hardness for pure PLA, untreated and chemically surface treated luffa-PLA biocomposite at different fiber volumes (5 to 20 wt%)

Effect of sodium hydroxide surface treatment on mechanical properties

The best overall mechanical properties were demonstrated in sodium hydroxide surface-treated luffa-PLA samples. The tensile and flexural strength was increased by 7.1 and 6.9%, respectively, at 15 wt% fiber volume compared with untreated luffa-PLA samples, as shown in Figs. 1 and 2. Mercerization strengthens the mechanical interlocking between luffa and PLA (Gupta *et al.* 2012; Anbukarasi and Kalaiselvam 2015). It improved the overall surface topography of luffa and thus, improved the adhesion between luffa and PLA. Moreover, waxy impurities, voids, and hydroxyl groups were omitted from the surface due to sodium hydroxide surface treatment. The chemical modification caused structural change on the surface of the luffa, which caused the surface to be rough. It increased the size of the pores and their quantity, which increased the surface roughness and absorption ability.

Effect of silane surface treatment on mechanical properties

The second-best overall mechanical properties were demonstrated by utilizing silane surface treatment. Compared with untreated luffa-PLA samples, an improvement of 5.7 and 1.4% was shown for tensile and flexural strength, respectively, at 15 wt.% fiber volume, as shown in Figs. 2 and 3. With the increased strength, it was evident that silane interacts with carbonyl groups present in the luffa, thus improving the interfacial interaction between luffa and PLA (Gupta *et al.* 2012; Orue *et al.* 2016). Furthermore, silane chemical surface treatment enhances the fiber's nucleation potential, which leads to the better formation of crystals, better bonding between the fiber with the polymer, and improved interfacial adhesion between the fiber and polymer (Gupta *et al.* 2012).

Effect of acetylation surface treatment on mechanical properties

The third highest mechanical properties out of the four samples were witnessed for acetylation surface treated samples. Compared to untreated luffa-PLA samples at fiber volume of 15 wt%, the tensile and flexural strength were increased by 4.3 and 0.4%, respectively, as shown in Figs. 2 and 3. The increase in flexural strength was negligible. However, the enhancement in tensile strength was due to the removal of waxy impurities and voids. Therefore, the acetylation surface treatment enhanced luffa's surface topology, which improved the interfacial adhesion between luffa and PLA (Gupta *et al.* 2012; Hajiha *et al.* 2014).

Water Absorption

Natural fibers are hydrophilic, so physical properties like water absorption should be measured. The water uptake (%) was determined using Eq. 1. The results are shown in Fig. 6. It was evident that as the volume of luffa increased, the uptake of water rose, irrespective of the fiber chemical surface treatments. However, water uptake was reduced using chemical surface treatments. Water uptake was lower due to eradicating the alkaline soluble hydroxyl groups. Silanol provides molecular continuity across the sample interface with the reaction between silanol and hydroxyl groups and hydroxyl and acetic groups using sodium hydroxide, silane, and acetylation chemical surface treatments, respectively (Anbukarasi and Kalaiselvam 2015; Chen *et al.* 2018; Halip *et al.* 2019).

The highest amount of water uptake was observed for sodium hydroxide surfacetreated luffa-PLA bio-composites. In contrast, acetylated luffa-PLA bio-composites recorded minimum water uptake. However, silane surface-treated luffa-PLA biocomposites showed improvements in water uptake.



Fig. 6. Water uptake for pure PLA, untreated and chemically surface treated luffa-PLA biocomposites at different fiber volumes (5 to 20 wt%)

Characterization

Mechanical testing showed that the optimum amount of luffa in PLA was 15 wt%; the PLA matrix could not fully encapsulate the luffa beyond this loading. The absorption of water in the sample was reduced with the help of sodium hydroxide, silane, and acetylation chemical surface treatment, regardless of the amount of luffa in PLA. Thus, the following characteristics were analyzed using 15 wt% luffa-PLA bio-composites.

Thermal analysis

Thermogravimetric analysis (TGA) was performed on PLA bio-composites enforced with untreated and chemically surface-treated luffa. These samples were also compared with a pure PLA matrix. Figure 7 shows the TGA plot. There was a mass loss for the untreated luffa-PLA bio-composite starting from 50 °C due to moisture and other impurities (Gupta *et al.* 2012; Parida *et al.* 2015). However, there was no substantial mass loss in this temperature range for treated luffa-PLA bio-composite and pure PLA matrix. The plot showed that the pure PLA matrix degraded at a higher temperature than chemically surface treated luffa-PLA bio-composites; the addition of luffa in the PLA matrix decreased the PLA matrix's thermal stability. Between 300 and 400 °C, all samples degraded approximately 85 to 90%. The thermal stability of chemically surface treated luffa-PLA was better than untreated luffa-PLA bio-composites. The improved interfacial bonding between luffa-PLA due to reduction of hydroxyl group from cellulose molecules in treated fiber. When the interfacial adhesion improved between luffa and PLA is improved, the thermal stability increases (Kaewtatip *et al.* 2012; Saw *et al.* 2013).



Fig. 7. TGA plot for Luffa-PLA bio-composites

Changes were anticipated in thermal analysis with the inclusion of luffa in the PLA matrix. Figure 8 shows the derivative thermogravimetry (DTG) plot contrasting the pure PLA, sodium hydroxide, silane, acetylated treated, and untreated bio-composites of luffa-

PLA. When observing the peaks in the region, it was apparent that the cellulose degradation on luffa caused these peaks. Sodium hydroxide surface-treated luffa-PLA peak was at 345 °C, silane surface-treated luffa-PLA peak was at 354 °C, and acetylated surface-treated luffa-PLA sample peak was at 358 °C. The peaks shifted to a higher temperature range than the untreated luffa-PLA peak, which was at 337.6 °C. This phenomenon was due to the surface of luffa having a higher level of celluloses exposed after sodium hydroxide, silane, and acetylation surface treatments (Gupta *et al.* 2012; Parida *et al.* 2015). Therefore, the degradation of cellulose moved to higher temperatures. Lignin, which degrades at 500 °C, showed no peaks in the plot, even though lignin was eliminated from luffa with sodium hydroxide, silane, and acetylated chemical surface treatments.

Moreover, the untreated luffa-PLA sample's small peak was seen in the range of 50 to 100 °C. This peak was caused due to the elimination of moisture from luffa because natural fibers are hydrophilic. No peaks were seen in this temperature range for chemically surface treated samples. Therefore, it was safe to assume that hemicellulose was removed through chemical surface treatments (Pandey *et al.* 1993).



Fig. 8. DTG plot of luffa-PLA bio-composites

The DSC thermogram in Fig. 9 shows the study results using the previously mentioned methodology. However, the results showed that the enthalpy of melting was highest in pure PLA samples 25.5 J/g; for luffa-PLA bio-composites, the enthalpy of melting decreased. Untreated luffa-PLA samples showed the lowest melting enthalpy, 12.7 J/g, due to impurities, but with the aid of sodium hydroxide, silane, and acetylation, surface treatment enthalpy of melting was improved. In addition, the crystallinity percentage showed a similar trend. The crystallinity values are shown in Table 1. This phenomenon demonstrated that untreated fiber specimens failed to induce crystallinity due to impurities.

Untreated fiber, therefore, prevented nucleation or crystalline formation (Parida *et al.* 2015). However, after luffa's chemical surface treatments, these impurities were eliminated, and thus better crystallization was encouraged, but not better than pure PLA.

Moreover, the introduction of luffa into the bio-composite helped produce lumps of luffa that may entangle the PLA matrix that restricted the crystallization of PLA. In addition, the melting temperature was unaffected for pure PLA, untreated luffa-PLA, silane surface-treated luffa-PLA, sodium hydroxide surface-treated luffa-PLA, and acetylation surface-treated luffa-PLA sample, respectively.



DSC Thermogram of pure/Luffa-PLA composites

Fig. 9. DSC plot of luffa-PLA bio-composites

	Pure PLA	Untreated	Silane	Sodium Hydroxide	Acetylation
$\Delta T_{\rm m}(^{\circ}C)$	177.7	177.3	176.9	176.3	178.2
$\Delta H_m(J/g)$	25.5	12.7	20.2	20.9	19.8
%X _c	27.4	16.1	25.6	26.4	25.1

Table 1. Melting Temperature (Δ Tm), Enthalpy of Melting (Δ Hm), and Crystallinity% (%Xc) for Pure PLA and Luffa-PLA Bio-composites

Fourier transform infrared spectroscopy

The plot was shown in Fig. 10 (a) represents the FTIR plot for untreated luffa samples. Using the FTIR plot, the -OH group's presence was confirmed by peaks shown in the range of 3200 to 3800 cm⁻¹. The presence of peaks for – OH groups was also noticed, which is a characteristic of natural fibers, which is hydrophilic. Moreover, a sharp peak in the range of 2300 to 2400 cm⁻¹ represents the presence of lignin, cellulose, and hemicellulose. The peak shown at 2870 cm⁻¹ represents the stretching of C - H bonds. The peak at 1730 cm⁻¹ represents carbonyl (C = O) stretching, which was an expected peak for natural fibers due to the presence of hemicellulose and cellulose. Furthermore, peaks present in the range of 1600 to 1850 cm⁻¹ represent the presence of waxy impurities (Fan et al. 2012; Krishnudu et al. 2020). The FTIR plot in Fig. 10 (b) denotes the plot for sodium hydroxide surface-treated luffa samples. The bending of CH_2 and O - H bonds was witnessed in the 1000 to 1500 cm⁻¹ range. The vibration of C = O bonds presents inside cellulose was seen in the 1500 to 1700 cm⁻¹ range. Peaks present in the range of 1700 to 2000 cm⁻¹ were insignificant, proving that impurities such as waxy impurities were removed from the surface of luffa utilizing sodium hydroxide surface treatment. In addition, little peaks were present in the range of 2300 to 2400 cm⁻¹, predicting that hemicellulose and lignin were removed (Boopathi et al. 2012; Gupta et al. 2012; Krishnudu et al. 2020).

The FTIR plot is shown in Fig. 10 (c) denotes the silane surface-treated luffa samples plot. The focus was to look for peaks representing Si - O - Si linkages and Si - O – Cellulose bonds. Peaks in the range of 700 to 800 cm⁻¹ confirmed the presence of Si - O – Cellulose bonds and confirmed the stretching of Si - O - Si linkages. Moreover, stretching Si - O – Cellulose bonds should represent stretching 1200 to 1250 cm⁻¹. Furthermore, siloxane peaks were also witnessed in the 2100 to 2200 cm⁻¹ range (Kumar *et al.* 2010; Hajiha *et al.* 2014). However, no significant peaks were present in this range. Figure 9 (d) denotes the FTIR plot for acetylated luffa samples. The plot showed that peaks in the range of 1500 to 1700 cm⁻¹ represent C – H bending, which occurred due to the esterification process. Bonding of C = O within acetyl functional groups was witnessed in the peaks ranging from 1700 to 1800 cm⁻¹. Peaks were seen in the range of 2300 to 2400 cm⁻¹; therefore, ester linkages were predicted between hydroxyl groups and acetyl ions. Furthermore, small peaks were witnessed in the 3200 to 3800 cm⁻¹. Thus, – OH groups were removed (Hajiha *et al.* 2014; Krishnudu *et al.* 2020).

It was evident from the FTIR analysis that most – OH groups were eliminated by acetylation, and the least amount of – OH groups were eliminated using sodium hydroxide. Therefore, acetylation chemical surface treatment predicted the least water uptake. Figure 4 shows that a low water uptake was recorded for acetylation surface-treated luffa-PLA bio-composites. The highest water uptake was recorded for sodium hydroxide surface-treated luffa-PLA bio-composites. However, most CH_2 and C = O bending were witnessed

for sodium hydroxide surface treated samples, followed by silane and acetylation surface treated samples. Therefore, the highest mechanical properties were expected for sodium hydroxide surface-treated luffa-PLA bio-composite, followed by silane and the acetylation surface-treated luffa-PLA bio-composites. Referring to Figs. 2 and 3, the highest tensile and flexural strength was recorded for sodium hydroxide surface-treated luffa-PLA bio-composites, followed surface-treated luffa-PLA bio-composites. Referring to Figs. 2 and 3, the highest tensile and flexural strength was recorded for sodium hydroxide surface-treated luffa-PLA bio-composites, followed by silane and acetylated surface-treated luffa-PLA bio-composites.



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Fig. 10. FTIR plots for untreated and chemically surface treated luffa composite samples

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Scanning electron microscopy

Scanning electron microscopy images obtained were 100x and 200x for untreated and chemically surface-treated luffa-PLA bio-composites. The untreated luffa-PLA sample is shown in Fig. 11.



(a)

(b)

Fig. 11. SEM analysis of untreated luffa-PLA bio-composite (a) x100, and (b) x200



Fig. 12. SEM analysis of sodium hydroxide surface-treated luffa-PLA bio-composite (a) x100, and (b) x200

Due to the presence of waxy impurities on the surface of the luffa, a smooth surface was seen. Hence, the interfacial adhesion between PLA and luffa was weak. However, luffa's rougher surface was observed when sodium hydroxide was used as a chemical for surface treatment was utilized to remove waxy impurities (Oushabi *et al.* 2017). Enhanced surface topography was seen for luffa once the waxy impurities were removed. Therefore, the interfacial adhesion was improved between luffa-PLA, as shown in Fig. 12, whereas better mechanical properties were recorded. There was no substantial difference on the surface of luffa using silane chemical surface treatment. The smooth surface of luffa is shown in Fig. 13 because of the silane particles deposited on the luffa (Hajiha *et al.* 2014).

Silane surface treatment increases fiber's nucleation potential, improving the interfacial adhesion between PLA and luffa (Gupta *et al.* 2012).



Fig. 13. SEM analysis of silane surface-treated luffa-PLA bio-composite (a) x100, and (b) x200.



Fig. 14. SEM analysis of acetylation surface-treated luffa-PLA bio-composite (a) x100, and (b) x200

The luffa's surface was smooth, similar to silane chemical surface treatment, utilizing acetylation chemical surface treatment. The smooth surface of luffa is shown in Fig. 14 was due to hydroxyl groups getting replaced with acetyl functional groups (Oushabu *et al.* 2017). In addition, surface impurities were removed. The elimination of surface impurities improved the surface topography of luffa and thus improved the mechanical properties by improving the interfacial adhesion between luffa and PLA. Moreover, enhanced mechanical properties were recorded due to improved interfacial adhesion between PLA and luffa.

CONCLUSIONS

- 1. The surface of luffa was observed to be flaky and waxy. The surface topography of luffa was improved, waxy impurities were removed, and interfacial adhesion between PLA and luffa was enhanced using sodium hydroxide, silane, and acetylation chemical surface treatments. In addition, the mechanical properties were improved with the addition of untreated luffa in PLA. However, with the help of chemical surface treatments, the mechanical properties were improved even further.
- 2. Sodium hydroxide surface-treated luffa-PLA bio-composites showed the highest tensile and flexural strength, followed by silane and acetylation surface-treated luffa-PLA composite samples.
- 3. The luffa-PLA bio-composites were also analyzed for water uptake. The addition of luffa-PLA composite increased water uptake due to natural fibers being hydrophilic. However, with the help of sodium hydroxide, silane, and acetylation chemical surface treatments, the water uptake was decreased considerably due to the removal of hemicellulose and –OH groups. Acetylation surface-treated luffa-PLA bio-composites showed minimum water uptake, and sodium hydroxide surface-treated luffa-PLA bio-composite showed the highest.
- 4. The luffa-PLA bio-composite thermal stability was improved due to improved interfacial bonding between luffa and PLA. With untreated luffa in PLA, the melting enthalpy (ΔH_m) was reduced due to impurities; however, the melting enthalpy was improved utilizing chemical surface treatments. A similar trend was seen for the percentage of crystallinity (% X_c). Untreated luffa specimens failed to induce crystallinity due to impurities. Untreated fiber, therefore, prevented nucleation of crystalline formation. However, after luffa's chemical surface treatments, these impurities were eliminated, and thus better crystallization was encouraged, but not better than pure PLA.

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