

Preparation and Properties of Pineapple Leaf Fiber Reinforced Poly(lactic acid) Green Composites

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Abstract: Green composites from Pattawia pineapple leaf fiber (PALF) and poly(lactic acid) (PLA) were prepared. The mechanical method was chosen to extract PALF from fresh leaves due to this method gave high yield of fiber, short extraction time, and environmental friendly. Tensile and thermal properties, together with morphology of the fibers were disclosed. The fibers were conducted into a specified length of 1-3 mm and blended with PLA, using a twin screw extruder, with the PALF content of 10-50 wt%. Tensile testing, morphology investigation and thermogravimetric analysis were applied. Preliminary results showed that tensile modulus of the composites depended on PALF content. The tensile modulus and elongation at break of the composite containing 40 % PALF was about 48 %, and 111 % increase, respectively, compared with that of PLA. With addition of maleic anhydride coupling agent, such the composite showed the tensile modulus of 5.1 GPa, which was 34 % higher than that of the non-coupling agent composite, and about 104 % higher than that of PLA. Although the elongation at break of the composite containing 40 % PALF was found to dramatically increase by 111 %, the introduction of maleic anhydride in such the composite caused only 57 % increase in the elongation at break compared with that of PLA. Finally, a pilot product of square boxes was produced successfully from the proposed composite, by conventional injection molding process.

Keywords: Pineapple leaf fiber, Fiber-reinforced composite, Green composite, Coupling agent

Introduction

The emphasis on environmentally sustainable materials and processes has made an increased interest in the development of natural fibers based biocomposites. Consuming, on average, 60 % less energy than the manufacture of glass fibers on their production, being derived from renewable sources and being biodegradable make natural fibers suitable for biocomposites production [1]. Research efforts are currently being harnessed in developing a new class of fully biodegradable green composites by combining natural or bio fibers with biodegradable polymers [2]. The chief attractions about green composites are that they are environmentally friendly, fully degradable and sustainable. At the end of their lives, they can be easily disposed of or composted without harming the environment.

Previously, polymers such as poly(propylene) [3-6], poly (amide) [7] and phenolformaldehyde [8] incorporating with natural fiber such as hemp [3], sugarcane bagasse [4], Curauá [7] and pineapple leaf fibers [5,6,8] can result in new materials with improved flexural and tensile modulus as well as tensile strength. With increasing interest on green composites, various systems based on biopolymers have been established. Those include flax fiber/poly(carpolactone) [9], flax fiber/PLA [10,11], wood flour/PLA [12], green coconut fiber/PLA [13], and recycled paper fiber/TPS [14]. Although those systems show the improvement in tensile and thermal properties in addition to impact performance, in

comparison with pure biopolymers, poor adhesion between matrix and fiber is still observed. Enhancing the matrix-particle interfacial adhesion by addition of a coupling agent is confirmed to be an attractive method in developing such adhesion [3,9,12,13].

Poly(lactic acid) (PLA) is a compostable biopolymer derived from renewable source. Due to PLA can satisfy many of the environmental criteria, many products those do not require high performance, such as plastic bags, food packaging, disposable cutlery and cups can be effectively produced [12]. However, its poor mechanical properties on top of higher price compared with oil-derived polymers, limit the use of PLA.

Among various natural fibers, PALF has the potential for use as reinforcing filler in green composites with satisfy mechanical properties. PALF exhibits excellent mechanical properties, associated with their high cellulose content, due to its main chemical constituents are cellulose (70-82 %), lignin (5-12 %) and ash (1.1 %) [15].

In this study, pineapple leaf fiber-reinforced poly(lactic acid) green composites were prepared by blending of poly(lactic acid) polymer and short-length-chopped Pattawia pineapple leaf fibers (1-3 mm) using a twin screw extruder. Effects of the fiber content and the addition of a coupling agent on mechanical properties and morphology of the composites were investigated. Finally, a pilot product was produced from such the green composite, which enclose optimum mechanical properties, by conventional injection molding.

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Experimental

Materials

High heat resistant grade (GP 330-1) PLA was supplied by Bio Green World Co. Ltd., Thailand. The Pattawia pineapple leaves were from Rayong province, Thailand. The leaves with 70-80 cm long were specifically chosen from pineapple plants at the age between 12 and 14 months. Maleic Anhydride (MA) coupling agent was purchased from Fluka, Germany and used as received without any further purification.

Preparation of PALF

Pineapple leaves were cleaned by water and transferred into the entrance channel of the extraction machine. After the fibers were separated from fresh leaves by mechanic blades, they were rinsed with a lot of water, and washed thoroughly in 2 % detergent solution at the temperature of 70 °C, followed by rinsing again with water. The clean fibers were allowed to dry at room temperature for 2-3 h before putting in a hot air oven at the temperature of 60 °C overnight. The dried pineapple leaf fibers with the length of about 70-80 cm were obtained. The PALF was manually chopped into short pieces of 1-3 mm in length, and stored in moisture-prevented bag, prior to compounding with PLA.

Preparation of PALF/PLA and PALF/MA/PLA Composites

To ensure that the adsorbed moisture was removed and to prevent void formation, the chopped PALF and the pure PLA were dried at 80 °C under desiccant drier for 4 hours prior to compounding. The PALF and PLA, mixed at various fiber contents (10, 20, 30, 40, and 50 wt%), were fed into a two-roll mill machine at room temperature and then the composite pellets were produced by a Brabender co-rotating twin-screw extruder. A uniform temperature of 120 °C was maintained for all the six zones of the extruder and strands of the extrudate were collected and chopped into pellets by the pelletizer. The obtained composite pellets were dried at 80 °C for 4 hours and kept in the moisture protectable bag. In case of the PALF/MA/PLA composite, 10 wt% of MA was firstly mixed with PLA using a high speed mixer. After good mixing, the mixture was loaded into the two-roll mill machine, in which the rollers surface temperature was set at 140 °C, for 5 minutes. In the meantime, the chopped pineapple leaf fibers were loaded into the mixture in the two-roll mill. Then the PALF/MA/PLA composites pellets were produced by the Brabender co-rotating twin-screw extruder, in which a uniform temperature of 120 °C was maintained for all the six zones of the extruder.

Preparation of Tensile Specimens

PLA and its composites pellets were injection molded to form type I tensile specimens according to ASTM D638 (Figure 1 and Table 1). In details, the pellets were dried in a desiccant drier at 80 °C for 4 hours to remove moisture prior

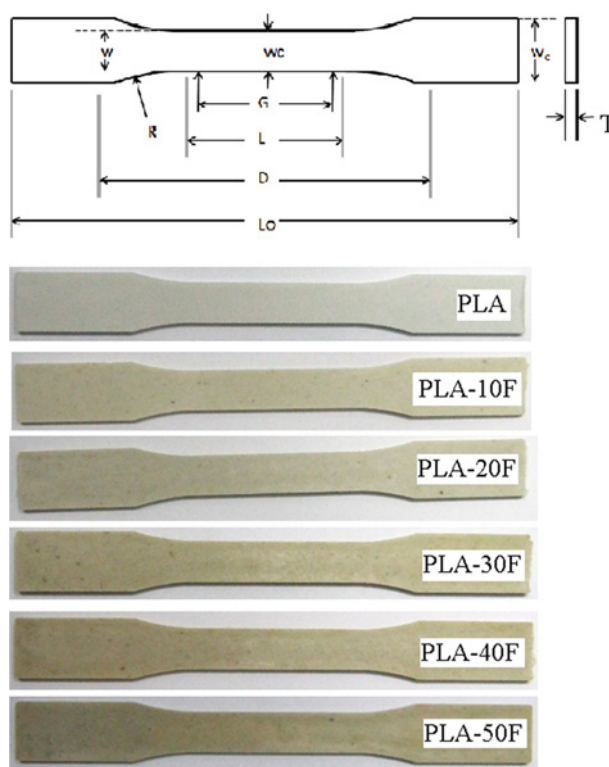


Figure 1. Tensile specimens of PLA/PALF composites with various fiber contents.

Table 1. Tensile specimen dimension, according to ASTM D638

Dimension	Value, mm (in)
Thickness < 7 mm (0.28 in), T	1.00±0.4 (0.13±0.02)
Width of narrow section, W	13 (0.5)
Length of narrow section, L	57 (2.25)
Width overall, WO	19 (0.75)
Length overall, LO	165 (6.5)
Gauge length, G	50 (2.00)
Distance between grips, D	115 (4.5)
Radius of fillet, R	76 (3.00)

to injection molding. The injection molding machine, ARBURG ALLROUNDER; Model 370U, (70 ton mold closing force) with four temperature zones on the cylinder was used to produce the tensile specimens. The nozzle temperature was set at 160 °C and the others zones were kept at the same temperature. The mold surface temperature was 50 °C and the cooling time was 25 s. Filling pressure and holding pressure were 130 and 70 MPa, respectively.

Preparation of a Pilot Product

A pilot product of rectangular boxes from PLA-MA-40F composite pellets was produced by conventional injection molding process on the Ferromatik Milakron E110 machine.

The nozzle temperature was set at 140 °C and the others zones were kept at the same temperature. The mold surface temperature was 50 °C and cooling time was 15 second. Filling pressure and holding pressure were 130 and 70 MPa, respectively.

Measurements

Tensile testing of PALF was carried out based on ASTM D3822-07 for tensile properties of single textile fibers. After separation into a single fiber, PALF was mounted on a paper cardboard with 2.54-cm gauge length. A small amount of glue was applied to the two edges on either sides of the gauge length along the length of the card, before carefully put the fiber into the place. The mounted single fiber was then individually placed between the grips of an Ametek LLOYD Instrument Ltd., tensile testing machine; model LRX Plus. The fiber was then tested to failure at a cross head speed of 0.5 mm/min using a 5N-load cell. Averaged values of Young's modulus, tensile strength, and elongation at break were calculated after 20 measurements.

Tensile testing of the composites was performed by 5500R Instron tensile testing machine with 10 kN load-cell, according to ASTM D638. At least 5 specimens were tested for each sample. The strain was measured using an Instron touching extensometer with 50 mm gauge length. Crosshead speed was 50 mm/min. The measurements were carried out in standard laboratory atmosphere of 23±2 °C and 50±5 % RH. The specimens were stored at these conditions for not less than 40 hours prior to the tensile test.

Thermal transition behavior of the PLA matrix was studied using a TA Instruments 2920 modulated differential scanning calorimeter (DSC), equipped with a cooling attachment, under nitrogen atmosphere from 25 to 260 °C at a constant heating rate of 5 °C/min. Thermal properties of PLA, PALF and their composites were studied using a Mettler Toledo TGA/SDTA851e, at a heating rate of 10 °C/min, under nitrogen atmosphere, from 25 to 600 °C. Morphology of fiber surface, fiber fractured surface, and composite fractured surface were investigated using a SEM, JSM-5410LV, Jeol Co., Ltd.

Results and Discussion

Inspection of PALF

The diameter of PALF was measured via an optical microscope with X200 magnification. Three parts, along the leaves of the fibers, were inspected: 1) fiber from leaf tip, 2) leaf center, and 3) leaf base. The diameter of a single fiber was inspected at three positions along the length of the fiber; A, B, and C (Figure 2). The averaged value of the fiber diameter was calculated from 20 measurements. The inspection data obtained are summarized in Table 2. It was found from the table that the averaged values of single fiber diameter were 0.197±0.043 mm, 0.199±0.050 mm, and 0.219±

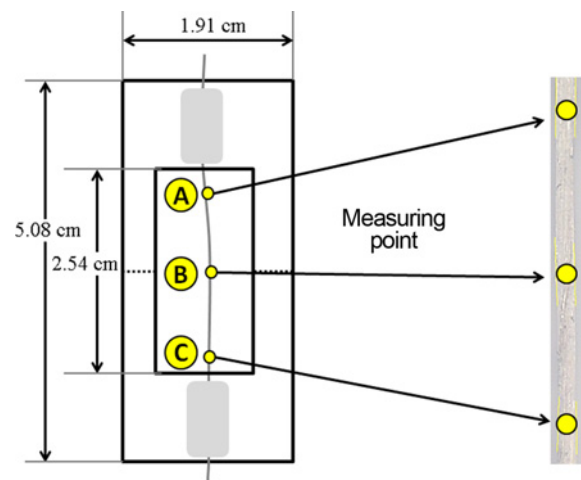


Figure 2. Schematic diagram illustrating PALF diameter measurement.

Table 2. Summary results for PALF diameter measurements

Fiber	Range of diameter (mm)	Averaged diameter (mm)
Fiber from leaf tip	0.127-0.268	0.197±0.043
Fiber from leaf center	0.136-0.296	0.199±0.050
Fiber from leaf base	0.139-0.334	0.219±0.052

0.052 mm for fiber from leaf tip, leaf center, and leaf base, respectively. These are in contrast with the diameter of PALF reported in literatures, which was in the range 0.02-0.08 mm [16,17]. It was because PALF used in this present work was mechanically extracted from the fresh leaves. Therefore, the fibers still contained more cellular residues such as lignin and hemicelluloses, which cemented the fibers together, compared with the PALF prepared by retting and scrapping [18]. The rough surface of mechanically extracted PALF seen in SEM images (Figure 3) indicated the ability in adhering between PALF and PLA matrix [19]. Such good adhesion will result in good mechanical properties since the rough surface morphology of the fiber is expected to assist with mechanical interlocking when being used in composites [12].

Tensile properties of the PALF were found to vary in different parts along the length of the fiber. Figure 4 shows tensile stress and tensile modulus of PALF. The fiber obtained from the leaf tip exhibited the ultimate tensile strength of 244 MPa, tensile modulus of 9.8 GPa and elongation at break of 1.5 %. The fiber obtained from the leaf center showed the ultimate tensile strength of 242 MPa which was slightly lower than that obtained from the leaf tip, tensile modulus and the elongation at break were 10.6 GPa and 2.3 %, respectively. The leaf base showed the lowest value of tensile strength of 146 MPa, and the lowest tensile modulus of 4.3 GPa, although it showed the highest elongation of

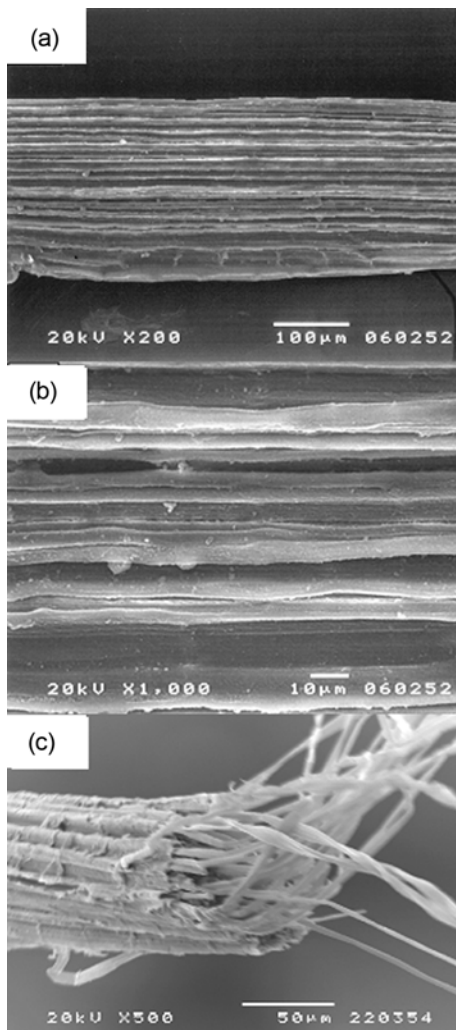


Figure 3. SEM micrographs showing surface morphology of PALF at the magnification of (a) $\times 200$, (b) $\times 1000$, and (c) fractured surface of PALF obtained from the center of the pineapple leaf.

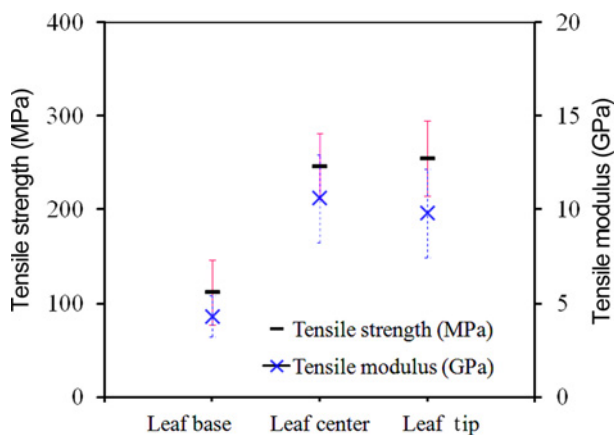


Figure 4. Tensile strength and tensile modulus of PALF obtained from different positions of the pineapple leaf.

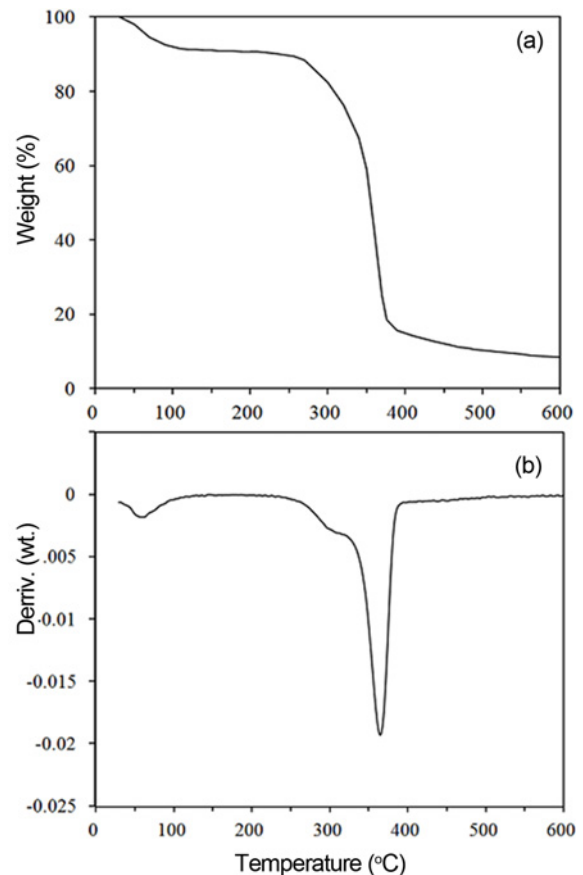


Figure 5. TGA (a) and DTG (b) thermograms showing thermal stability of PALF.

3.1 %. Therefore, in this study the PALF obtained from the leaf center was chosen as a filler for the composites preparation. According to Arib *et al.* [5], the reported tensile strength, tensile modulus and elongation at break of PALF were 126 MPa, 4 GPa and 2.2 %, respectively. This implied that the PALF obtained in our study showed better mechanical properties than those of the PALF prepared by Arib *et al.*

Figure 5 shows the degradation behavior of PALF. The initial weight loss occurred in the temperatures range 30 to 100 °C was due to the evaporation of water containing in the PALF. There was no significant weight loss in the range 100-250 °C, until the PALF began to degrade near 250 °C, due to the degradation of cellulose, hemicelluloses and lignin in PALF. The non-cellulose in the fiber started to decompose at about 330 °C, and continued to decompose until ~ 385 °C, giving the char residue of ~ 10 % [20,21], while the fastest weight change was observed at 362 °C. The results are in good agreement with the degradation behavior of PALF studied by Costa *et al.* [22].

Inspection of PLA

The DSC thermogram of PLA (Figure 6) displayed both glass transition (T_g) and melting (T_m) temperatures at 85 and

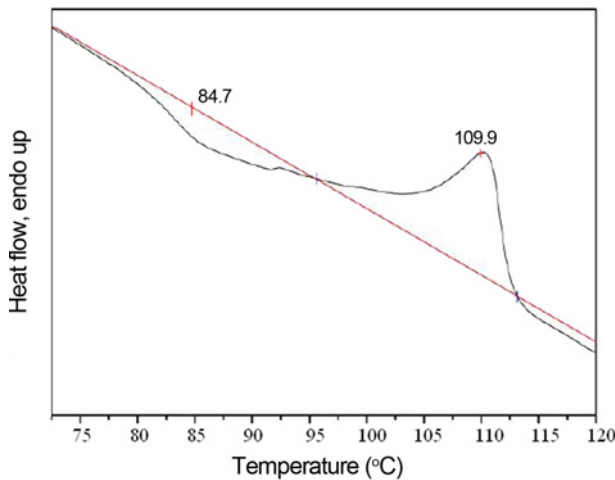


Figure 6. DSC thermogram for PLA.

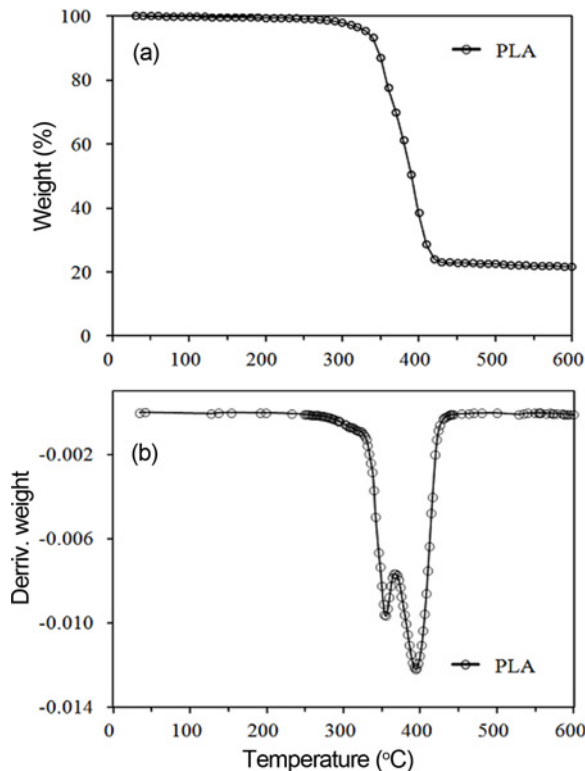


Figure 7. TGA (a) and DTG (b) thermograms showing thermal stability of PLA.

110°C, respectively, demonstrating its semi-crystalline structure. The temperature behavior of PLA, especially T_m , had to be considered when it was mixed with PALF to prepare the composites. Hence, the mixing temperature of 120°C was chosen to process the composites using co-rotating twin screw extruder in order to melt PLA granules and prevent it from thermal degradation.

TGA and DTG curves of PLA are shown in Figure 7. PLA

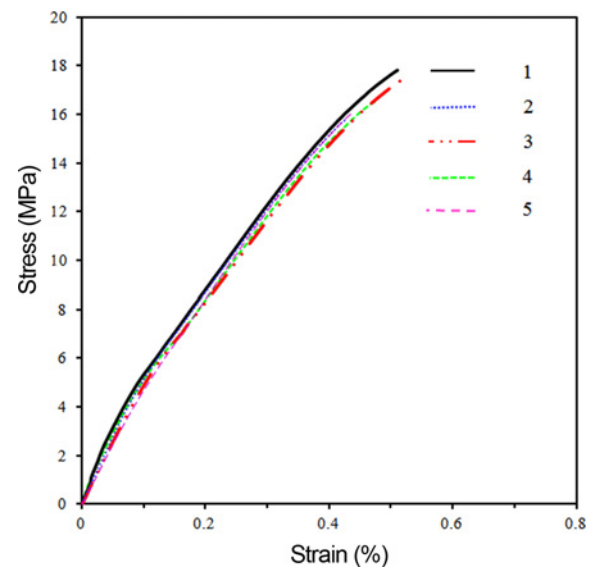


Figure 8. Stress-strain curves of five PLA specimens.

showed the initial weight loss around 100°C due to moisture evaporation. The first decomposition peak was found at 356°C indicating the decomposition of the heat resistant additive in the PLA. The second peak was shown at 394°C, indicating the decomposition of PLA, which is in accordance with that reported in literature [12]. Together with the data obtained from DSC, the decomposition information from TGA analysis was used as the useful information to choose the optimum temperature for the composite preparation, in order to prevent the degradation of both PLA and PALF during processing. Therefore, the processing temperatures at 120°C (in the twin-screw extruder), 140°C (in the two-roll mill) and 160°C (in the injection molding) were suitable to process the composites in molten state without causing any significant degree of degradation for both PLA and PALF.

Figure 8 demonstrates the typical stress-strain curve of 5 specimens of PLA, showing failure pattern of brittle materials. The elongation at break of PLA was $0.3 \pm 0.05\%$, while the tensile strength and tensile modulus were 8.5 ± 1.1 MPa and 2.7 ± 0.1 GPa, respectively.

Characterization of PALF/PLA Composites

Thermo Gravimetric Analysis

TGA was carried out to evaluate the thermal behavior of the composites. TGA and DTG curves for the PALF/PLA composites are illustrated in Figure 9. In the figure, all the PALF/PLA composites showed almost the same thermal behavior. There was an initial transition in the range 30-100°C, due to volatile materials and moisture evaporation, followed by two main regions of degradation. The first region of degradation occurred in the temperature range 225-370°C, showing the decomposition peak at 350°C, was due to the thermal degradation of cellulose, hemicelluloses

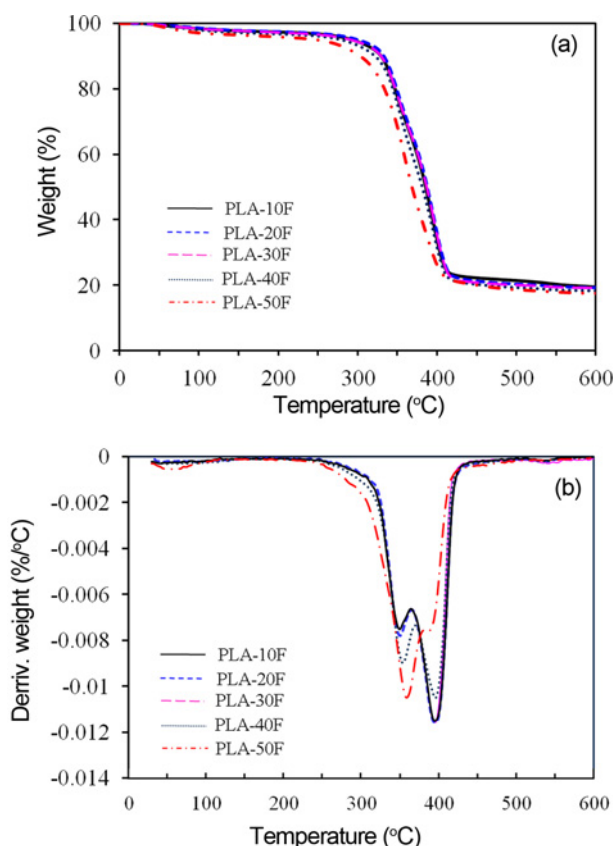


Figure 9. TGA (a) and DTG (b) thermograms showing thermal stability of PALF/PLA composites.

and lignin in PALF [20,21]. The second region occurred at higher temperatures, ranging from 370–415 °C, showing the decomposition peak at 396 °C, was attributed to depolymerization of the PLA matrix [23]. Moreover, it's clearly seen in the DTG curves that the composites with higher PALF content showed higher amount of moisture released. The degradation of cellulosic substances such as hemicellulose and cellulose in PALF started at about 225 °C, followed by the decomposition of PLA, starting at 370 °C, and the degradation of such composites completed at about 500 °C, leaving char residue of 17–20 % depending on the amount of PALF. The higher the PALF content, the lower the amount of char residue was. Additionally, the thermal stability of the composites also depended on the amount of PALF. The composites with lower amount of PALF showed higher thermal stability. Conclusively, the results obtained from TGA indicated that all the PALF/PLA composites are thermally stable up to 225 °C.

Tensile Properties

Figure 10 exhibits tensile properties of PALF/PLA composites as a function of PALF content. It can be seen from Figure 10(a) that both the tensile strength and tensile modulus of the composites were significantly improved with increasing PALF loading content. Figure 10(b) shows the elongation at

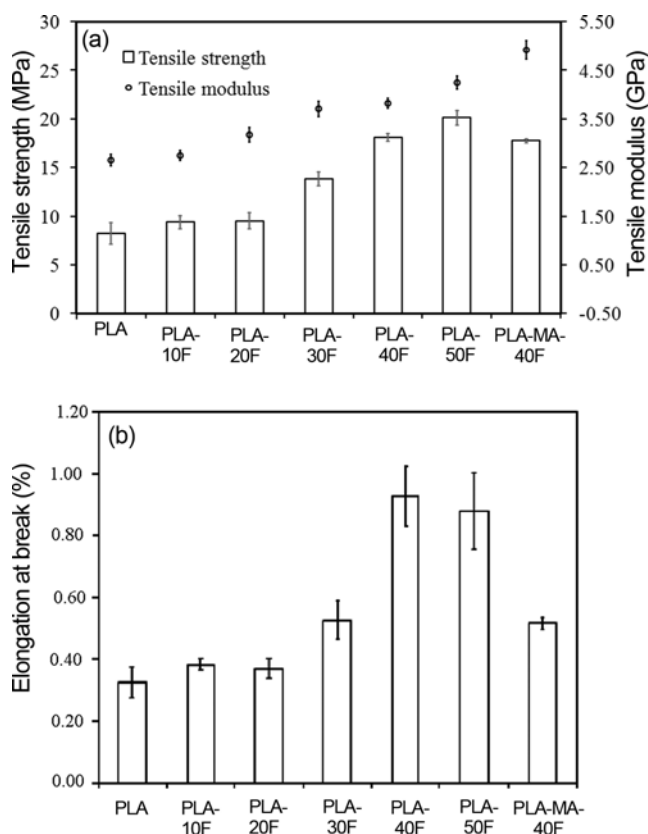


Figure 10. Tensile properties of PALF/PLA composites showing (a) tensile strength and tensile modulus and (b) elongation at break.

break of composites. Such the composites displayed higher elongation at break when PALF content increased from 10 to 40 wt%. However, when the fiber content was increased up to 50 wt%, the composites showed the decrease in the elongation at break, due to the aggregation of PALF.

In order to choose the optimum composition of PALF/PLA composite to mix with MA coupling agent for improving their mechanical properties, the composites with different amount of PALF were mixed in a two-roll mill machine. Then the composite pellets were produced by a Brabender co-rotating twin-screw extruder. At 50 wt% PALF content, it was very difficult for the rollers to move during mixing by two-roll mill machine, due to the increment of frictional forces, experienced during processing. Too high content of PALF resulted in long milling time and high energy consumption, in order to obtain homogeneous distribution of the fibers in PLA matrix. In addition, the composites pellets released from two-roll mill were also difficult to be further conveyed into the twin screw extruder. Thus, the composites with 40 wt% PALF content was chosen to mix with MA coupling agent, namely PLA-MA-40F. The tensile testing results showed the improvement in tensile strength and tensile modulus of such the composite with addition of 10 wt% maleic anhydride (MA) coupling agent. However,

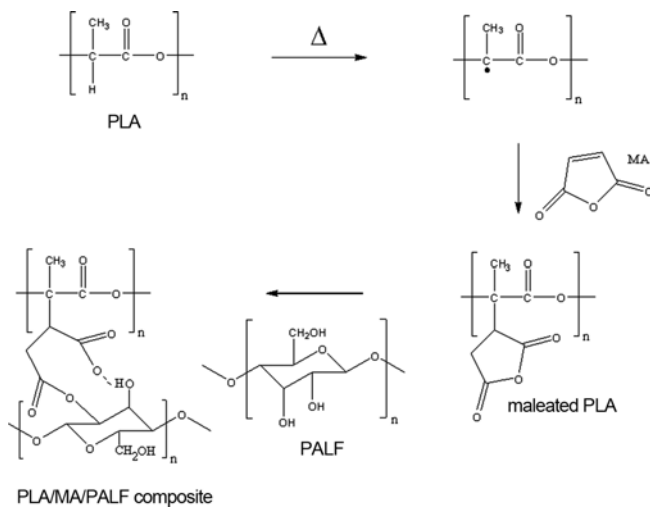


Figure 11. Proposed chemical reactions of PLA, MA, and PALF.

PLA-MA-40F showed the lower elongation at break compared with PLA-40F. The improved tensile modulus (by 34 %) and the lower elongation at break (by 40 %) were the results of the formation of branched and cross linked macromolecules in PLA-MA-40F by reactions between anhydride carboxyl groups in PLA-g-MA and the hydroxyl groups of PALF [13,24], as illustrated in Figure 11. Hence the interfacial adhesion between the matrix and the fibers was improved (as also evidenced by SEM micrographs demonstrated in Figure 13). The results are in good agreement with the results presented in literature [25].

Fractured Surface Morphology

The fractured surface morphology of PALF/PLA composites is shown in Figure 12. The figure indicated well dispersion of PALF fibers in PLA matrix when the fiber content was 10 %. As the fiber loading increased to 40 and 50 %, the aggregation of the fibers as well as void formation were

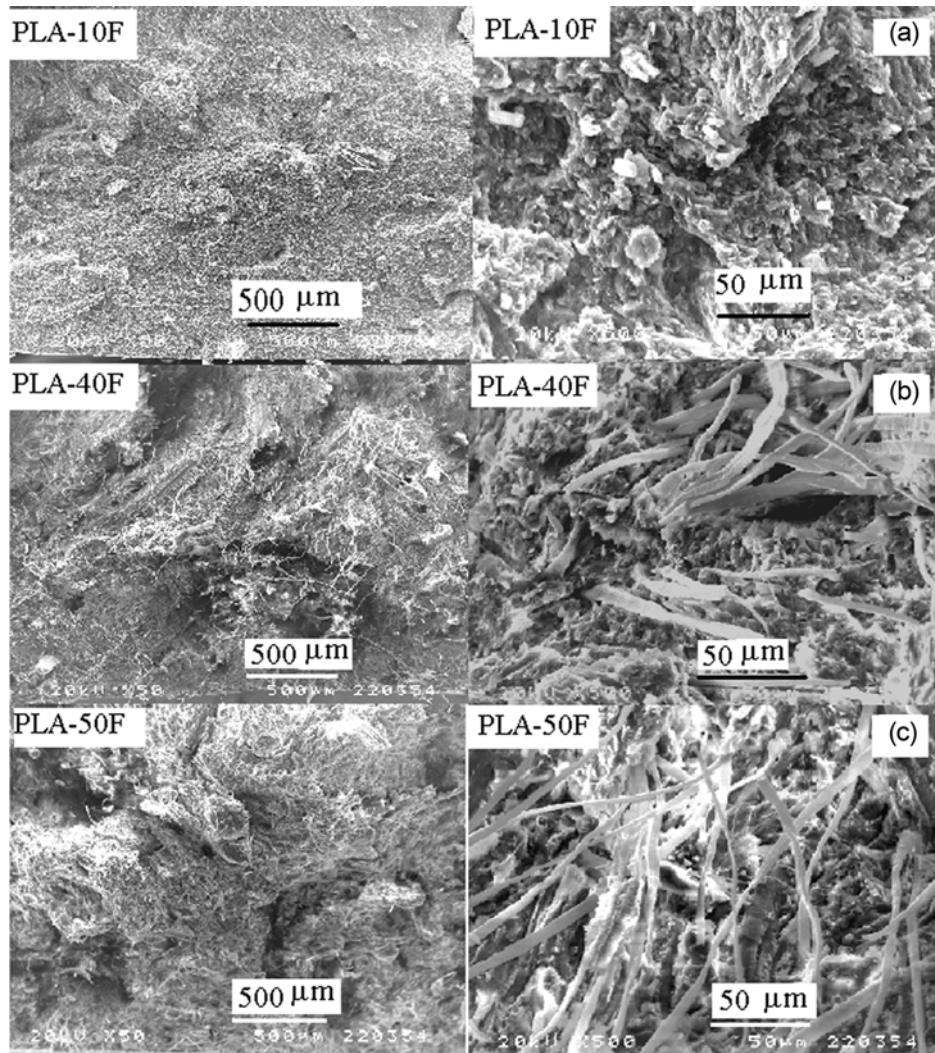


Figure 12. SEM micrographs demonstrating fractured surfaces of PALF/PLA composites containing; (a) 10, (b) 40, and (c) 50 wt% of PALF at the magnifications of $\times 50$ and $\times 500$.

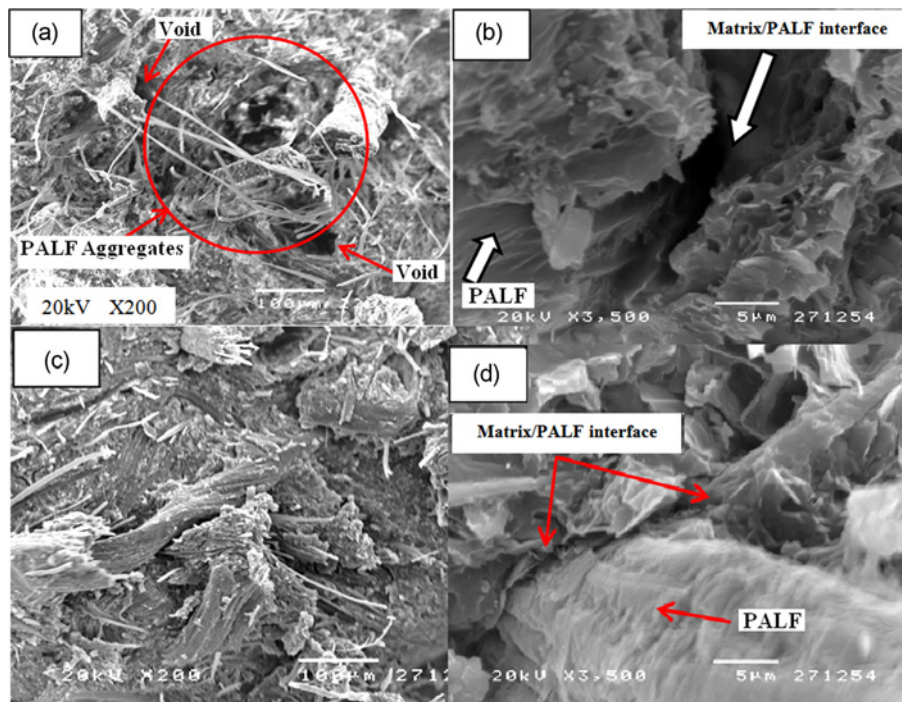


Figure 13. SEM micrographs showing fractured surface morphology of PALF/PLA composites containing 40 % PALF; (a) PALF aggregation in the composites without MA, (b) poor adhesion between PALF and PLA matrix, (c) better PALF dispersion in PLA matrix after the introduction of MA, and (d) good adhesion between PALF and PLA matrix.

clearly evidenced. Figure 13(a) shows SEM image of fractured surface for PLA-40F. The figure indicated poor dispersion and voids. The PALF aggregation was highlighted with a circular, and voids indicated by the arrows. The wide gap at the interface was shown in Figure 13(b). This was the feature that made the composite poor in tensile modulus. Figure 13(c) showed the fractured surface of PLA-MA-40F. It can be seen from the figure that the fibers became more dispersed, and the fiber aggregation and voids were decreased, bringing about good adhesion between PALF and PLA matrix, at the interface (Figure 13(d)). These reflect that with addition of a coupling agent, the adhesion between PALF-PLA interface was improved, resulting in the better mechanical properties of the composite. The results are in good accordance with the results reported in literatures [19,25].

Pilot Product from the Composites

To evaluate the prospective for industrial use of green composites, the possibility to be produced by conventional manufacturing process is vary important. Figure 14 shows a pilot product of rectangular boxes, made from PLA-MA-40F composite. It can be confirmed that the molten composite (at 140 °C) could flow through the flow path and filled-up the mold cavity. This reflected the processability of the proposed composite, using conventional injection molding technique, and PLA worked very well as the matrix for PALF composite. Moreover, the results shown previously confirmed that the mechanical properties of PLA-MA-40F were high enough

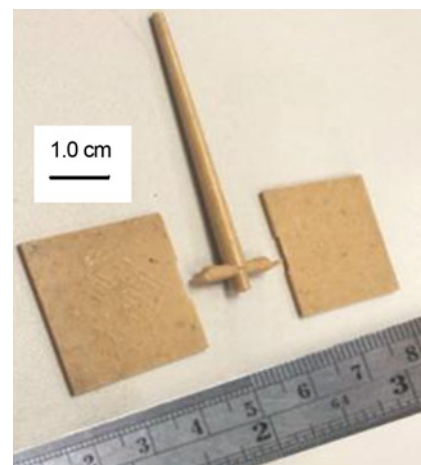


Figure 14. A pilot product made from PLA-MA-40F by conventional injection molding process.

for use instead of some conventional thermoplastic composites, which are used today in many industrial applications such as car seat [26], automotive panels [10], and construction materials [27,28].

Conclusion

In this investigation, it was shown that pineapple leaf

fiber-reinforced poly(lactic acid) green composites were successfully prepared, using a twin screw extruder. Mechanical properties of PALF, at different positions along the leaf length, were significantly different. The PALF obtained from the leaf tip and the leaf center showed slightly different in tensile strength and tensile modulus, which were obviously greater than those of the PALF obtained from the leaf base. Moreover, PALF exhibited rough surface, indicating the ability to be used as reinforcement for PLA matrix and resulting in good adhesion between PALF and PLA matrix, by mechanical interlocking. Tensile properties of PALF/PLA composites were significantly improved by increasing PALF loading content. PALF reinforced PLA composite containing 40 % fiber showed optimum tensile properties. Although the introduction of 10 wt% MA coupling agent helped to further improve in tensile modulus of the composite, it reduced the elongation at break. The fractured surface morphology of the composite containing MA showed well dispersion of the fibers in PLA matrix, as well as the reduction in their aggregation and voids, resulting from better adhesion at the interface between the fiber and PLA matrix.

The possibility to use conventional manufacturing processes is a very important factor for industrial use of green composites. In this study, PALF/PLA composites with 40 % PALF did not show any difficulty in extrusion and injection molding processes and can be processed in a similar way as other commodity plastics.

Acknowledgements

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