Jurnal
Teknologi

Full Paper

THE EFFECT OF ALKALINE TREATMENT AND FIBER LENGTH ON PINEAPPLE LEAF FIBER REINFORCED POLY LACTIC ACID BIOCOMPOSITES

Article history
Received
30 August 2016
Received in revised form
13 November 2016
Accepted
13 March 2017

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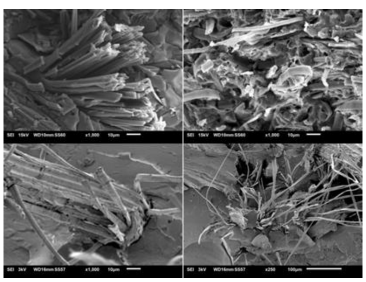
Graphical abstract



Abstract

The awareness of natural fibers as alternative materials to synthetic fibers in composite applications have increased briskly due to lightweight, non-toxic, low cost and abundantly available. To-date, there are still limited works on fully biodegradable composites also known as biocomposites, especially using long pineapple leaf fiber (PALF) reinforced poly lactic acid biocomposites. Thus, this study presents an investigation of the effects of alkaline treatment and use of different fiber length on the mechanical performance of pineapple leaf fibers reinforced poly lactic acid, biocomposites. Flexural testing was conducted via ASTM D790. The results showed enhancement in flexural properties of the biocomposites when the PALF fibers were treated with alkaline treatment, suggesting an effect of improving mechanical interlocking between matrix and reinforcement due to rougher fiber surface. The flexural strength and modulus of long treated fibers increased from 56.47 MPa and 4.24 GPa to 114.03 MPa and 5.70 GPa respectively compared to long untreated fibers. In addition, the effect of fiber length is also proven to affect the overall performance of the biocomposites, in which the long PALF fiber composites exhibit superior flexural properties to those of the short fiber reinforced PLA biocomposites, i.e. flexural modulus of 5.7 GPa and 0.22 GPa for the long fiber composites and short fiber composites respectively. The existence of sodium hydroxide, (NaOH) on PALF fibers were confirmed by FTIR analysis. Surface morphology of both untreated and treated samples was studied by using a scanning electron microscope (SEM). Results from both analyses suggest removal of lignin and hemicellulose on the alkaline-treated PALF fiber reinforced composites led to a rougher fibers surface and formed a better fiber-matrix adhesion, as reflected in the flexural properties of the biocomposites as reported above.

Keywords: Biocomposites, pineapple leaf fiber, microstructure, chemical treatment, fibre length

1.0 INTRODUCTION

Recently, there is a growing attention in the development of research on natural fiber reinforced composites or biocomposites, in widespread applications, including automotive, construction and aerospace [1–3]. Typically, synthetic fibers like aramid, carbon and glass are used to fabricate the composites along with synthetic polymer. However, there are two crucial issues, which are (i) relatively higher material cost and (ii) alarming issues with the environment, leading to the urge to find substitute materials, such as biocomposites [4, 5].

Malaysia ranked ninth among exporter country in the world market with total production of 452,019.75 metric ton for pineapple annually [6]. Pineapple leaf fibers (PALF) exhibits better mechanical properties compared to other naturals fibers due to their high cellulose (70 – 82 %) and low lignin (5-12 %) contents [7]. Table 1 shows the detail mechanical properties of some natural fibers over the world production.

Table 1 The mechanical properties of natural fibers [8, 9]

Fibers	Density (g/cm)	Tensile Strength (MPa)	Elastic Modulus (GPa)	World production (10^3 tonnes)
Bamboo	0.6-1.1	140-1150	11-17	30000
Bagasse	1.25	290	17	75000
Jute	1.3	393–773	26.5	2300
Kenaf	1.45	930	53	970
Pineapple	0.8-1.6	400-627	14.5	2200

Poly lactic acid (PLA) is a biodegradable polymer, produced from fermentation process that possesses promising strength in most practical applications. However, one of the disadvantages of PLA is brittleness, and a way to improve the mechanical properties of PLA is by adding reinforcement or filler materials [10, 11]. Therefore, it is necessary to introduce a suitable chemical treatment prior to fabricating the biocomposites samples. Furthermore, these allow reduction in the hydrophilic nature of the natural fibers as well as removing the impurities within the fibers [12–14], resulting in an improvement in adhesion between the fiber and the matrix [12, 15]. According to Huda *et al*. [16], the treated kenaf fibers with NaOH resulted in an improvement from 5.6 MPa for untreated kenaf to 8.3 GPa for treated Kenaf, with a 34% increase in flexural strength. Meanwhile, in flexural modulus, a 48% increase for untreated to treated kenaf fibers was observed, which is from 42 MPa to 56.3 MPa, respectively. Recently, it is proven that short PALF fiber treated with NaOH resulted in superior mechanical properties, in comparison to the untreated short PALF fiber with enhancement from 33.64 MPa to 107.53 MPa and 0.22 GPa to 0.32 GPa of flexural strength and flexural modulus, respectively [17].

The goal of this research is to study the effect of alkaline treatment as well as fiber length on mechanical properties of the PALF fiber reinforced PLA biocomposites. Three different samples were tested; (i) untreated-short PALF fiber reinforced PLA biocomposites (PALFS), (ii) alkaline-treated short PALF fiber reinforced PLA biocomposites (PALFSNA), (iii) long untreated PALF fiber reinforced PLA biocomposites (PALFLO) and (iv) long alkaline-treated PALF fiber reinforced PLA biocomposites (PALFLONA). Mechanical properties of the biocomposites.

2.0 METHODOLOGY

Poly lactic acid (PLA) of 6100D grade supplied by NatureWorks, LLC, USA is used as a matrix material for the biocomposites. Pineapple leaf fibers (PALF) from Josephine species were used as reinforcement from Pontian, Johor. The properties of PALF and PLA are given in Table 2. Sodium hydroxide (NaOH) was purchased from Merck Chemicals Sdn. Bhd.

Table 2 The properties of the PALF and PLA

Properties	PALF [9]	PLA 6100D
Density g/cm³	1.53	1.08
Tensile strength (MPa)	170	62
Tensile Modulus (GPa)	1.44	-
Elongation (%)	14.5	10-70
Glass transition temperature (°C)	-	55-60
Melting Temperature (°C)	-	165-180
Transition Temperature (°C)	-	60

2.1 Surface Modifications Treatments

PALF fibers were soaked in water bath solution containing 5% NaOH at room temperature for an hour. Following this, the PALF fibers were rinsed with distilled water repeatedly until reaching pH value of 7 to ensure that the NaOH solution was fully removed. Consequently, the treated fibers were air dried for 2 days. To ensure that the treated PALF fibers were completely dried, the treated PALF fibers were dried using a vacuum oven overnight at temperature of 60°C. The fibers were cut to final fiber length of 30 mm and 200 mm respectively.

2.2 Biocomposites Preparation

In this study, both types of biocomposites samples were fabricated with 30 wt. % of fiber loading and 70 wt. % of PLA matrix. For the short PALF reinforced PLA biocomposites, melt-mixing process was considered. Here, PALF fiber used is of 30 mm in length. The raw materials were fed into the internal mixer via a ThermoHaake machine for 15 minutes at temperature up to 175°C and rotor speed of 50 min^{-1}. The same steps were repeated for both untreated and NaOH treated fibers. The composite blend was then compression molded using a Hot Isostatic Press using a stainless steel mold platen. The mold was pre-heated for 2 minutes and then pressed under a pressure of 200 psi at a setting temperature of 175 °C for 10 minutes and followed by cooling process. Meanwhile, the long biocomposites were produced by using hand lamination. PALF long fibers (100 mm) were sandwiched in between 0.3 mm-thick PLA thin film which were compressed molded. The processing temperature was set up to 175ºC and a maximum pressure of 1700 psi, with a contact time of 10 minutes, prior to cooling under zero pressure. The biocomposites were cut into 74 mm x 15 mm x 3 mm for flexural testing.

2.3 Mechanical Characterization via Flexural Testing

A Universal Testing Machine (UTM) model INSTRON 5585 was used to measure the flexural properties according to ASTM D790. The test was carried out at crosshead displacement rate of 2 mm/min using a span ratio of 16:1. A minimum of five samples were tested for each types of biocomposites produced.

2.4 Fourier Transform Infrared Spectroscopy Analysis (FTIR)

FTIR analysis was run to examine the changes in functional groups of untreated and NaOH treated fibers. The samples were analyzed in transmittance mode within the range of 600-2200 cm and a wavelength resolutions of 2 cm^{-1}.

2.5 Scanning Electron Microscopy

The fracture morphology of PALF reinforced PLA biocomposites were studied using JEOL JSM-6010 Plus/LV (Joel, Japan) at accelerated voltage of 3kV. Prior to the test the sample was platinum coated in sputter coater of JEOL JEC-3000FC, to reduce the charging effect. The samples were viewed perpendicular to fracture surfaced.

3.0 RESULTS AND DISCUSSION

3.1 The Effect of Alkaline Treatment on Mechanical Properties of Short Fibers

Figure 1 shows the flexural properties of the short PALF fibers reinforced PLA biocomposites. Both the flexural strength and flexural modulus of short PALF fibers reinforced PLA biocomposites (untreated and treated) exhibit notable enhancement due to the effect of fiber surface modifications.

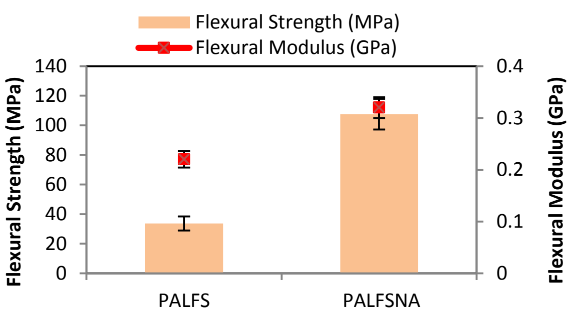


Figure 1 Flexural properties of short PALF fiber reinforced PLA biocomposites

Clearly, it is proven that NaOH-treatment enhanced the flexural properties of the biocomposites, with an increase in flexural strength and modulus of 46% and 220% for the untreated and treated biocomposites respectively.

It can also be suggested that the NaOH treatment created rougher surface of the fibers, resulting in enhanced interfacial adhesion, therefore inducing better fiber-matrix interlocking and consequently enhance the mechanical performance of the composites [10].

3.2 Effect of Fiber Length on Flexural Properties of PALF Biocomposites

Figure 2 illustrates the flexural properties of short and long PALF fibers reinforced PLA biocomposites, for both untreated and treated samples. In general, the long fiber reinforced biocomposites exhibit much higher strength and modulus, regardless of whether the fibers were alkaline-treated or not. Moreover, with the introduction of alkaline treatment on the fibers, there is a significant increase in the flexural properties of the composites, with the long PALF fiber reinforced PLA biocomposites showing a maximum strength of approximately 114.03 MPa, in comparison to only 33.64 MPa for the untreated PALF short fiber reinforced PLA composites.

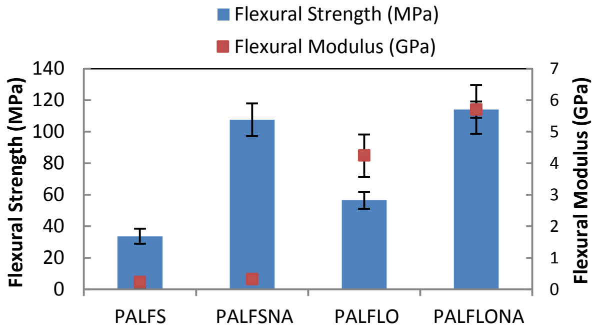


Figure 2 Flexural properties of PALF biocomposites

In terms of stiffness, the flexural modulus of the long fiber reinforced biocomposites is approximately 5.70 GPa, in comparison to only 0.22 GPa for the untreated PALF short fiber reinforced PLA biocomposites. These findings suggest that long fibers result in better mechanical properties in comparison to the short fibers. These results reflect the significant contribution of fiber length on the mechanical properties of PALF fibers reinforce PLA-based biocomposites. According to Lee *et al*. [11], the randomly oriented chopped fiber reinforcement, resulting in the less degree of fiber alignment in the matrix.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3 shows the FTIR spectra, revealing several changes which occurred in both the untreated and treated PALF biocomposites. The peaks corresponding (a) the vibrations peaks at 1174 cm^{-1}, which belongs to a C-O stretching vibrations of acetyl group in lignin component and (b) the peaks at 1735 cm^{-1}, assigned to a C=O stretching vibration of carboxylic acid or ester, indicates the disappeared in the spectrum of NaOH treated PALF.

Both peaks correspond to the stretching vibrations in cellulose and hemicellulose [18]. The decreased peaks indicated the chemical treatment of NaOH removed some of the hemicellulose. These results indicated that the NaOH treatment leads to the partial removal of lignin and hemicellulose.

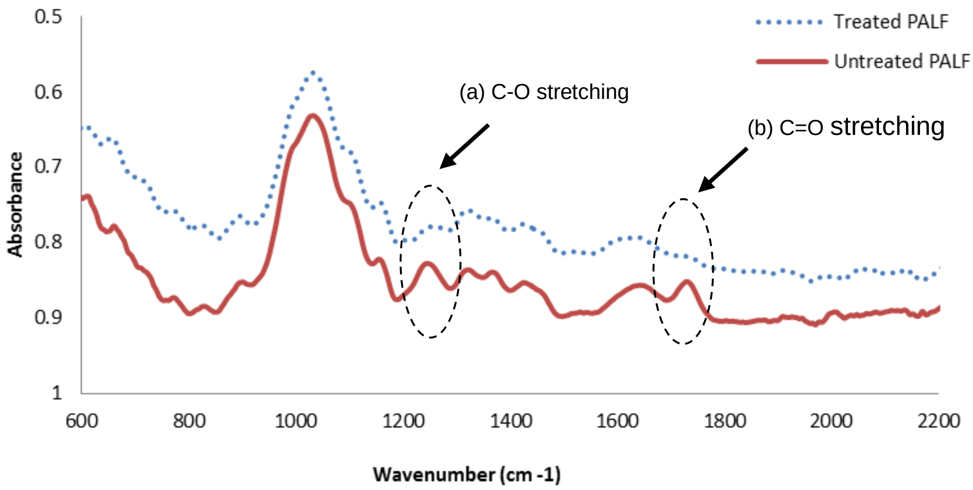


Figure 3 FTIR spectra showing (a) treated PALF fibers and (b) untreated PALF fibers

3.4 Scanning Electron Microscopy (SEM)

Figures 4 to 6 demonstrates the SEM micrographs of short and long PALF reinforced biocomposites of untreated and treated samples following flexural testing. In Figure 4 and 5, the effect of surface treatment via NaOH treatment on the fractured surface of PALF fibers are observed, showing the interface between the PALF fibers and PLA matrix. The micrographs revealed smooth surface in the untreated short PALF/PLA biocomposites as shown in Figure 4. Meanwhile, in Figure 5, it is evident that physical microstructural alterations occurred on the treated short PALF reinforced PLA biocomposites, with rougher surface. Improved adhesion between treated PALF fibers and PLA matrix are achieved resulting from elimination of impurities during the alkaline pre-treatment process of the fibers.

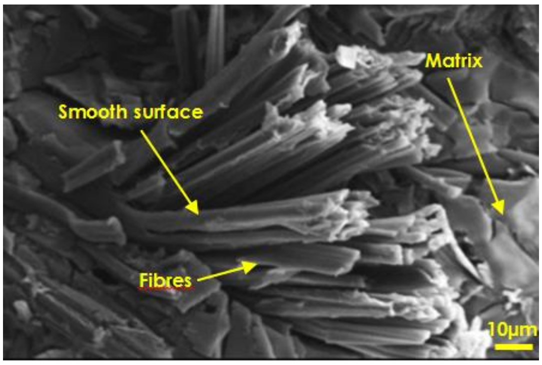


Figure 4 SEM micrograph of untreated short PALF reinforced PLA biocomposites following flexural test

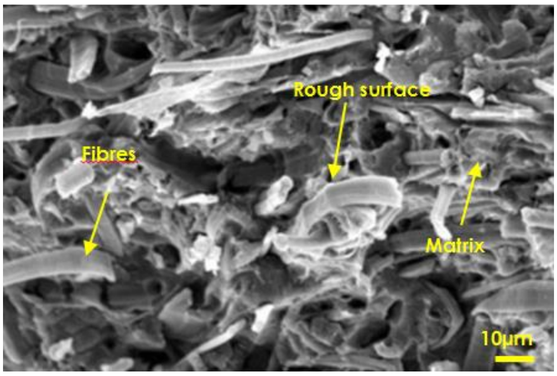


Figure 5 SEM micrograph of treated short PALF reinforced PLA biocomposites following flexural test

In addition, SEM micrograph (Figure 6) of the fractured long treated PALF fiber reinforced biocomposites sample is given. Figure 6 (a) shows presence of voids at the surface and fibers breakage. Fibers pull-out is an indication of poor wettability or matrix/fibers adhesion. Meanwhile, in Figure 6 (b), for the treated-PALF fiber reinforced PLA biocomposites, it is apparent that good wetting between the PLA matrix and the treated PALF fibers promotes better adhesion at the interface between PLA and PALF. These observations suggest that the addition of sodium hydroxide and long fibers enhance the adhesion between PLA and PALF interface which results in better mechanical properties of the biocomposites by increasing the fiber surface roughness.

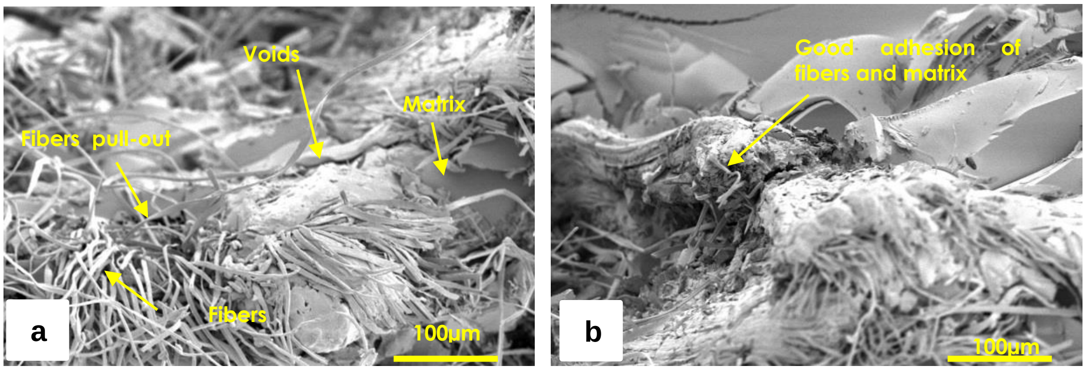


Figure 6 SEM micrograph of treated-long PALF fiber reinforced biocomposites following flexural test at magnifications of X250

5.0 CONCLUSION

Experimental results from this study suggest an enhanced performance in the mechanical properties of the biocomposites is due to an improve adhesion achieved by introducing alkaline treatment of the fibers, thereby causing rough surface at the fiber-matrix interface. In addition, the decrease in the spectra peaks of the FTIR analysis suggest removal of lignin and hemicellulose on the alkaline-treated PALF fiber reinforced composites in comparison to those of the untreated composites. SEM images revealed that alkaline surface treatment is effective in removing impurities and creating a rougher fibers surface and formed a better fiber-matrix adhesion. An extended study on this composites will be focused on the dynamic and quasi-static response of the alkaline-treated long PALF reinforced PLA biocomposites.

Acknowledgements

The authors are grateful to the Ministry of Higher Education (MOHE), Malaysia Ministry of Science, Technology and Innovation for sponsoring this work under RAGS/1/2014/TK04/FKM/02/B00069 research grant. Special thanks to Advanced Material Research Group (A-MAT), Faculty of Mechanical Engineering, University Teknikal Malaysia Melaka (UTeM) for technical support involved throughout this research project.

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