Fabrication of non-woven hybrid natural fiber/poly(lactic acid) composite via prepreg lamination

J Khieomuang and C Thongpin*

Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000, Thailand

*Corresponding author: THONGPIN_C@su.ac.th.

Abstract. Hybrid natural fiber-reinforced polylactic acid (PLA) composites were prepared using a prepreg lamination. Two types of the long continuous natural fibers, i.e. sisal fiber (SF) and pineapple leaf fiber (PALF) were used in this work. The SF and PALF were treated using alkalization (NaOH) and then silane coupling agent (APS) to improve the interfacial bonding between fiber and PLA. After the surface treatment, the chemical group on the surface of SF and PALF were analyzed by Fourier transform infrared (FTIR). The FTIR result confirmed that hemicellulose and lignin were removed and also silane was grafted on the fiber surface. The micrographs by scanning electron microscopy (SEM) of the fibers observed morphological change of the fiber surface. The surface treatment improved the thermal stability of fiber as detected by thermogravimetry analyzer (TGA). The tensile strength of single SF and PALF were increased after surface treatment by alkalization and silane, respectively. Moreover, the tensile strength increases as an increase in the fiber length. Thus, the hybrid natural fiber/PLA composites showed high tensile properties compared with SF/PLA, PALF/PLA composites and pure PLA.

1. Introduction

Nowadays, the automotive industry is growing and widely used. The automobile parts are generally manufactured from plastics derived from the petroleum industry. When the cycle life is expired or damage occurs from the accident, it will become refuse and affect the environment because it cannot be naturally decomposed. Various agencies have seen problems with the issuance of regulations regarding the production of equipment. For example, end-of-life vehicles or ELVs in Europe declared new rules and regulation for vehicle recycling. [1] In addition, the entrepreneurs are turning to the use of bioplastics instead of plastic from petroleum industrial. The interesting bioplastic is polylactic acid (PLA) because the price is not very high and the physical and mechanical properties of PLA are comparable to other plastics used in the automotive industry. PLA has better young modulus values that can be used to replace these plastics but PLA has brittle. [2] Therefore, reinforcement of PLA by natural fibers to make the material stronger is one of interesting approaches. Natural fiber has high strength and lightweight. [3] Moreover, there are many types of fiber in Thailand such as pineapple leaf fiber and sisal fiber. Both of the fibers have good mechanical properties. The reinforcing natural fiber in PLA matrix can improve mechanical properties of composites and the surface treatment of fiber will improve interfacial properties between fiber and polymer were proposed in the literature. [4-6] Asaithambi et al. studied the effect of fiber surface treatment by benzoyl peroxide (BP) of banana/sisal fiber (BSF) reinforced Polylactic acid (PLA), had on the mechanical properties of the composite. It was found that tensile and flexural modulus of BP treated BSF increase compared with virgin PLA and untreated BSF
reinforced composites. [7] The concept of this work is to use the pineapple leaf and sisal fibers in continuous and non-woven fiber to reinforce PLA and study the effect of surface treatments as well as fiber length on mechanical properties of single sisal and pineapple leaf fibers. The mechanical properties of hybrid long natural fiber reinforced PLA composites were also evaluated, which is eco-friendly environment materials for application in automotive application.

2. Experimental

2.1. Materials
PLA pellet was provided from Nature Works LLC (Minnetonka, USA). In this work, the sisal fiber (SF) and pineapple leaf fiber (PALF) obtained from Phetchabun and Songkhla Province, Thailand. The length of both fibers was 150±3.0 mm and the diameter was 0.14±0.04 mm (L/D ratio of 1093.5±330.1). Sodium hydroxide pellet supplied by RCI Labscan Limited (Bangkok, Thailand) and 3-aminopropyl triethoxysilane, APS (supplied by Sigma-Aldrich (San Luis, USA)) were used as fiber surface modifiers. Glacial acetic acid was also supplied by RCI Labscan Limited.

2.2. Fiber surface treatments
The SF and PALF, they were treated with 5 wt% NaOH solution for 3 h at room temperature using a fiber/NaOH solution ratio of 1:10 (w/v) to remove hemicellulose and lignin. And then the fibers were washed and dried at 60 °C for 12 h. After that, the alkalized fibers were soaked in silane aqueous solution (5% v/v) at room temperature for 3 h. The pH of solution was adjusted to 3-4 with glacial acetic acid and fiber/silane solution ratio of 1:10 (w/v). Finally, the fibers were washed in reverse osmosis water to neutralize the fiber surface and dried at 60 °C for 12 h.

2.3. Preparation of prepreg laminate composites
Before fabrication of the prepreg laminate composites, The PLA pellet and fibers (SF and PALF) were oven-dried at 60 °C for 12 h. The preparation of prepreg laminate composites contained two stages. In the first stage, PLA sheet was prepared with thickness of 0.8 mm using compression moulding at pressure 800 psi and temperature 170 °C. The fiber were threaded around aluminium frame (15×15×0.15 cm). The PLA sheet was placed on top and bottom of the frame and then pressed inside compression moulding at 170 °C to obtain unidirectional fiber prepreg with PLA as a matrix in thickness 1.5 mm. SF prepreg and PALF prepreg were laminated and pressed as the same condition. Finally, the unidirectional hybrid natural fiber/PLA composite with 15% fiber content (The PALF/SF ratio of 0.5:0.5 (v/v)) was obtained.

2.4. Characterization and Testing
Fourier transform infrared (FTIR) spectroscopy was used to analyse the characteristic functional groups of natural fibers before and after chemical surface treatment. In order to study the thermal stability of untreated and treated natural fiber a TGA (Mettler Toledo) was used and carried out in nitrogen atmosphere between 50 to 600 °C at a heating rate of 10 °C/min. Morphology of fiber surface and fractured surface of prepreg laminate composite were investigated using a Hitachi TM3030 SEM. The tensile test of natural fiber was carried out based on ASTM D3288. Natural single fiber was randomly chosen, mounted and glued on a paper tape before measurement. The tensile testing was performed using Instron 5969 with the sample gage length of 2.5, 5 and 10 cm and crosshead speed of 1 mm/min with a 5kN-load cell. The tensile test of prepreg laminate composites was carried out using Instron 5969 with 5kN-load cell according to standard methods ASTM D638 type IV. The crosshead speed of 50 mm/min and the wide and thickness of tensile specimen are 6 mm and 3 mm, respectively.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy
FTIR spectra of untreated sisal fiber (Un SF) as presented in Figure 1(a) showed the board peak around 3400 cm⁻¹ attributed to OH stretching whereas peak at 2900 cm⁻¹ is CH stretching of alkyl group in
aliphatic bond of cellulose, hemicellulose and lignin. After Alkaline treatment (Na_SF), peak at 1724 cm$^{-1}$ of C=O stretching vibration and 1222 cm$^{-1}$ of C-O-C symmetrical stretching were decreased. This result confirmed that hemicellulose and lignin were partially removed from the surface of fiber. The fibers after silane treatment (APS_SF) showed peak at 1506 cm$^{-1}$ of NH$_2$ vibration indicating that silane successfully grafted on the fibers. Similar result of untreated pineapple leaf fiber (Un_PALF) and its surface treatment (Na_PALF, APS_PALF) was found in other researchs. [8-9]

3.2. Thermogravimetric analysis
The Figure 2 presents TGA and DTG thermograms of SF and PALF. Both of Un_SF and Un_PALF show three stages of thermal decompositions. The first stage is evaporation of water around 70 °C. The second stage around 295 °C indicating degradation of hemicellulose and the late stage around 358 °C attributed to degradation of cellulose and lignin. After surface treatment fiber with alkaline and silane coupling agent, the thermograms reveals two stages of decomposition which indicates that hemicellulose and lignin were removed, in agreement with FTIR spectra. The thermal decomposition temperation of Na_SF, APS_SF, Na_PALF and APS_PALF were 360.35, 353.27, 363.71 and 359.41 °C, respectively. The thermal stability of treatment fiber was higher than untrearment fiber because remaining cellulose had natural crystalline structure. It can also be seen that the thermal stability of alkali-treated fiber was slightly higher than those of APS-treated and untreated fiber. In addition, the residue of APS-treated fiber has higher char percentage than those of alkali-treated and untreated fiber. [6-9]
3.3. Surface morphology of fibers

The Figure 3 display surface morphology of untreated and treated SF and PALF. Un_SF has rough surface due to a presence of some component such as lignin and hemicellulose covering on the surface. The Na_SF surface in figure 3(b) seems become smoother than the untreated fiber due to remove of hemicellulose and lignin on the fiber surface. APS_SF as showed in figure 3(c) has smooth surface and appears siloxane deposited on the surface. The surface morphology of PALF (Figure 3(d)-(f)) like same as sisal fiber. Thus, these morphology results confirm the change of fiber surface after surface treatment. [8-9]

3.4. Tensile properties of fiber

The effect of surface treatment and fiber length on tensile strength, Young’s modulus and elongation at break of SF and PALF is shown in figure 4. The tensile strength and Young’s modulus of SF and PALF increased when modified surface because hemicellulose and lignin were removed, resulting in an increase in degree of cellulose. Moreover, the tensile strength and Young’s modulus of fiber increased when fiber length increased because long fiber have more surface area than short fiber. Elongation at break of SF and PALF increase after alkaline treatment and decreased after silane treatment. Moreover, the variability of tensile properties was probably related to a microstructure of fiber. [9-10]
3.5. Tensile properties of prepreg laminate composites
The effect of surface treatment on tensile strength, Young’s modulus and elongation at break of hybrid fiber reinforcement PLA composite is shown in figure 5. The tensile strengths of composite with untreated pineapple leaf fiber (Un_PALF) and untreated sisal fiber (Un_SF) were higher than that of pure PLA. In the case of composite with untreated hybrid natural fiber (Un_HF) has higher tensile strength and Young’s modulus but lower elongation at break compared with pure PLA, Un_SF and Un_PALF. The composite with APS-treated hybrid natural fiber (APS_HF) had lower tensile strength and Young’s modulus but higher elongation at break compared with Un_HF composite. This may be attributed to weak improvement effect of silane on fiber surface. Moreover, acid catalyst condition in silane surface treatment of fiber may be destroyed bond of cellulose structure. [8]

3.6. Fracture surface morphology of prepreg laminate composites
The SEM micrographs of fracture surface shown in Figure 7. The Un_PALF, Un_SF and Un_HF laminated composites (Figure 6(a)-(c)) showed a fiber breakage, fiber pull out and matrix debonding, indicating poor interfacial bonding between fiber and matrix. In the case of APS_HF composite shown in Figure 7(d) seen that some fiber well trapped with PLA matrix, which expected that mechanical properties of APS_HF composite should improve. However, the tensile properties of APS_HF composite were lower than Un_HF composite.
Figure 6. SEM micrographs of prepreg laminate composites. (a) Un_PALF, (b) Un_SF, (c) Un_HF and (d) APS_HF.

4. Conclusion
In this work, the hybrid long natural fiber/PLA composites were prepared using prepreg laminate method. The natural fiber, i.e. sisal and pineapple leaf fiber were treated with different chemical surface methods. It was found that alkali treatment removed some hemicellulose and lignin as confirmed by FTIR and TGA. Also, the fiber after silane treatment showed amino group that attributed to successfully graft the silane on the fiber. The SEM micrograph revealed smoother surface after the alkaline surface treatment. The tensile properties of the fibers were increased when fiber length increased and after surface treatment. Moreover, the hybrid natural fiber/PLA composites showed higher tensile properties compared with SF/PLA, PALF/PLA composites and pure PLA.

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