Preparation and properties of silane-treated banana fiber/poly(lactic acid) biocomposites

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Abstract. Poly(lactic acid) (PLA) reinforced with silane-treated banana fiber (BFSi) at various fiber contents was studied. Banana fiber surfaces were firstly treated by sodium hydroxide and subsequently by 3-aminopropyl triethoxysilane. The biocomposites were then prepared by melt blending method in a twin-screw extruder. The effect of BFSi fiber contents on the mechanical and thermal properties of the biocomposites were investigated. Scanning electron microscope (SEM) was used to reveal the cryo-fractured surfaces of the composites. Mechanical properties, thermal characteristics and thermal stability were carried out by universal testing machine, differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA), respectively. Interfacial adhesion between PLA matrix and BFSi fibers was significantly improved even fiber content up to 40% by weight. There were few fiber pull-outs or voids appeared. With increasing fiber contents, tensile modulus and strength increased while elongation at break decreased. Moreover, glass transition temperature ($T_g$) and cold crystallization temperature ($T_c$) decreased, whereas, crystallinity ($X_c$) significantly increased, however, melting temperature ($T_m$) was almost intact when fiber contents increased. The composites with higher amount of fibers exhibited faster thermal decomposition and higher residue contents at 550°C.

1. Introduction

Biodegradable plastics have been received much attention to be used as green materials. Poly(lactic acid) (PLA) is one of these plastics which can be synthesized from renewable resources. Recently, many countries are making every effort to develop natural fibers to replace synthetic fibers. Natural fibers are not only inexpensive, but also hypoallergenic. Moreover, the advantages of such fibers over man-made fibers include low density, low cost, recyclability, and biodegradability. Fiber from the banana stem is a natural fiber derived from plants. Natural fibers compose of cellulose which enhances the strength and uniformity of the fiber; hemicellulose which increase strength to the fibers; and lignin which increases the flexibility of the fiber. It has been discovered that a natural fiber derived from banana, the amount of cellulose, hemicellulose and lignin ranges in 60-65, 6-8 and 15-10%, respectively. Fibers from banana stem have density, tensile stress and Young’s modulus of 1.3 g/cm³, 791 MPa and 30 GPa, respectively. The amount of cellulose from banana trees is high then the fibers from banana trees show high toughness. The fibers are also suitable to be used to produce textile products [1]. In this study, we actively manufactured high performance banana fiber reinforced PLA biocomposites. Banana fiber surfaces were modified in order to improve the compatibility between banana fibers and PLA in order to enhance the mechanical strength, to reduce the cost of the materials, and to meet the request of eco-friendly composites. Effect of BFSi contents on the properties of biocomposites was investigated.

2. Experimental
2.1. Materials
Poly(lactic acid) was purchased from NatureWorks®, USA (product name – NatureWorks® PLA Polymer 7000D), USA. Banana fibers were obtained from “Musa Sapientum Linn” by Agriculture Women’s Club in Hua-Hin, Prachuap Khiri Khan, Thailand. Aminopropyltriethoxysilane (APS) was purchased from Merck, Germany. Sodium hydroxide (NaOH) was purchased from Better Syndicate, Thailand.

2.2. Banana fiber surfaces modification
The chopped banana fibers (6 mm) were soaked in 10% w/w NaOH solution for 1 h at room temperature together with stirring by mechanical stirrer. The fibers were washed with distilled water containing small amount of acetic acid until neutralized and were dried in a hot-air oven at 60°C for 48 hr. Banana fibers treated with NaOH (BFNa) were then undergone silane treatment. 5 wt% APS was dissolved in a mixture solvent of water:ethanol (40:60 %v/v). The pH of solution was adjusted to 4 by acetic acid and stirred continuously for 1 hr. Next, the BFNa fibers were soaked in the solution for 3 hr. NaOH treated Banana fibers followed by silane treatment (BFSi) were washed several times in distilled water. Finally, BFSi fibers were dried in hot-air oven at 60°C for 48 hr.

2.3. BFSi reinforced PLA biocomposites preparation
Silane-treated banana fibers (BFSi) were molten mixed with PLA in a twin screw extruder. BFSi/PLA biocomposites with three different amounts of the fiber at 20, 30 and 40 wt% were prepared. Finally, an injection molding machine was used to produce testing specimens.

2.4. Morphological study
Scanning electron microscope (CamScan, Bruker, UK) was used for the morphological characterization of banana fiber surfaces and cryo-fractured surfaces of BFSi/PLA biocomposites.

2.5. Thermal properties
Differential scanning calorimetry (DSC) measurement was taken on the Mettler Toledo DSC 1 using nitrogen as the purge gas at a scanning temperature ranges from 25-200°C at a heating rate of 10°C/min. Thermogravimetry analysis (TGA) measurement was taken at a scanning temperature ranges from 35-550°C whilst maintaining a nitrogen airflow with a constant heating rate of 10°C/min.

2.6. Mechanical properties
The tensile specimens were tested according to the ASTM D638 standard using an Instron-5969 universal testing machine. Load cell of 50 kN and crosshead speed of 50 mm/min were set for testing. At least 10 specimens were tested.

3. Results and discussion

3.1. Morphological studies
Scanning electron micrographs of each banana fiber and BFSi/PLA biocomposites at different BFSi contents were shown in Figure 1. It can be seen that surfaces of the banana fibers can be altered after the alkali and silane treatments. The untreated fiber (BF) surface (Figure 1a) is found to be slightly smooth due to the presence of oils and waxy substances including lignin that makes the fiber surface shiny and smooth [2]. The morphology of BFSi fiber shows different structures. Smoother surface can be observed in Figure 1b which is due to the deposition of the silane compound on the fiber surface [3]. Figure 1c-f describes the effect of fiber contents on the fractured surface morphology of the composites. It can be seen from Figure 1c that neat PLA normally shows smooth surface. With increasing the fibers contents from 20-40 wt% (Figure 1d-f), the fibers become closer together but do not show any sign of agglomeration. There are few fiber pull-outs or voids appeared on the surfaces. However, there is no gap observed at the interphase between the fiber and the matrix. This indicates that the interfacial adhesion between PLA matrix and BFSi fibers is significantly improved even fiber content up to 40 %
by weight [4]. Moreover, the fiber breakages can be seen in Figure 1f which supporting the interfacial adhesion improvement.

![Figure 1](image1.png)

**Figure 1.** SEM micrographs of (a) BF fiber, (b) BFSi fiber, (c) neat PLA, and BFSi/PLA composites at (d) 20, (e) 30 and (f) 40% by weight of BFSi fiber.

### 3.2. Thermal characteristics

![Figure 2](image2.png)

**Figure 2.** DSC thermograms of neat PLA, BFSi fiber and BFSi/PLA biocomposites at different fiber contents.

The thermal characteristics obtained from DSC experiment are shown in Figure 2 and summarized in Table 1. It can be seen that $T_g$ and $T_c$ decrease with the addition of BFSi to the PLA which resulting from density of crystalline state [5]. Moreover, the addition of BFSi to PLA results in an increase in crystallinity ($X_c$) of the PLA matrix. This can be explained by the nucleating ability of BFSi which promoting the crystallization of PLA. As a result of the silane modification on the fiber surfaces, bonding between the fiber and PLA matrix is improved due to the increasing in interfacial interaction by potential...
hydrogen bonding and mechanical interlocking between them [4]. The better the interfacial interaction between BFSi fibers and PLA matrix the more the fiber surfaces act as nucleation sites for the crystallization of PLA [6]. However, $T_m$ seems not significantly affected by BFSi fiber contents. It can be seen that peak intensity at $T_m2$ is higher than that of $T_m1$ when fiber contents increase. This indicate that more crystallites nucleated with more BFSi fibers loading.

### Table 1. Thermal properties obtained from DSC study of neat PLA and BFSi/PLA biocomposites at different fiber contents.

| Sample       | $T_g$ ($^\circ$C) | $T_{cc}$ ($^\circ$C) | $T_m1$ ($^\circ$C) | $T_m2$ ($^\circ$C) | $X_c$ (%) |
|--------------|-------------------|----------------------|-------------------|-------------------|-----------|
| Neat PLA     | 55.62             | 116.8                | 147.3             | -                 | 30.94     |
| 20BFSi/PLA   | 55.95             | 106.6                | 144.9             | 153.0             | 35.77     |
| 30BFSi/PLA   | 53.59             | 100.3                | 142.4             | 151.4             | 37.40     |
| 40BFSi/PLA   | 54.51             | 101.9                | 143.3             | 152.6             | 37.74     |

3.3. Thermal stability

TGA thermograms of neat PLA, BFSi fiber and BFSi/PLA composites are shown in Figure 3. PLA matrix, BFSi fiber, BFSi/PLA composites at the fiber content of 20, 30 and 40wt% show maximum decomposition temperature ($T_d$) at 385.8, 342.8, 343.7, 322.0 and 316.0$^\circ$C, respectively. The BFSi fiber and the composites with different fiber contents clearly show two-step decomposition. The first step during 40-100$^\circ$C is due to the loss of water molecules and the second step during 250-375$^\circ$C is due to the decomposition of cellulose in the fiber together with PLA because they decompose in the same temperature range. $T_d$ of the composites becomes lower as the fiber content increases. This is due to BFSi fiber has less thermal stability than neat PLA. In addition, the composites with higher BFSi loading shows the higher residue content at 550$^\circ$C toward the BFSi fiber itself [7].

![Figure 3. TGA thermograms of neat PLA, BFSi fiber and BFSi/PLA biocomposites at different fiber contents.](image)

3.4. Mechanical properties

Table 2 displays the summary results of mechanical properties from the tensile testing of PLA and BFSi/PLA composites. Tensile modulus of the composite increases with increasing amount of the BFSi fibers because the transcrytallization at the surfaces of fibers enhances the degree of crystallinity in the
composites [8]. The tensile strength of the composites increases when the loading of BFSi fibers in the composites increase. There is interfacial adhesion enhancement between PLA matrix and BFSi fibers which produces the good force transfer along the fibers. Moreover, the orientation of the fibers in the composites produce positive effect of tensile strength [9]. However, the elongation at break of the composites becomes decreased with the fiber loading contents. Because the fibers hinder the conformation of the PLA molecules, subsequently, slippage between PLA molecules hardly takes place.

Table 2. Tensile properties of neat PLA and BFSi/PLA biocomposites at different fiber contents.

| Sample       | Tensile modulus (MPa) | Tensile strength (MPa) | Elongation at break |
|--------------|-----------------------|------------------------|---------------------|
| Neat PLA     | 1,127±90              | 67.39±0.97             | 9.82±1.32           |
| PLA/20BFSi   | 1,367±41              | 67.83±1.01             | 6.86±0.64           |
| PLA/30BFSi   | 1,684±133             | 68.94±1.74             | 5.41±0.21           |
| PLA/40BFSi   | 1,892±75              | 76.16±2.00             | 5.21±0.44           |

4. Conclusions
This work demonstrated that the eco-friendly composites with good mechanical and thermal properties can be successfully developed using banana fibers as a reinforcement and PLA as a matrix. Silane treatment improves the compatibility between banana fibers and PLA resin. Thermal characteristic slightly changes compared to neat PLA, though crystallinity obviously increases with fiber contents. Thermal stability of the composites becomes more unstable with increasing amount of the fiber. Mechanical properties of BFSi/PLA biocomposites was significantly higher than those of the PLA matrix.

5. References
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