

Mechanical and Thermal Properties of Poly(lactid acid) Bamboo Fiber Composites

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Abstract

The effect of natural fiber, unbleached bamboo fibers (BF) on poly(lactid acid) (PLA) composite by means mechanical and thermal properties on the presence of plasticizer, triacetine was investigated. Wet processing was chosen by dissolving PLA on dicloromethane then BF with different fiber loading i.e 30, 40 and 50% were added. Thermal properties were analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA). The result showed that BF could increase the flexural strength and modulus of pure PLA by increasing the fiber loading. Moreover, it decreased at high fiber content (50%) due to the agglomeration of the fiber; however, the mechanical properties are still better than those of neat PLA. The best performances were shown by increasing the strength and modulus by 49.55% and 122.71% at 40% fiber content, respectively. DSC showed that fiber loading and plasticizer decreased glass transition temperature (T_g), meanwhile melting temperature (T_m) not significantly influence. Beside that TGA analyze showed that PLA/BF 60/40 composite start to decompose at 230 °C. Microscopic surface fracture of composites revealed by Scanning Electron Microscopy (SEM) showed fibers pull out, may due to lack of fiber-matrix bonding.

Key words: bamboo fibers, composites, DSC, poly(lactic acid).

Introduction

Recently, natural fibers reinforced polymer material has gaining attention among researchers, due to the benefit such as low cost, low density, high specific strength and renewable (Bledzki *et al.* 1999). Vary of polymer, e.g. polypropylene (PP), high density polyethylene (HDPE), polyvynil chloride (PVC)) successfully reinforced by abundant biopolymer on earth, cellulose. Dynamic oil prices and ecological concern awareness emphasized researcher to find some renewable polymer. PLA has properties that are comparable to many commodity polymers (petroleum based) such as high stiffness, clarity, gloss and UV stability (Garlotta 2001). Natural fiber-filled biopolymers are often referred to as “green” composites as

they are fully biodegradable and renewable.

The mechanical properties of composite material depend on several factors such as the interfacial interaction between the matrix and fiber, type of matrix and fiber, aspect ratio, and fiber loading. Poor dispersion fibers as reinforcing agent on matrix lead to lower mechanical properties of composites (Iwatake *et al.* 2008). Many attempts have been conducted to improve interfacial interaction between hydrophilic nature of cellulose fiber and hydrophobic polymer. Coupling agent (i.e Maleated-g-Polypropylene, MAPP) was introduced to fulfill requirement for better properties of PP composite (Masruchin *et al.* 2010). Besides that, modification to fiber (mechanically or chemically) and process

manufacturing of composites also influence significantly to fiber dispersion.

Shah *et al.* (2008) reported that maleated PLA is not available commercially and would be expensive and time-consuming to produce as part of composite manufacturing process. On the other hand, maleated polylactide (MAPLA) was used as compatibilizer in jute-PLA composites (Plackett 2004). The result showed that a reduction in the tensile strength resulting from addition of MAPLA to the fibers. Moreover, Graupner (2008) was investigated the addition of lignin as bio-compatibilizer, the result showed that lignin has an influence on the composite properties cotton/PLA. However, the utilization of lignin as biocompatibilizer composite has not been exploited.

Since the processing methods (e.g. injection, compression, extrusion) for natural fibre-thermoplastic composites are all based heating, understanding the thermal properties of such composites at their processing temperature is very important for studies on controlling and optimizing the manufacturing process (Li *et al.* 2008).

In this study, a composite made from PLA and unbleached-bamboo fibers was manufactured. Aspect ratio factor was obtained by making unbleached-bamboo fiber (lignin kept as bio-compatibilizer) into fibrillated pulp. Authors assumed that bamboo fiber flour had low aspect ratio and resulting lack on reinforcing agent, because of the nature PLA are hard and brittle. Therefore, filler and plasticizer were used to improve the flexibility and impact resistance of PLA. In our previous research (Subyakto *et al.* 2009), optimal concentration plasticizer (7% by weight) was obtained and will be used in this study. Composites manufactured by wet

processing was chosen to prevent undesirable agglomeration of fibers when it was manufactured on dry processing (Suryanegara *et al.* 2009). Moreover, stirring of compounding will improve homogeneity and fiber dispersion. Finally, the effect of different fiber loading (30, 40 and 50%) on the mechanical and thermal properties of fully biodegradable composites (PLA/BF) was investigated. Mechanical performance tested by flexural test using Universal Testing Machine (UTM) and Thermal properties was analyzed using Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA). Microstructure of unbleached-bamboo fibers and composite was also studied by Optical Microscopy and Scanning Electron Microscopy, respectively.

Materials and Methods

Materials

PLA (LACEA H-400) was supplied by Mitsui Chemicals, Inc, Japan. The melt flow rate (MFR) was 3 g per 10 min. (190 °C, 2.16 kg). Bamboo fibers (*Dendrocalamus asper*) was collected from Bogor area, West Java, Indonesia. Plasticizer, Triacetine, was supplied by local chemical supplier.

Preparation bamboo fiber

250 g (oven dried weight) of fiber was cooked in NaOH 2.5% (1 part of fiber soaked in 10 part of solution) for 2 hours. Cooked fibers were separated from the cooker liquid and washed until clean. Fibers then processed using beater Hollander for 90 minutes (mechanical beating). Then, fibers were grinded using stone grinder for 5 times cycle (mechanical fibrillation). The never dried unbleached bamboo pulp was stored in a freezer before use, to prevent fiber-fiber bonding (Hult *et al.* 2001).

Preparation of composites

Composite of PLA/fiber was prepared by soaking PLA in dichloromethane, stirred until dissolve completely, wet pulp and triacetin 7% by weight were added, and mixed until homogenous, for 2 h. Ratio of PLA/bamboo fiber were 70/30, 60/40, and 50/50. The compound was spread in trays, and the solvent was evaporated in oven at temperature below T_g, 60 °C for 8 h. Dry compound was processed in a Laboplastomill 30R150 at 170 °C, 60 rpm for 20 min. Compound then hot pressed at temperature of 180 °C, pressure of 1 MPa for 30 s. Immediately compound was taken and cold pressed at pressure of 1 MPa for 5 min, and sample was taken.

Optical microscopy

Morphology of bamboo fibers was observed under Optical Microscopy NIKON eclipse 80i, Japan. Image was capture and analysis with Motic Images Plus 2.0 software to know the fiber dimension.

Mechanical testing

Flexural properties were determined by using UTM (SHIMADZU type). Sample dimension were 150 mm x 50 mm x 3 mm. At least 4 specimens of each sample were performed with UTM at crosshead speed of 50 mm per minute at span 100 mm.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on DSC Perkin Elmer type Jade. The test was programmed with two steps. First, a heating step from 50 to 250 °C at 20 °C min⁻¹. Second step, involved cooling the sample from 250 to 50 °C at 20 °C min⁻¹. T_g, T_m, ΔH_m data were obtained from each step.

Thermogravimetry (TGA)

TGA/DTG was carried out by METTLER TOLEDO STAR^c System, at rate of 20 °C min⁻¹ in three steps. First, from 50 to 600 °C under inert, N₂ (nitrogen), second, sample was kept isothermally at 600 °C for 5 min under inert, N₂. Finally, sample was totally burn, 600-900 °C under oxygen to obtain char as residue.

Scanning Electron Microscopy (SEM)

Fracture surfaces of flexural test specimens were observed using a JEOL JSM 5310 LV. An accelerating voltage of 20kV was used. The samples were gold-coated in a sputter conter before collecting the image.

Results and Discussion

Morphology of BF as reinforcing agent

To obtain a high aspect ratio (L/d) mechanical and chemical treatments were applied to the natural fiber. The morphology of the bamboo fibers showed in Figure 1a-d. On nature, Bamboo fibers are a bundle of fiber, (Figure 1b). Grounded fibers into passed 40 meshes, familiar called by bamboo flour still could not separate the fibers, (Figure 1a). These agglomerated fibers will difficult to disperse into matrix, besides, not homogenized dimension result on un-homogenized performance of material composite. Clearly showed on Figure 1c, fibrillated pulp bamboo fibers had millimeter in length and micron in diameter, comparable to Figure 1a-b. During stirring on wet processing and mixer on kneader, fibers were well dispersed into matrix polymer easily in the form of high aspect ratio and fibrillated. Liu *et al.* (2007) reported that modulus and impact strength composite increase with increasing fiber length. Further implication by conducting mechanical and

chemical treatment to the fibers reported on changes of crystallinity cellulose (Bisanda 2000, Gumuskaya *et al.* 2005). Amorphous non cellulose component on fibers such as hemicellulose, pectin and lignin on large portion removed from the fibers during alkali treatment, these lead to increase thermal stability of the fibers (Masruchin *et al.* 2010). Figure 1d showed the smooth surface of unbleached bamboo pulp, no external fibrillation occurred during mechanical treatments (beating and fibrillation).

Mechanical properties composites

Typical stress-strain curve was shown in Figure 2. The flexural strength of PLA was 43.3% increase when fiber loading was 30% up to 100.83 MPa. The same trend

was also found for 40% fiber loading, flexural strength increase 49.55% than pure PLA up to 105.23 MPa. At higher fiber loading (50%), composite drop in strength due to agglomeration of the fibers and its difficult to disperse in the matrix during processing, however the strength is still greater than the strength of pure PLA. The agglomeration leads micro cracks and cause failure in material strength. The young modulus (E) increased in the presence of fiber in the matrix and elongation decreased compared to the pure PLA.

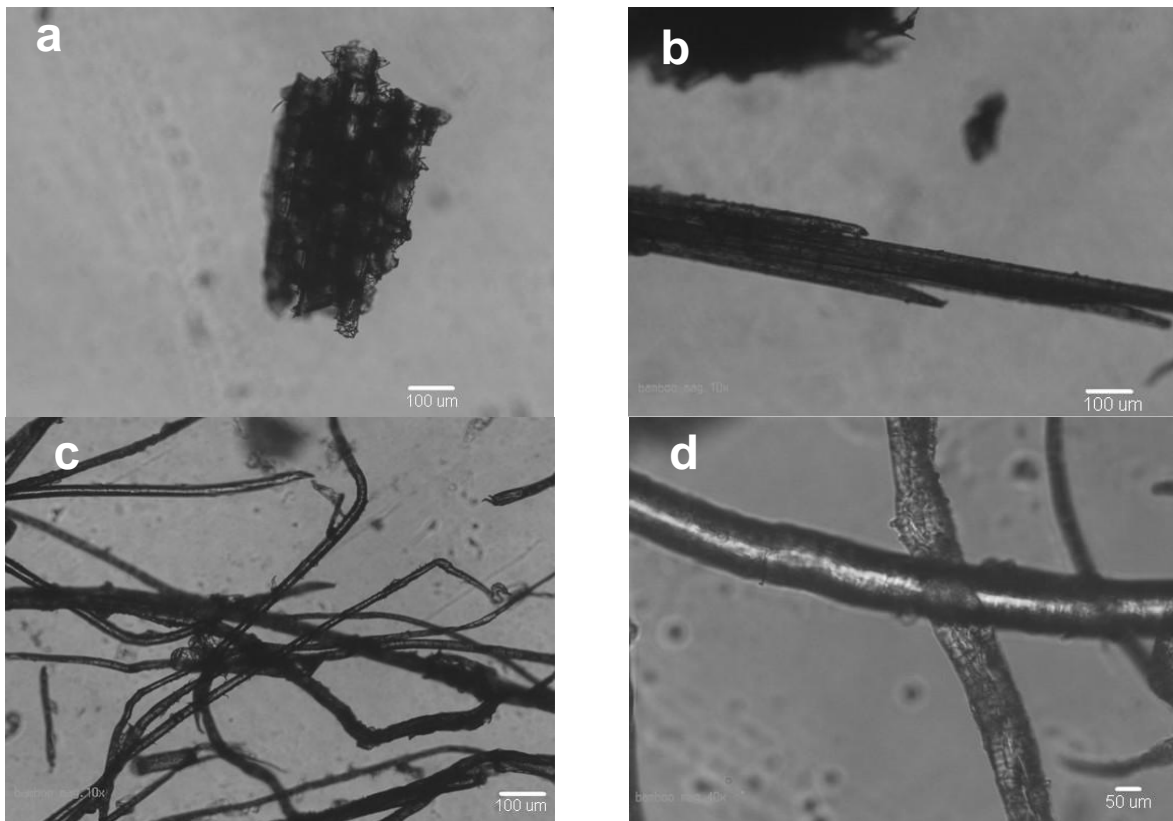


Figure 1 The morphology of bamboo fiber, (a) bamboo flour, passed 40 mesh (mag.10X), (b) bamboo fiber bundle (mag 10X), (c) fibrillated pulp bamboo fibers (mag 10X), (d) surface of single pulp bamboo fiber (mag 40X).

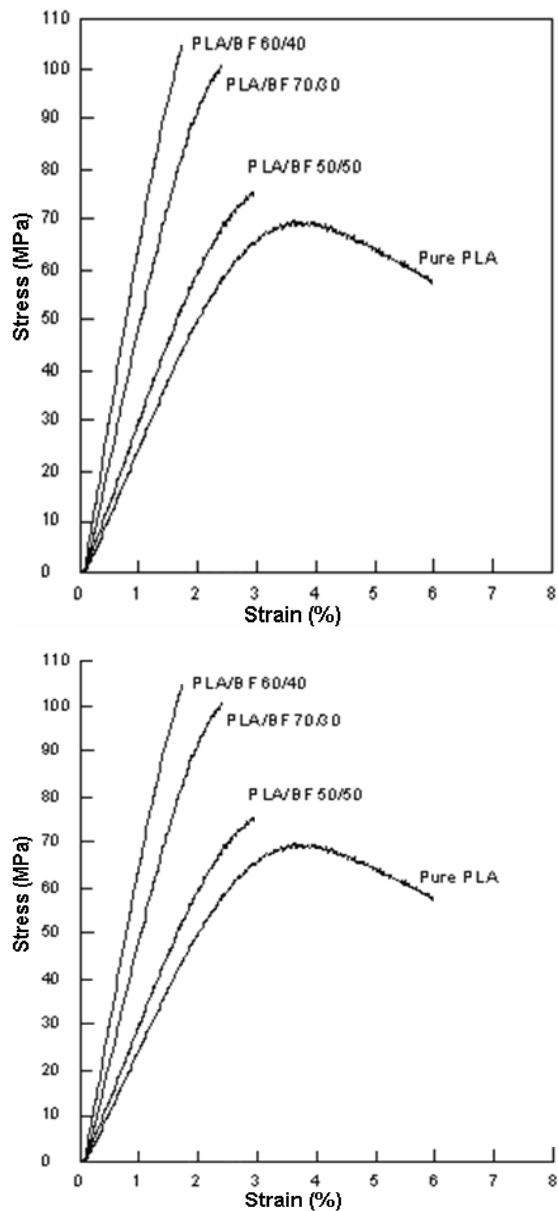


Figure 2 Typical stress-strain curves of pure PLA and PLA/BF with various fibers loading.

Table 1 Glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m)

Sample	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	Area (T_g), mJ	Area (T_m), mJ	ΔH_m (J/g)
Pure PLA	72.15	164.49	19.89	53.24	18.91
PLA/BF = 70/30	66.92	162.91	23.46	70.99	24.29
PLA/BF = 60/40	66.52	162.88	46.05	94.03	21.42
PLA/BF = 50/50	68.96	161.99	20.48	40.02	19.22

Scanning electron microscopy

SEM was conducted to investigate the fracture of PLA/BF 50/50, since this composition showed drops on mechanical properties. Figure 3 showed many holes left during fracture indicate fiber pull out.

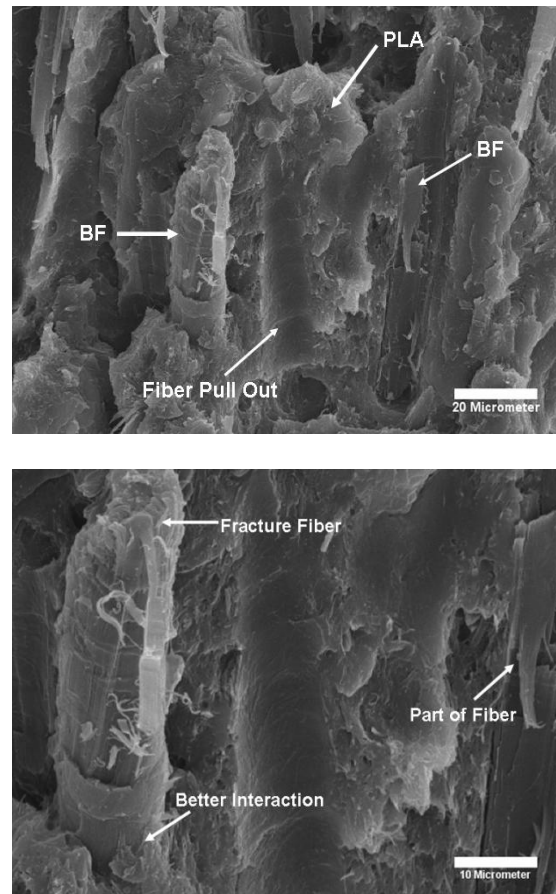


Figure 3 SEM image of fracture of specimens tested for PLA/BF 50/50, top 1000X mag. bottom 2000X mag.

This figure also evident that the morphology of fibers influences the reinforcing effect to matrix polymer, for instance, rough surface will lead a better mechanical interlocking than smooth surfaces (Figure 1d). For these reasons, lignin will be an important role to make cellulose compatible with polymer by covered and made more hydrophobic, better interaction showed in Figure 3 (bottom) on 2000X magnification.

Thermal analysis (DSC and TGA)

Figure 4 showed Tg and Tm of pure PLA and composites with different fiber loading. Tg decrease when BF was added, this way improve the brittle characteristic

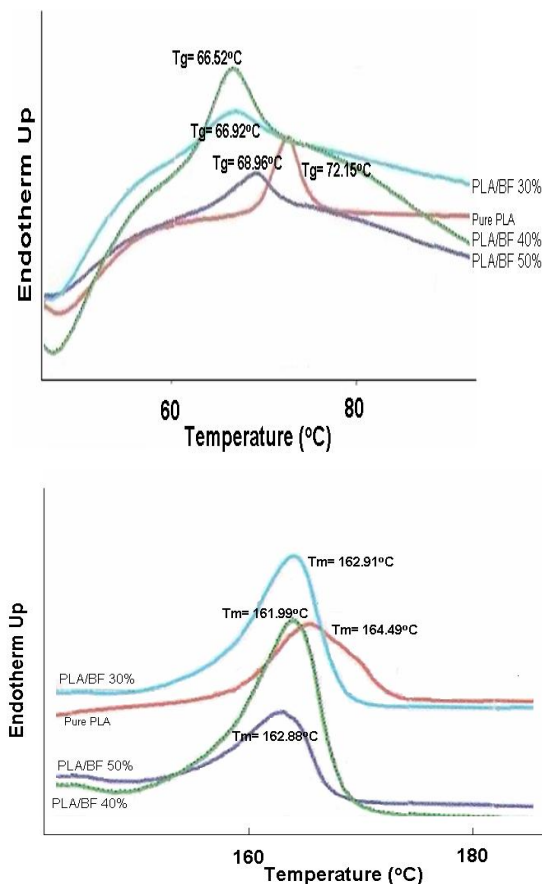


Figure 4 DSC curves of endothermic peak for Tg (top) and Tm (bottom), all composites at heating step.

of PLA. From this study BF may also play the role as a plasticizer. Significant decreased Tg showed at BF 40% with increasing area under Tg curve (Table 1). Even though, Tm was decreased when fiber was added, fiber loading does not significant influence on Tm. Same result reported by Mohanty *et al.* (2004) and Shah *et al.* (2008). Beside fiber loading, according to the study of Kulinski *et al.* (2005), plasticizer such triacetine strong influence on decreasing Tg also.

The cooling step analysis from DSC analysis showed in Figure 5. There is no peak exist, except a narrow, on fiber loading 40 and 50% close to Tm at heating step. The presence of plasticizer does not implying on crystallization mechanism of PLA (Xiao *et al.* 2009). It is depend on the filler that could act as nucleating sites. Crystallization mechanism occur depend on the nature of polymer used, it might be caused by raw material PLA (LACEA H-400) that we used is semicrystalline with lower crystallinity. From Table 1, Heat of fusion energy (ΔH_m) was increase by the presence of BF indicating the changes on crystallinity of PLA. Crystallization rate and nucleation of natural fiber on polymer will be the topic for further study.

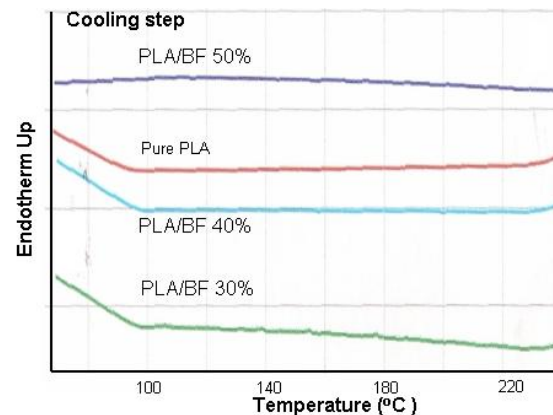


Figure 5 DSC curves of composite at cooling step.

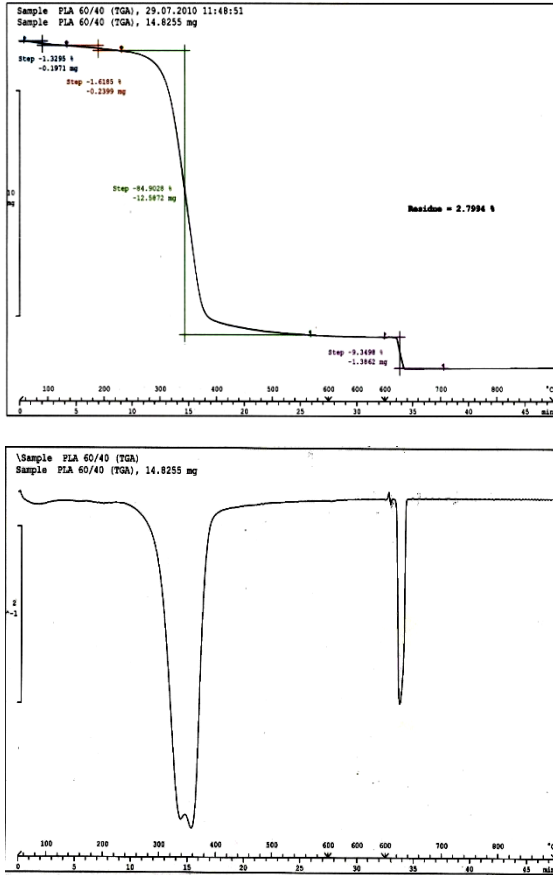


Figure 6 TGA (top)/DTG (bottom) curves of PLA/BF 60/40 composite.

Figure 6 showed TGA/DTG curves for the PLA/BF 60/40 composite. On the first heating, under N_2 gases, the weight loss of PLA/BF occurred in a two step process. This result can be confirmed by the presence of two peaks in the DTG curve. But, for the second extremely weight loss, there are two peak showed. This is caused by the decomposition of BF as filler as well as the original PLA as matrix follow. First weight loss is due to the evaporation of volatile and water compound until 110 °C, second weight loss occurring on 230 °C. This temperature is known as decomposition temperature for PLA/BF 60/40. The amount of residue (char) after final heating was 2.80%

Conclusions

Mechanical and thermal properties of PLA and unbleached bamboo fiber composites were studied in the presence of plasticizer. Flexural strength and modulus of pure PLA were increase by increasing the fiber loading. Moreover, it decreased at higher fiber content (50%); however, the mechanical properties are still better than those of neat PLA. The best performances of composite were shown by composition at PLA/BF 60/40. Thermal properties analysis showed that the addition of bamboo fiber and the presence triacetine were influenced on decreasing T_g , but not significantly on T_m . Thermogravimetry study showed PLA/BF 60/40 start to decomposed at 230 °C.

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