
Thermal Property of Poly(lactic acid)/Polypropylene/Bamboo Fiber Composite for Injection Molding application

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Abstract.

Polymer composites of poly(lactic acid)/polypropylene/bamboo fibers (PLA/PP/BF) were prepared using polypropylene-graft-maleic anhydride (PP-g-MAH) as a compatibilizer. The ratio of PLA/PP was 40/60 by weight with 3 phr of PP-g-MAH. The content of BF in the composite was varied for 5, 10 and 20 phr (part per hundreds of resins). To improve the surface contact of BF and the polymer matrix, treatment of BF with alkali solution to remove lignin and hemicellulose was studied. The thermal analysis of composite was carried out using a differential scanning calorimetry (DSC) method to verify the property for injection molding application. Morphology of surface area was investigated by a scanning electron microscope (SEM). Chemical property of composite was measured to verify the functional groups by FT-IR. Crystallinity of composite was calculated from XRD analysis. Morphology of fracture structure of PLA/PP blend showed smooth surface area with clear and no phase separation between fiber and polymer matrix. The BF content of 10 phr composite showed satisfied thermal property. The interactions between BF and polymer matrix was confirmed their functional groups of PLA/PP/BF composite by FT-IR spectroscopy. The crystallinity of the composites decreased while the crystallization temperature (T_c) shifts to lower values with increasing BF content which indicated nucleating effect of BF.

Keywords. -

1. INTRODUCTION

Natural fibers have been used as reinforcement materials in polymers from their advantages of low specific gravity, non-abrasive and their abundant available from renewable resource. Polymer composites reinforced with natural fibers exhibit high stiffness

properties, high specific properties, easily recyclable. Unlike brittle fibers the natural fibers are not fractured during processing, low energy consumption and low cost. Wide variety of fibers are available throughout the world.

Currently bamboo is considered as an important plant natural fiber and has a great potential to be used as reinforcement materials in polymer composites. Mechanically grounded bamboo present its structure as fibers rather than particles. On the basis of BF characterization, bamboo has 60% cellulose and high lignin content. The microfibrillar angle of BF is 2–10°, which is comparatively small. According to bamboo fiber (BF) structural variation, treatment of BF including extraction of fibers, chemical modification had made it versatile for the use in polymer composites which resulted in improvement of their mechanical and thermal properties [1-2]. The composites can be effectively applied in the automotive, building, appliance and other applications [3].

The limitation of application of natural fibers as reinforcements for polymers is their property inconsistency which depend on high moisture absorption and incompatibility with polymer matrices [4]. To overcome the above limitations, treatment the fibers surface, addition of compatibilizers and coupling agents such as maleic anhydride, acetic anhydride, and silanes have been reported to facilitate better fiber-polymer interfacial interactions and efficient load transfer [5].

Recently, biodegradable polymers have been used as composite polymer matrices with the purpose to replace the non-degradable polymers. Poly(lactic acid) (PLA) have become a topic of great interest in research and development of biobased and biodegradable polymers. PLA exhibits excellent mechanical properties such as high modulus, and biodegradability. However, PLA has disadvantages on low toughness and gas barrier properties [6].

Polypropylene (PP) is widely used for injection molding products. PP possesses applicable properties for packaging such as high heat distortion temperature, transparency, dimensional stability and outstanding flow ability. PP shows excellent characters for composite fabrication as a matrix material because PP is suitable for filling, reinforcing and blending. The study on PP reinforced with natural fibers composites was reported [7]. Zhang Ying-Chen, et al studied the blending of PLA/PP using PP-g-MAH as a compatibilizer. Block or graft copolymers were produced from reaction of maleic anhydride and the side chain of PLA by melt free radical copolymerization The copolymers acted as a compatibilizer for the PLA/PP blend [8]. However, the reinforcement of PLA/PP with natural fiber has not been reported.

2. EXPERIMENTAL PROCEDURE

2.1. Experimental Materials

Poly(lactic acid) (grade: 3052D, Mn 1.39 x 10⁵, Mw 2.07 x 10⁵, polydispersity 1.48) was purchased from NatureWorks LLC. Polypropylene (grade: HP500N) produce by HMC Polymers Company Ltd. PP-g-MAH was produced from Dupont with maleic anhydride functionalized. Bamboo fiber (BF) was purchased from Kanchanaburi province, Thailand.

2.2. Preparation of compound process

PP, PLA, PP-g-MAH, and bamboo fiber were first vacuum-dried at 80 °C for 8 h prior to mixing. The PLA/PP blending ratio was 40/60 w/w, PP-g-MAH compatibilizer was 3 phr, and bamboo fiber content was varied between 5, 10, and 20 phr. The blending was carried out using a twin screw extruder (CTE-D20L800) at 200°C.

2.3. Preparation of injection molding process

PLA/PP/Bamboo compounds were oven-dried at 80°C for 8 h before injection molding (Toyo Machinery & Metal Co., Ltd (TI-30F6). The configuration of injection temperature zones was 200/180/180/180/170 °C. The samples were subjected to mechanical property analysis

2.4. Morphology analysis

Samples for morphology analysis are from tensile test specimens. The morphology of polymer blends was examined by scanning electron microscopy (SEM) (JEOL, JSM-S410LV), operating at 15 kV. The samples were fixed on supports and coated with gold.

2.5. Thermal analysis

DSC scans were recorded on a differential scanning calorimeter Perkin Elmer, DSC 800 in inert atmosphere (nitrogen), with a heating rate of 10 °C/min. The samples (~10 mg) were placed into alumina crucibles. After the first heating 20 °C to 250 °C at a rate of 10 °C/min, held at that temperature for 5 min, then cooled to 20°C with cooling rate of 10°C/min before second step where the samples were heated again and thermograms for second heating were recorded. Glass transition temperature (T_g), cold crystallization temperature (T_c), melting temperature (T_m).

2.6. Fourier Transform Infrared Spectroscopy

FTIR spectra were recorded Nicolet iS5 FTIR Spectrometer equipped with a universal attenuated total reflectance. The spectra were recorded between 4000 and 500 cm^{-1} frequency ranges.

2.7. X-Ray Diffractometry (XRD) measurement

XRD analysis of PBS and its blend was performed on Panalytical X'Pert Pro (model-PW 3040/60) diffractometer with Cu $K\alpha$ radiation ($\lambda= 1.54\text{\AA}$) generated at voltage of 40 kV and current of 30 mA. Scanning was done in the 2θ angle of 5–80° with a scan step size and time per step of 0.01° and 0.5 s, respectively.

3. RESULTS AND DISCUSSION

3.1. Morphology (SEM)

Figure 1 shows an SEM image of fracture surface of PLA/PP (40/60 by weight) composites. PLA/PP without BF in (a) shows no phase separation which may due to the effect of a compatibilizer, PP-g-MAH (3 phr), addition. In Figure 1 (9-11) the yellow cycles indicate the bamboo fiber in matrix. With 5 and 10 phr the bamboo fibers were

found to distribute on the PLA/PP matrix. However high BF content of 20 phr, the fillers were agglomerate and phased separation of polymer matrix and BF was clearly observed.

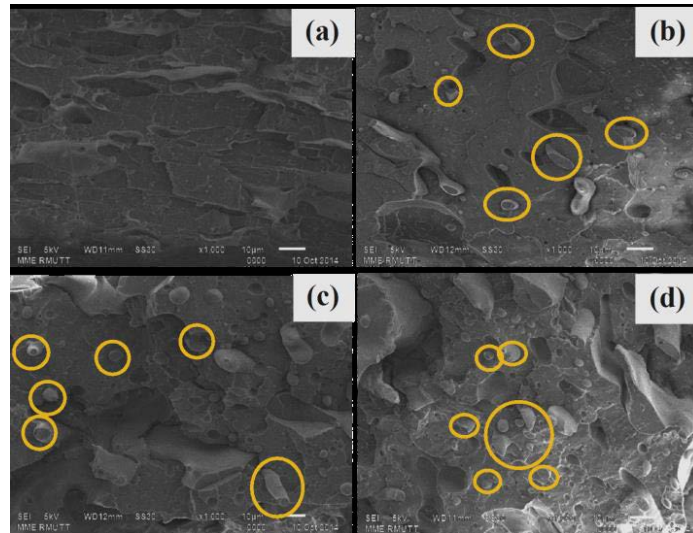


Figure 1 Morphology of PLA/PP/BF composites (3 phr PP-g-MAH) at different BF contents (a) without BF (b) 5 phr (c) 10 phr and (d) 20 phr

3.2. Chemical properties (Fourier Transform Infrared Spectroscopy, FTIR)

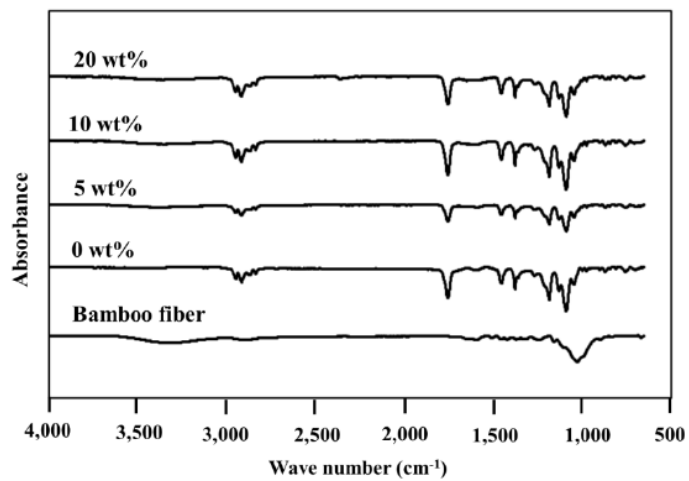


Figure 2 FT-IR spectrum of PLA/PP/BF composite at different BF content

Figure 2 exhibits the FT-IR absorptions bands of PLA/PP/BF composites. The absorbance peak at 3330 cm^{-1} of bamboo fibers represented the stretching vibration of OH and the intensity peak at 2890 cm^{-1} was attributed to the asymmetric stretching vibration of CH_2 in cellulose, hemicellulose, and lignin. The spectrum of hemicellulose (ester linkage of the carboxylic group of ferulic and p-coumaric acid of hemicellulose, $\text{C}=\text{O}$ in hemicelluloses) of the bamboo fibers showed peak at 1735 , 1596 and 1506 cm^{-1} (aromatic skeletal vibration of lignin), 1456 cm^{-1} (C-H deformation combined with aromatic ring vibration), and 1230 cm^{-1} (methoxyl groups of lignin) [10, 11]. The peak at 1735 cm^{-1} , attributed to hemicellulose, disappeared for the alkali treated BF. This disappearance of spectrum indicated that the removal of hemicellulose was successful. [10] The peak area within the region $3200\text{--}3500\text{ cm}^{-1}$ of the OH stretching vibration was found to be intensified after NaOH treatment. The peak located in 2922 cm^{-1} is attributed to a hydrocarbon (C-H) stretching vibration. The typical absorption peaks of cellulose are observed at 1422 and 1159 cm^{-1} . It could be highlighted that the peak was shifted to the lower value of 1032 cm^{-1} which derived from C-O and C-C stretching vibration, which may be expected as a result of alkaline treatment for the change in molecular orientation [12-13].

The FT-IR spectrum of PP observed at 2956 , 2910 , and 2830 cm^{-1} are attributed to $-\text{CH}_2-$ and $-\text{CH}_3$ groups. The absorption bands at 1452 and 1377 cm^{-1} are attributed to $-\text{CH}-$ and $-\text{CH}_2-$ groups [14]. PLA shows characteristic frequencies at 1746 , 2995 , 2946 and 1080 cm^{-1} for $\text{C}=\text{O}$, $-\text{CH}_3$ asymmetric, $-\text{CH}_3$ symmetric, and C-O stretching, respectively [15-17].

For the composites, after addition of BF into PLA/PP, the O-H stretching vibration at 3657 cm^{-1} was shifted to 3650 cm^{-1} , which indicated the interactions between the BFs and polymer matrix. Treatment of BF surface by NaOH resulted in removals of the impurities which led to smaller sized and higher crystallinity of the cellulosic fibers and increased the fiber surface area [18].

3.3. Crystallinity of composites (XRD)

Figure 3 shows the XRD pattern of PLA/PP/BF composites at difference BF contents. Bamboo fiber displayed XRD peaks at 2θ 14.9° , 16.1° , 22.1° , and 34.5° , are corresponding to the (101), (110), (200), and (004) crystallographic planes, respectively [19-21]. The intensity of reflections at the angular positions 14.2° , 16.8° , 18.6° of 2θ are in agreement with the (110), (040) and (130) planes of PP [8, 22-24]. The peaks at 16.7° , 19.1° of 2θ are corresponding to the (110) and (020) plane of PLA [24]. The XRD patterns of PLA/PP/BF composites with difference bamboo fiber content was not change but the reduction of peak intensity was observed, The crystallinity of the composite was found to decreased when the amount of bamboo fibers increased. The results may arise from restriction to deformation capacity of the matrix in the elastic zone [25].

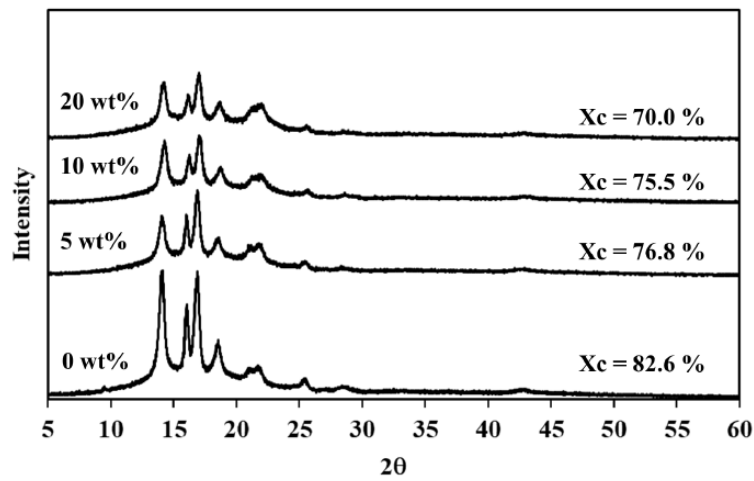


Figure 3 XRD pattern of of PLA/PP/BF composite at different BF content

3.4. Thermal property analysis

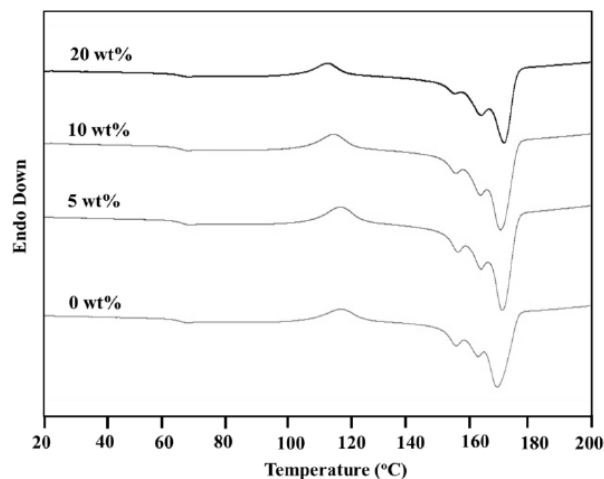


Figure 4 DSC thermogram of PLA/PP/BF composite at different BF content

Figure 4 and Table 1 depict the DSC thermogram of composites of PLA/PP (40/60 by weight) at difference BF contents. The melting temperature (T_m) of PP and PLA of all samples are not significantly changed. Two melting peaks of PLA in the composites are observed which are attributed to size distribution of crystalline lamella if the melting points are not produced due to the matrix polymorphism [26-27]. The peak of crystallization temperature (T_c) of composite was shifted to lower values with increasing the bamboo fiber contents. The results indicated the nucleating effect of BF [5] and the

presence of a transcrystalline zone form at the BF-PP interface [26]. The enthalpy of melting (ΔH_m) of main crystalline parts of PLA is in agreement with the nucleating effect of BF.

Table 1 Thermal property of PLA/PP/Bamboo fiber composites

BF (wt%)	T_g (°C)	T_c (°C)	ΔH_c (g/J)	PLA				PP	
				T_{m1} (°C)	ΔH_m (g/J)	T_{m2} (°C)	ΔH_m (g/J)	T_m (°C)	ΔH_m (g/J)
0	63.29	116.83	6.57	154.46	11.25	160.92	7.59	167.80	109.87
5	64.64	116.74	6.39	153.91	10.33	161.60	13.97	169.43	113.39
10	64.53	114.30	5.02	153.60	8.05	161.92	14.10	168.76	112.18
20	63.91	112.43	3.99	153.33	4.00	161.98	16.17	169.94	85.67

4. CONCLUSION

This research study the production of green composites from poly(lactic acid) (PLA) and polypropylene (PP) blend reinforced with bamboo fibers using an injection molding process. The polymer blend ratio of PLA/PP was 40/60 by weight with addition of polypropylene-grafted-maleic anhydride (PP-g-MAH) for 3 phr as a compatibilizer. The contents of BF reinforced in the PLA/PP blend were varied from 5, 10 and 20 phr. The composites were subjected to morphology of surface area by SEM, chemical property as a functional group by FT-IR, crystallinity of composite calculated from XRD and thermal property was analyzed by DSC. Morphology of fracture structure of PLA/PP blend showed smooth surface area with clear and no phase separation between fiber and polymer matrix which may due to addition of polypropylene-grafted-maleic anhydride (PP-g-MAH) for 3 phr as a compatibilizer. However, increasing the BF content to 20 phr the agglomeration of fiber and phased separation were occurred. FTIR spectrum confirmed functional group of PLA/PP/BF composite which indicated the interactions between the BFs and matrix. The XRD patterns of PLA/PP/BF composite with difference bamboo fiber contents were not changed but the intensity of peak was reduced. The crystallinity of the composite decreased with increasing BF content which may due to restriction to deformation capacity of the matrix in the elastic zone. Addition of bamboo fiber has no effect to melting temperature (T_m) of composites but the crystallization temperature (T_c) shifts to lower values with increasing the bamboo fiber contents. The results indicated nucleating effect and the presence of a transcrystalline zone form at the BF-PP interface.

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