

Study on Poly(lactic acid)/Natural Fibers Composites

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ABSTRACT: Recently, the natural fibers-reinforced composites have attracted substantial attention as a potential structural material for low cost applications. The composites of poly(lactic acid) (PLA) with three kinds of natural fibers, such as bamboo fibers, wood fibers, and coconut fibers (CTFs), were prepared by solution-casting technique. The natural fibers were modified by aluminum acid ester coupling agent and stearic acid to improve compatibility. To compare the mechanical and thermal properties of composites, tensile test, dynamic mechanical analysis, differential scan calorimeter, scanning electron microscopy (SEM), and Vicat softening point test were carried. The results showed that the addition of three kinds of natural fibers all could improve the mechanical and thermal properties of composites, and natural fibers after modification could further

improve tensile strength of composites. And in comparison, the composite of PLA/CTF had highest tensile strength and best thermal properties. When the content of natural fibers were 2%, the highest tensile strength of PLA/modified CTF composites was highest, and it reached 22.5 Mpa which was 20.4% higher than that of pure PLA, and VST of this composite increased compared with pure PLA. Meanwhile, the results of SEM indicated that the modified CTF had best interfacial compatibility to PLA. These results indicated that PLA/natural fiber composites had higher strength and better heat resistance than pure PLA. This study provided the application of PLA industry with a feasible method. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: composites; natural fibers; PLA; heat resistance

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable polymer produced from renewable resources, and it has a broad market prospect and is universally recognized as the most promising biomedical materials and new-style packing materials in the new century. Besides, PLA which is expected to be substitute of general plastics is environmental and sustainable.¹ However, some factors such as hydrophobic, brittleness, low impact resistance, and high cost, especially, the sensitivity to the temperature of PLA, limit the use of PLA in the engineering field. Except for chemical modification of PLA, physical blending is also used to improve the properties of PLA. Polyesters such as poly(glycolic acid) (PGA), poly(hydroxyalkanoates) (PHA), and poly(caprolactone) (PCL) were selected to blend with PLA. Some natural materials such as

chitosan and hydroxyapatite were also used to modify PLA.^{2–5} In addition, natural fiber-reinforcing is one possibility to enhance thermal stability and mechanical properties of PLA. Natural fibers have many advantages compared to synthetic compounds, such as low weight, low cost, and they are recyclable and biodegradable. They are also renewable and have relatively high strength and stiffness. Several research papers focused on natural fiber-reinforced PLA composites, used natural fibers such as kenaf fiber, flax fiber, hemp fiber, etc. Some investigated biodegradability, others looked for ways to improve heat resistance or mechanical characteristics of the composites. Table I lists some literature about PLA composites with different kinds of fibers prepared by compression and injection molding.^{6–34}

However, only a small number of studies have been so far reported for PLA composites based on wood fiber and coconut fiber (CTF)-reinforced PLA. Particularly, as the low addition of the micro-sized natural fiber, the report of the mechanical and thermal properties of PLA thin film is very few. The method we used is solution-casting while the method most of the studies reported is extrusion. And the natural fibers play an important role in promoting the crystallization of the composites as nucleating agent. The goal of this work was to produce composites by solution-casting based on PLA and natural fibers including bamboo fiber (BF),

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TABLE I
Used Natural Fibers for PLA Composite Preparation by
Compression and Injection Molding⁶

	Kind of fibers and references		Kind of fibers and references
Preparation method:	Kenaf ⁷⁻¹⁰	Preparation method:	Kenaf ²⁵⁻²⁸
compression	Hemp ¹¹⁻¹³	injection	Hemp ²⁹
molding	Bamboo ¹⁴⁻¹⁶	molding	Bamboo ³⁰
	Sugar beer pulp ¹⁷		Sugar beer pulp ³¹
	Flax ¹⁸⁻²¹		Wood pulp ³²
	Jute ^{8,22,23}		Pine (Wood) ³³
	Henequen ⁸		Silk ³⁴
	Ramie ²⁴		

wood fiber, and CTF which had low cost and specific strength. The natural fibers used in this study were modified by high-speed stirring with aluminum acid ester coupling agent and stearic acid, the untreated natural fibers were used as a reference in this experiment. The mechanical properties and thermal properties of the materials were studied using tensile test, dynamic mechanical analysis (DMA), differential scan calorimeter (DSC) and vicat softening point test (VST). Besides, distribution of natural fibers and interfacial compatibility between natural fibers and PLA matrix were investigated by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

PLA (M_w 10×10^4) was supplied by Beijing Huabo Union Biodegradable Materials Technologies (Beijing, China). BF, wood fiber (WF), and CTF with 80 mesh fineness provided by Hebei Baoding Cellulose Factory (Baoding, China). These fibers were dried at 80°C for 24 h. Aluminum acid ester coupling agent and stearic acid were purchased from Beijing Chemical Reagents (Beijing, China).

Natural fibers pretreatment

Natural fibers were pretreated by high-speed stirring with 1.6 wt % aluminum acid ester coupling agent and 1.2 wt % stearic acid for an hour at 80°C. The modified natural fibers were preserved in a sealed envelope at room temperature.

Composites films preparation

The composites were prepared by solution-casting. A series of different natural fibers and PLA (10 wt %) were prepared as solution in chloroform. The suspensions were dispersed by using ultrasonic oscillation for 20 min. And then the suspensions were casted in Teflon dishes and evaporated at 25°C for 6 days. Pure PLA samples, without fiber-rein-

forcement, acted as reference for all experiments. Finally the films were formed, and the thickness of prepared composite film was 0.65 mm.

Characterization

Mechanical test

The mechanical properties were investigated by tensile test. The tensile tests were carried out according to GB/T 1042-1992 at a rate of 10 mm/min using an Instron 1185 testing, and the 4 × 50 mm dumbbell-shaped specimens were used. The tensile strength and elongation of composites at break were recorded. At least 10 specimens were tested for every material.

Dynamical mechanical analysis

DMA was carried out to study the glass transition temperature and storage modulus of the composites. The dynamical mechanical spectra of the different specimens were obtained using a dynamic mechanical analyzer (NETZSCH instrument, model 242C). Rectangular specimens (45 mm × 5 mm × 0.65 mm) were tested in tensile mode. The analyzer is operated at 1 Hz from -50°C to 150°C at a heating rate of 10 °C/min.

Differential scanning calorimetry

The melting behavior of the composites was measured using a differential scanning calorimeter (NETZSH 204F1, Germany) at a heating rate of 5 °C/min and nitrogen atmosphere. The sample weight was 5 mg, and each sample was heated from 20 to 180°C.

Vicat softening point test

Vicat softening temperatures (VST) of the composites were tested using a XRW-300 Vicat softening point tester at heating rate of 50 °C/h. The specimens were 5 mm thickness and the load was 10.0 N.

Scanning electron microscopy

Fractured surfaces of the materials were observed with a scanning electron microscope (Hitachi S-4700) with an acceleration of 20 kV. All specimens were obtained from films fracture under liquid nitrogen. The sample surfaces were sputter coated with gold. Distribution and morphology of the natural fibers in composites were observed.

RESULTS AND DISCUSSION

Mechanical test

Figure 1 shows the effect of fiber content on the mechanical properties of PLA matrix. As seen in

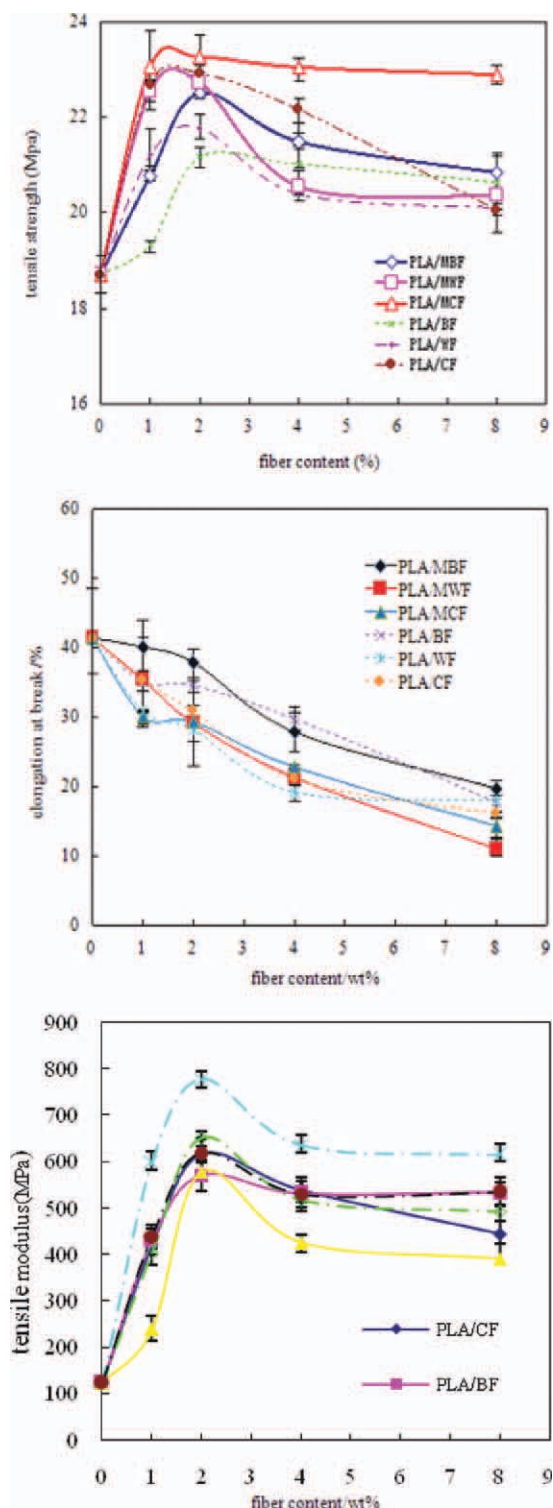


Figure 1 Effect of fiber content on the tensile properties of fiber/PLA composites: (a) tensile strength, (b) elongation at break, and (c) tensile modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 1(a), the tensile strength of each fiber composite sample in our experiments is higher than that of pure PLA sample, whether fibers were modified or not. And the tensile strength of PLA first

increased and then decreased with increasing the content of fiber from 1 to 8 wt %, and reached the highest when the fiber content was 2 wt %. A maximum value of 23.3 MPa (increment of 25%) was reached for the MCF/PLA composite sample with MCF content of 2 wt %.

It implies that the strength of PLA matrix was effectively improved by the incorporation of certain amount of natural fiber, which is less than 8 wt % in this case. This phenomenon may be due to fact that natural fibers could disperse the external force and played a role of nucleating agent in PLA matrix to accelerate crystallization, which could improve the tensile strength of the material. However, as the natural fibers amount increased, aggregation of fibers leading to defects and stress concentration in material made the tensile strength descend. In addition, modification of natural fibers could improve the tensile strength of the material, which also could be easily found from morphology of different composites. In the three kinds of composites, the modified CTF/PLA had the highest tensile strength.

Figure 1(b) shows the elongation at break of the different samples, the value obtained was 30–40% at 2 wt % of fiber content, and lower than that of pure PLA sample. And the elongation at break of the samples further decreased with increasing fibers content. However, the decrement is less than 10% when the fiber content varies from 0 to 2 wt %, which is acceptable for applications that do not require high ductility capability.

The decrease of elongation at break was partial because natural fibers as nucleating agent could improve the crystallization of materials, which made elongation of samples decrease. Besides, the defects and aggregations of fibers were another reason making the elongation decrease. Among three kinds of composites, the elongation at break of PLA/MBF was the highest.

Figure 1(c) shows the tensile modulus of PLA/raw fiber composites and PLA/modified fiber composites. The result showed that all composites had higher modulus than pure PLA. The tensile modulus increased significantly with the addition of 2 wt % CTFs. This revealed that the incorporation of CTFs into the matrix provided effective reinforcement, but it decreased with the fiber loading.

Thermal properties

In this study, DSC, DMA, and VST were carried out in order to investigate the thermal properties of the produced materials.

Differential scanning calorimetry

The DSC heating thermograms of materials produced were shown in Figure 2. Except for pure PLA, all the

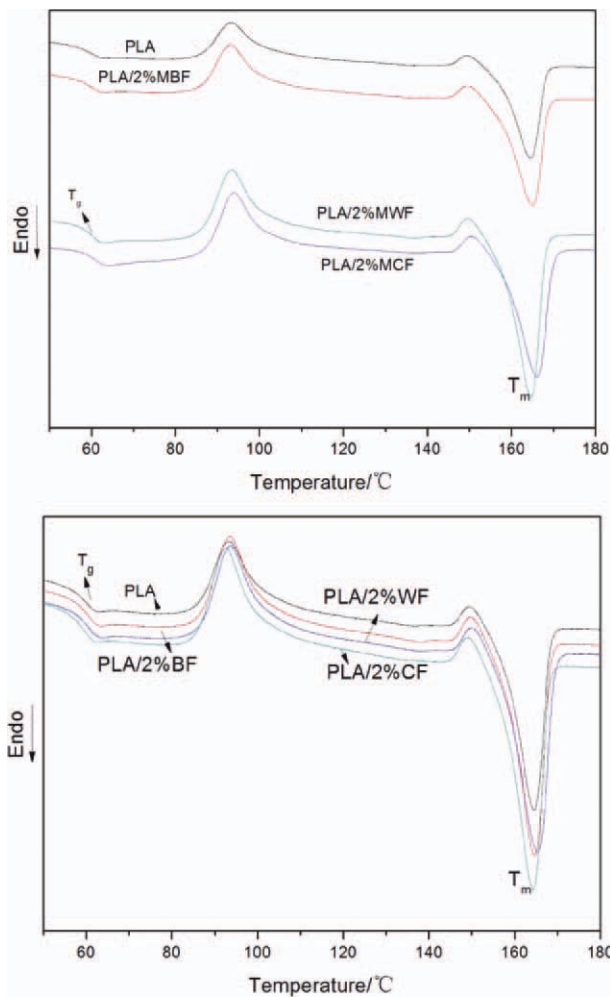


Figure 2 DSC curves of different composites: (a) storage modulus, (b) $\tan \delta$. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

samples contained 2% natural fibers content. The results showed that the melting temperatures (T_m) of pure PLA and its composites do not showed much difference, as the melting peak points were relatively close to each other. Composites were slightly increased about 1°C in comparison with pure PLA, respectively.

The crystallinity of PLA is computed using the following equation:

$$\chi_c (\% \text{ Crystallinity}) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{\omega} \quad (1)$$

where,

$$\Delta H_m^0 = -93.7 \text{ J/g}$$

ω is the weight fraction of PLA in the sample, ΔH_m is the enthalpy for melting, ΔH_m^0 is the enthalpy of melting for a 100% crystalline PLA sample.

The heat of melting of the PLA matrix in the composites increased in the order $\text{PLA} < \text{PLA}/2\%\text{MBF} <$

TABLE II
The DSC Data of PLA with 2% Content Modified Fiber

	T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_m (J g^{-1})	χ_c (%)
PLA	59.7	93.4	164.6	25.7	27.4
PLA/2%MBF	59.7	93.1	165.1	31.4	34.2
PLA/2%MWF	60.7	93.9	166.0	38.2	41.6
PLA/2%MCF	61.0	93.5	164.6	43.8	47.7
PLA	59.7	93.4	164.6	25.7	27.4
PLA/2%BF	60.2	93.6	164.8	30.0	32.7
PLA/2%WF	60.3	93.7	165.3	30.7	33.4
PLA/2%CF	58.8	92.5	164.2	31.8	34.6

$\text{PLA}/2\%\text{MWF} < \text{PLA}/2\%\text{MCF}$, and the crystalline degree of PLA were 27.4%, 34.2%, 41.6%, and 47.7%. In contrast, $\text{PLA} < \text{PLA}/2\%\text{BF} < \text{PLA}/2\%\text{WF} < \text{PLA}/2\%\text{CF}$, and the crystalline degree of PLA were 27.4%, 32.7%, 33.4%, 34.6% as seen Table II. These results indicated that 2% content fiber improved the degree of crystallization of PLA matrix.

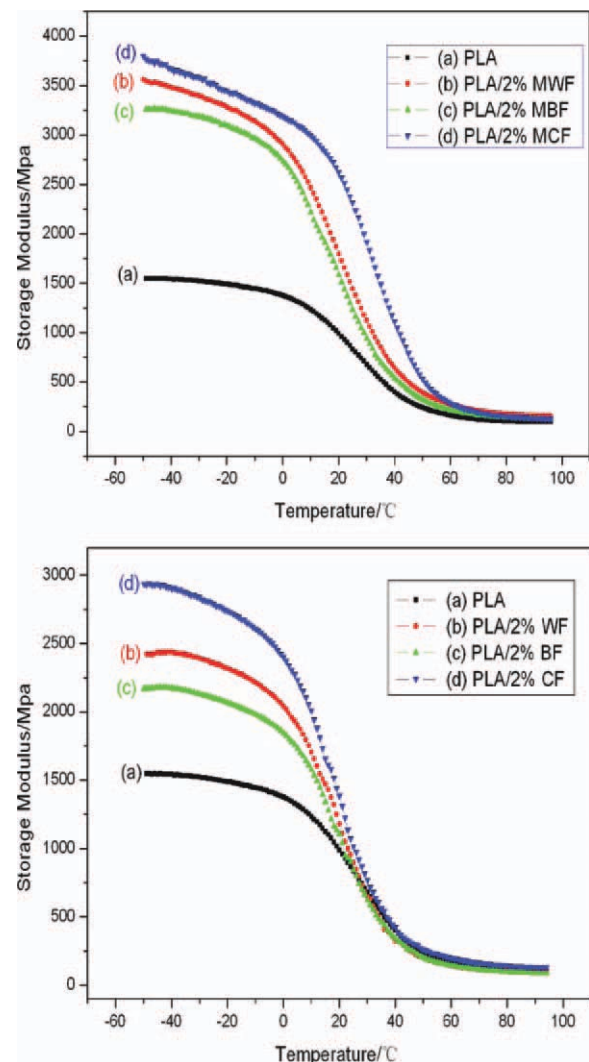


Figure 3 Storage Modulus of different biocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

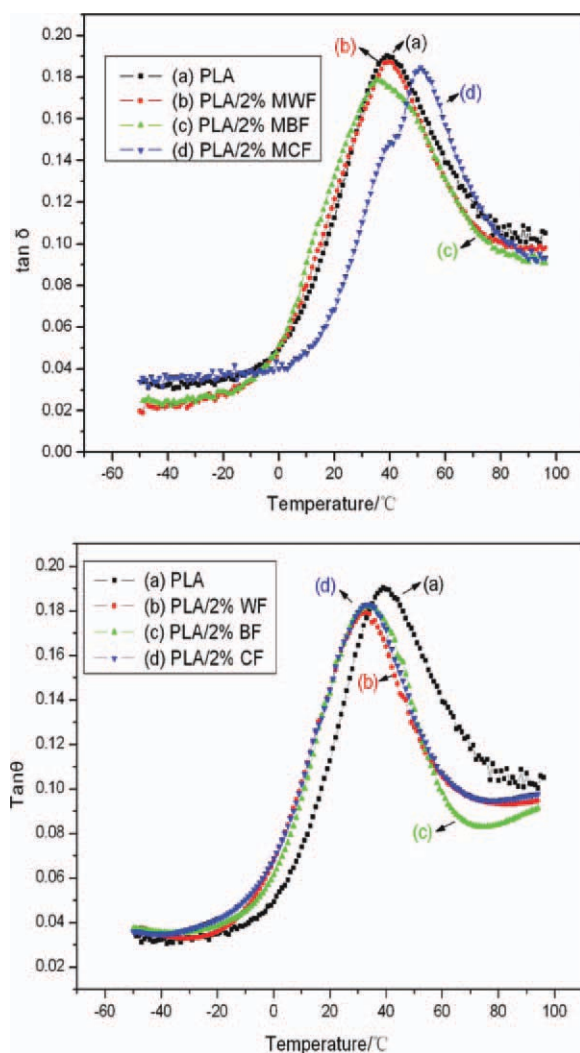


Figure 4 Tan δ of different biocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The addition of natural fiber improved the degree of crystallization of PLA and accelerated crystallization. The effects of different kinds of fibers were different. It is considered that the surface roughness of CTFs was expected to initiate, while smooth surface of BFs was expected that crystal formation was not initiated on the fiber surface. In conclusion, the addition of NF increased the crystallinity by acting as a nucleating agent. It may be due to the occurrence of nucleating effect of natural fibers in agreement with the case of PLA/hemp composites in the literature.¹⁸

Dynamic mechanical analysis

DMA was performed to investigate how the stiffness of natural fiber/PLA composites was affected by exposure at elevated temperature. The values of dynamic storage modulus E' for pure PLA and its

composites with different kinds of fibers were compared in Figure 3. The test temperature increased gradually from -50 to 100°C , the results showed that all kinds of natural fibers used in the experiment were able to improve the storage modulus of pure PLA at ambient temperature, whether fibers were modified or not. And the storage modulus of PLA/2%MCF was the highest of all, and reached a maximum gain 1.5 times when compared to pure PLA. In this analysis, on the one hand, the stress can be transferred from PLA matrix to fibers, on the other, the addition of natural fibers increased the crystalline degree of PLA matrix, so the mobility and deformation of the matrix is reduced.

Tangent delta ($\tan \delta$) is a function of temperature which is given by:

$$\tan \delta = E''/E'$$

where E'' is the loss modulus. A comparison of $\tan(\delta)$ for pure PLA and its composites is shown in Figure 4. The glass transition temperature T_g can be deduced from the peak of $\tan(\delta)$ curve. Figure 4 showed that pure PLA has a T_g of 59.7°C , the T_g of PLA/2%MBF, 2%MWF, and 2%MCF composites are 59.7 , 60.7 , and 61.0°C . No appreciable change in $\tan(\delta)$ values was observed in comparison to pure and pure/2%MWF samples. It is highlighted that the introduction of MBF into PLA matrix reduced the value of $\tan(\delta)$, which is in agreement with the results from previous literature.^{35,36} Generally, the damping in the transition region measures the imperfection in the elasticity and that much of the energy used to deform a material during DMA testing is dissipated directly into heat. Hence, the mobility of the composites decreases and the mechanical loss to overcome inter-friction between

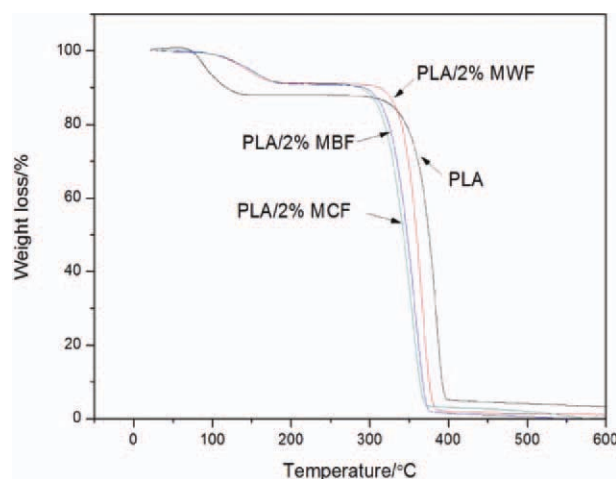


Figure 5 TGA curves of PLA and its composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

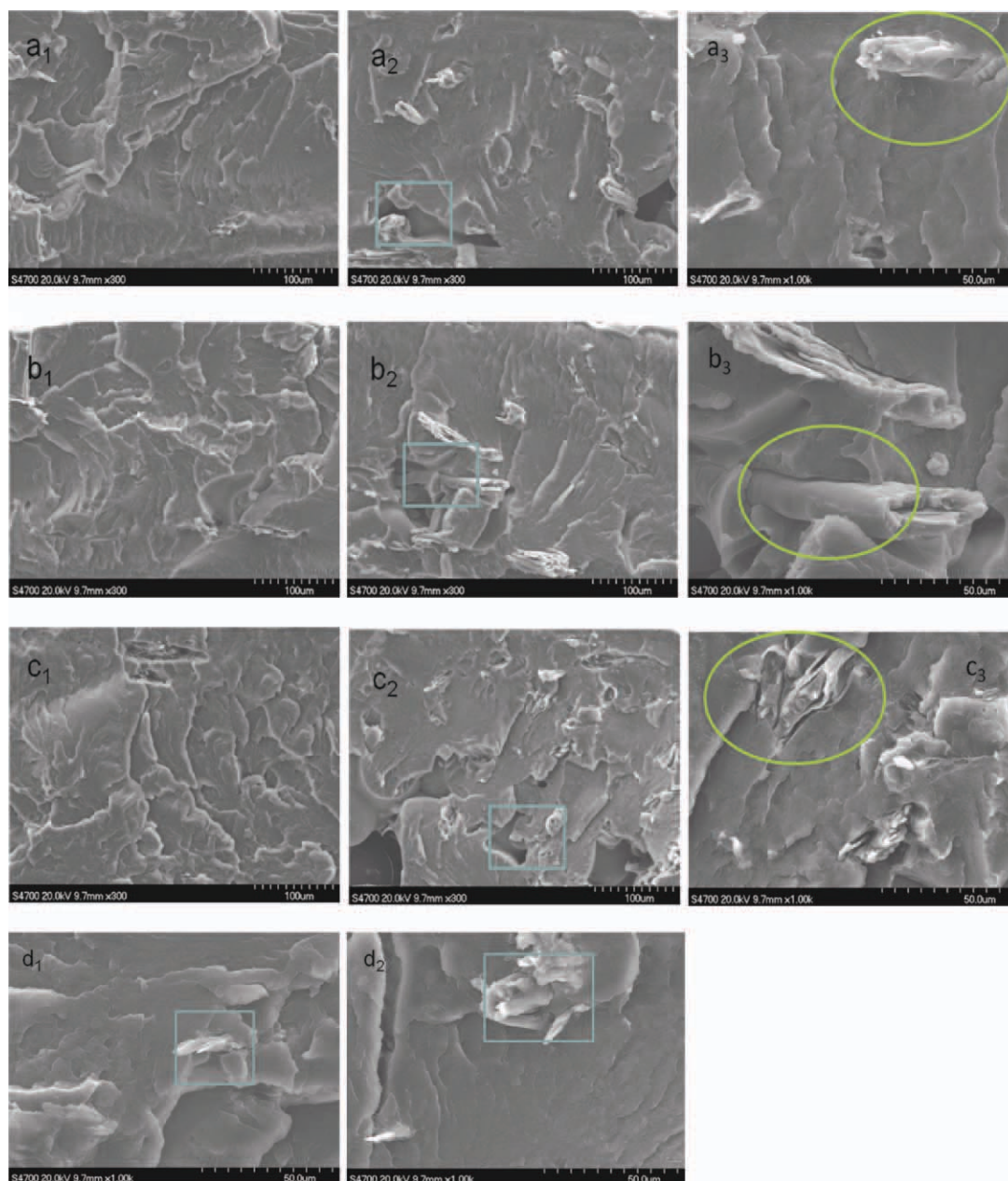


Figure 6 SEM images for fracture surfaces of PLA/fiber composite with 2 wt% and 8wt% of fiber content a₁: PLA/2%MBF; a₂: PLA/8%MBF; a₃: PLA/8%MBF; b₁: PLA/2%MWF; b₂: PLA/8%MWF; b₃: PLA/8%MWF; c₁: PLA/2%MCF; c₂: PLA/8%MCF; c₃: PLA/8%MCF; d₁: PLA/2%MBF; d₂: PLA/2%BF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular chains is reduced in the presence of MBF. Conversely, MCF increased the value of $\tan(\delta)$ of PLA matrix, this may be due to the fact that PLA/MCF composite has a higher crystallinity.

Vicat softening point test

The CTF-reinforce PLA composites had the best heat resistance, which could be concluded from the VST. The results showed that the VST of pure PLA was 135.0°C. And for PLA/MCF, PLA/MBF, and PLA/MWF, the VST were 143.3°C, 139.3°C, and 139.8°C,

respectively. All results of DSC, DMA, and the VST indicated natural fiber could improve the thermal stability of PLA.

Thermogravimetric analysis

Thermal stability of pure PLA and its composites were investigated by thermogravimetric analysis (TGA). Figure 5 shows the TGA curves for pure PLA, PLA/2%MBF, PLA/2%MWF, and PLA/2%MCF composites. Overall, PLA and its composite degraded through three main stages: (i) the moisture absorbed during storage is released from the fibers

first at nearly 100°C; (ii) a second transition occurs from 300 to 370°C, and the natural fibers undergo thermal degradation; and (iii) after 370°C, the composites started to thermal decompose. As seen as Figure 5, in comparison, fibers composites are more difficult to lose adsorbed moisture as the natural fibers are hydrophilic. For example, at first stage composites started to lose weight from 100°C, and pure PLA starts to form at 50°C, and percent weight loss is about 10%. In addition, the addition of natural fibers slightly decreased the thermal degradation temperature of PLA, this may be due to the fact that adsorbed moisture played some promotion role on the thermal degradation of PLA.

Scanning electron microscopy analysis

The morphology of the fracture surfaces of the specimens is presented in Figure 6. When the content of fibers was 2%, the fibers were separated from each other during the process of solvent evaporation and well-dispersed in the PLA matrix. And few voids are found on the fracture surface, as the fibers are trapped by the PLA matrix. As the fibers content reached 8%, some defects and aggregations of fibers formed, which would weaken the mechanical properties of materials. The micrographs in higher magnification for the composite sample with 2 wt % of fiber content are shown in Figure 6(c₃) (PLA/MCF) and Figure 6(a₃) (PLA/MBF). It can be noticed that many MCF fibers broke off together with PLA matrix, instead of being drawn out of MBF when the samples were ruptured under liquid nitrogen. It reveals the fact that MCF has good adhesion to PLA matrix. In case of PLA/MWF [Fig. 6(b₃)], obvious gaps between fibers and PLA indicated poor adhesion between MWF and PLA. A better adhesion meant a better mechanical property, so it was in accordance with the results of tensile test.

Besides, the influence of fiber modification is shown for images of d₁(modified BF) and d₂(unmodified BF) in Figure 6. It was easy to find that the BF after modification had better adhesion to PLA than the unmodified, for more agglomerates exist in the composites of PLA with unmodified BF, which is one of the reasons why fiber modification could improve the mechanical properties of materials.

CONCLUSIONS

This study was carried out as an initial step toward the use of a combination of modified natural fiber, such as MBF, MCF, and MWF as reinforcements in the PLA matrix. The evaluation of the composite mechanical properties demonstrated that the tensile strength was improved in the presence of natural fiber, and the PLA/2%MCF system had highest

modulus. Moreover, the modified natural fibers/PLA system had higher strength with respect to unmodified ones. However, the elongation at break of the samples was down after the higher content of natural fibers blended in PLA. It was thought that the aggregations and defects were main factors that led the elongation down. Besides, the natural fibers could also improve the heat resistance. The evidence of this result was provided by the testing of DMA, DSC, and vicat softening point.

Further study will be focused on the improvement of interfacial bonding, improving fibers content in composites, and changing process method. With such improvements, it is possible to achieve optimum dispersion of fibers, fiber-matrix adhesion, good mechanical properties, and heat resistance.

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