# Synthesis of Polylactide-*graft*-Glycidyl Methacrylate Graft Copolymer and its Application as a Coupling Agent in Polylactide/Bamboo Flour Biocomposites

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**ABSTRACT:** In this study, a novel graft copolymer, polylactide-*graft*-glycidyl methacrylate (PLA–GMA), was synthesized by the grafting of glycidyl methacrylate onto the polylactide (PLA) chain via free-radical polymerization. Fourier transform infrared spectroscopy and $^{1}$H-NMR were used to characterize the structure of the copolymer. Furthermore, PLA–GMA was used as a coupling agent to improve the interfacial adhesion between bamboo flour (BF) and PLA in PLA/BF biocomposites. The mechanical properties and crystallization behavior of the PLA/BF biocomposites were investigated. The results show that with the addition of PLA–GMA, the flexural strength and flexural modulus of the biocomposites increased significantly. The mechanical properties increased with increasing PLA–GMA amount. The PLA–GMA also enhanced the crystallization rate of PLA in the PLA/BF biocomposites. The property improvement of the biocomposites was due to enhanced interfacial adhesion between the PLA and BF. This was confirmed by scanning electron microscopy.  J. Appl. Polym. Sci. 000: 000–000, 2012

**Key words:** compatibility; composites; crystallization; graft copolymers; mechanical properties

## INTRODUCTION

Recently, with worldwide environmental awareness, many efforts have been focused on the study of natural-fiber (NF)-reinforced polylactide (PLA) fully biodegradable biocomposites.[1] NFs, such as jute, flax, and sisal, which have some advantages, including low cost, low density, and acceptable mechanical properties, are potential alternatives to traditional reinforcing fibers (e.g., glass fiber (GF) , carbon fiber (CF), Kevlar).[2,3]

However, the hydrophilicity of NFs and their poor compatibility with hydrophobic polymer matrices limit their use as reinforcements in polymer composites. Many physical and chemical treatments of fiber surfaces (e.g., mercerization, acetylation[4–6]) have been applied to improve the interfacial adhesion between NFs and the PLA matrix. However, these fiber surface treatments always destroy the fiber structure or produce a lot of wastewater. The use of a coupling agent in NF-reinforced composites is a relatively efficient and environmentally friendly method for improving the interfacial adhesion. A coupling agent is a substance capable of reacting with both the reinforcement and the matrix and, thus, creates a bridge between the reinforcement and the matrix. Several coupling agents are extensively used in NF-reinforced composites. Methylenediphenyl diisocyanate, the isocyanate groups of which can react with hydroxyl and carboxyl groups, has been widely used as a coupling agent in NF-reinforced composites. Petinakis et al.[7] increased the tensile strength and tensile modulus of wood-flour/PLA composites with the addition of methylenediphenyl diisocyanate. Lysine-based diisocyanate has also been used as a biobased coupling agent in PLA-based biocomposites.[8] Maleic anhydride (MA) and maleated polymers are two other commonly used coupling agents in NF-filled composites. Kim et al.[9] obtained MA-grafted PLA via reactive extrusion and used it as a coupling agent in bamboo-flour (BF)- or wood-flour-reinforced PLA composites. They found that the tensile strength and heat deflection temperature of the PLA–MA treated biocomposites were greater than those of untreated ones. Another coupling agent widely used in NF-reinforced composites is silane coupling agents.[10]

Glycidyl methacrylate (GMA) is a well-known bifunctional monomer, which consists of acrylic and epoxy groups. The epoxy group of GMA can react with many other groups, such as hydroxyl and carboxyl groups, whereas acrylic groups show the

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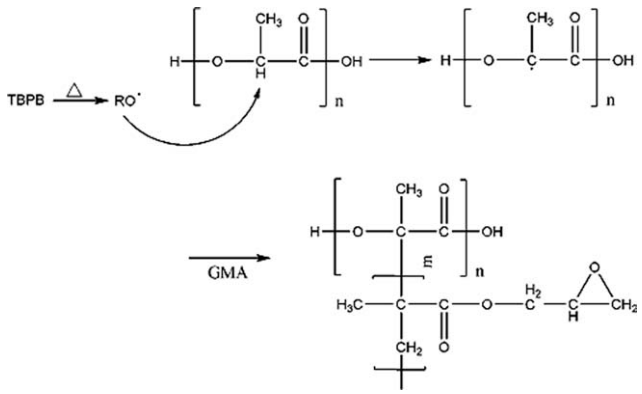


**Figure 1** Mechanism of the grafting of GMA onto the PLA chain.

capability of free-radical grafting of GMA onto the polymer chain. The GMA-grafted copolymer is a potential compatibilizing agent for reducing the interfacial tension in polymer blends or a coupling agent in polymer-based composites. In recent years, several kinds of GMA-grafted polyolefins have been prepared through reactive extrusion or solution copolymerization.[11–15] In our previous work, the reactive grafting of GMA onto PLA was achieved in the process of BF-reinforced PLA biocomposite blending extrusion. The mechanical properties of PLA/BF biocomposites were improved. However, there was always some residual GMA in the composites, which was volatile, and the crystallization properties of PLA were affected by the broadened molecular weight distribution of the PLA. So, in this study, polylactide-*graft*-glycidyl methacrylate (PLA–GMA) was prepared in solution and used as a coupling agent to improve the interfacial adhesion in PLA/BF biocomposites. The mechanical and crystallization properties of biocomposites with or without PLA–GMA were investigated.

## EXPERIMENTAL

### Materials

Commercial PLA (4032D) was purchased from NatureWorks LLC., (Minnetonka, MN) BF (<400 μm) and alkali treated with a 2% sodium hydroxide solution were obtained from a local source. GMA and *tert*-butyl perbenzoa (TBPB) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China) and were used with no further purification. All of the other reagents and solvents were obtained from commercial companies and with no further purification.

### Preparation of PLA–GMA

The grafting of GMA onto the PLA chain was carried out under nitrogen in a toluene solution. PLA (20 g) was dissolved in toluene (300 mL) at 115°C. When all of the PLA was dissolved, a mixture of 5 g of GMA and 2 g of TBPB was added dropwise. The reaction mixture was stirred, and the grafting reaction went on for 5 h. The solution was then cooled to 25°C, and the graft copolymer was precipitated. The precipitated product was dissolved further in chloroform and precipitated in ethanol several times to remove residual GMA, TBPB, and GMA homopolymer and then dried in a vacuum oven at 75°C.

### Fabrication of the PLA/BF biocomposites

Before processing, all of the BF and PLA were dried in a vacuum oven at 75°C for 12 h. The blending of PLA–GMA, BF, and PLA was carried out at 185°C with a laboratory-scale conical twin-screw extruder (SJSZ-10A), which could run in circulation mode. The screw rotational speed and cycle time were kept at 40 rpm and 6 min, respectively. PLA/BF biocomposites with various amounts of BF and PLA–GMA were fabricated and evaluated.

### Characterization

Fourier transform infrared (FTIR) spectra of PLA and PLA–GMA were acquired on a Nicolet 6700 spectrophotometer with a resolution of 4 $cm^{-1}$ and 32 scans in the range 4000–400 $cm^{-1}$. The $^1$H-NMR spectrum of the graft copolymer PLA–GMA was recorded with a Bruker instrument (400-MHz AVANCE III). The PLA-GMA sample was dissolved in $CDCl_3$, and tetramethyl silane was used as an internal standard. The molecular weights of the pure PLA and PLA–GMA were obtained by a Waters 1515 gel permeation chromatograph with chloroform as the solvent at a flow rate of 0.8 mL/min. The morphologies of the fractured surfaces of the PLA/BF biocomposites

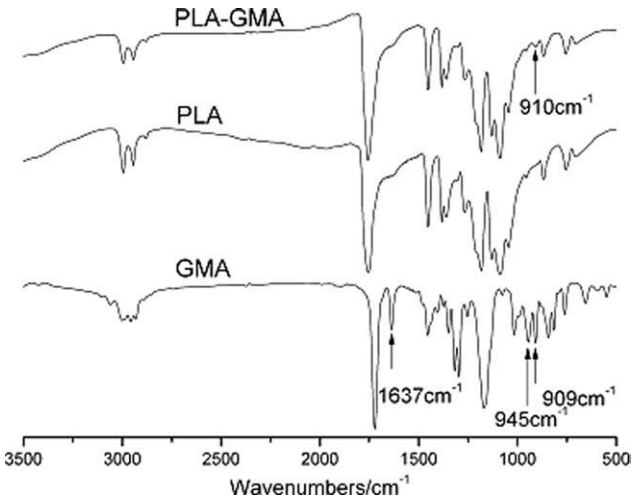


**Figure 2** FTIR spectra of PLA, GMA, and PLA–GMA.

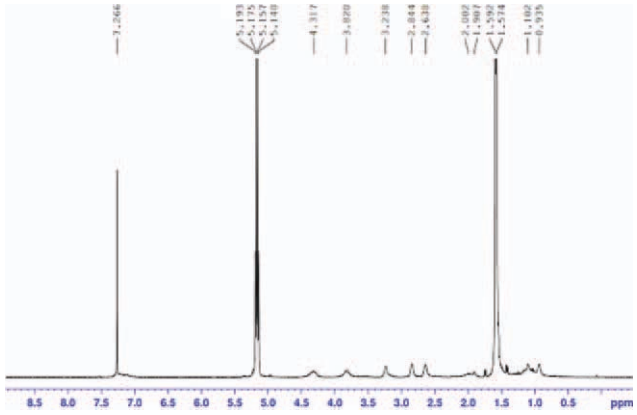

**Figure 3** $^{1}$H-NMR spectrum of PLA–GMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were observed with a scanning electron microscopy (SEM) instrument (Hitachi TM-1000, Tokyo, Japan). The samples were coated with gold particles before observation.

### Mechanical properties testing

The melt blends from the extruder were injected to flexural bars according to ISO 178 : 2010 standard with a miniature plastic injection machine (SZ-15, Wuhan, China). The flexural properties of the biocomposites were measured on an Instron 5567 (Boston, MA) instrument. The crosshead speed was set at 2 mm/min. The values reported for the flexural strength and modulus were the averages of at least five replicated tests.

### Crystallization behavior

The nonisothermal and isothermal crystallization behaviors of the pure PLA and PLA/BF biocomposites were researched with a differential scanning calorimetry (DSC) instrument (Mettler-Toledo, TGA/DSC 1, Zurich, Switzerland). In the nonisothermal crystallization process, the samples were first heated to melting at 200°C for 3 min to remove the heating history. The melted samples were cooled to 25°C at a rate of 5°C/min and then heated to 200°C at a rate of 10°C/min. The degree of crystallinity

**TABLE I**
**Molecular Weights of the Pure PLA and PLA–GMA**

| Sample | $M_n$ (g/mol) | $M_w/M_n$ |
|---|---|---|
| PLA | 118,900 | 1.72 |
| PLA–GMA | 119,200 | 1.76 |

$M_n$, number-average molecular weight; $M_w$, weight-average molecular weight.

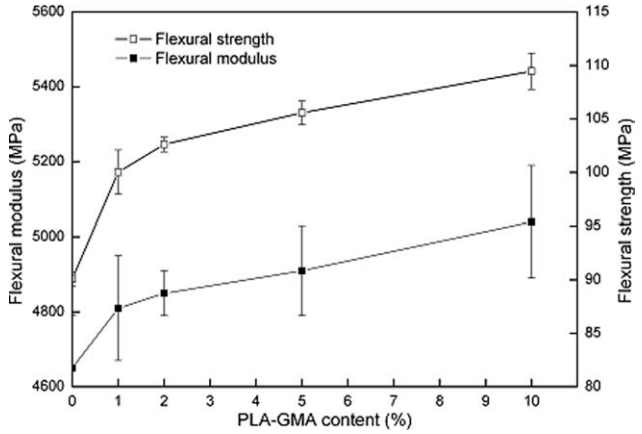


**Figure 4** Effect of the PLA–GMA content on the flexural properties of the PLA/BF biocomposites. The content of BF was 20 wt %.

($X_c$) values of the pure PLA and PLA in the PLA/BF biocomposites were computed by eq. (1):[16,17]

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \times \frac{1}{\omega} \quad (1)$$

where $\Delta H_m$ and $\Delta H_{cc}$ are the melting enthalpy and cold crystallization enthalpy in the heating process and ω is the weight fraction of PLA in the PLA/BF biocomposite. $\Delta H_m^o$, which is the melting enthalpy of an infinitely large crystal, was taken as $\Delta H_m^o = 93.6$ J/g.

In the isothermal crystallization process, the samples were also melted at 200°C for 3 min to remove the heating history. The melted samples were then cooled to a desired temperature at a rate of 100°C/min, crystallized at this temperature for 30 min, and subsequently heated to 200°C at a rate of 10°C/min.

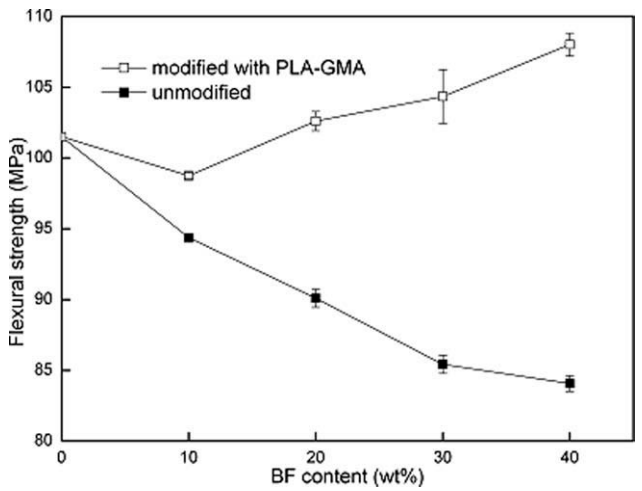


**Figure 5** Effect of the BF content on the flexural strength of the PLA/BF biocomposites modified with or without PLA–GMA.

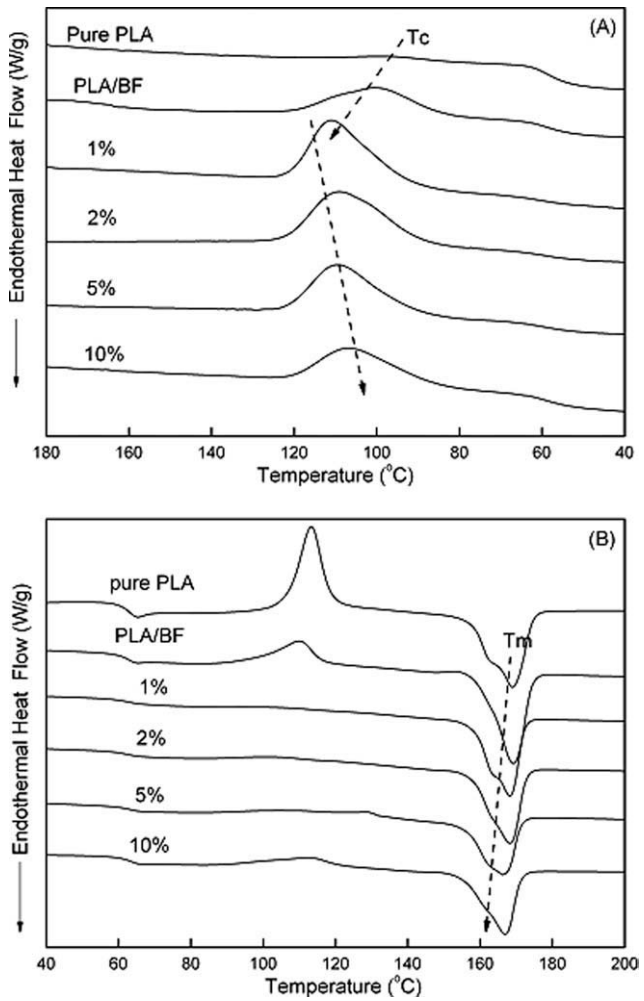


**Figure 6** DSC curves of the (A) nonisothermal crystallization at a cooling rate of 5°C/min and (B) subsequent heating process at a heating rate of 10°C/min of the pure PLA and PLA/BF biocomposites.

## RESULTS AND DISCUSSION

### Synthesis of the PLA–GMA graft copolymer

The graft polymer PLA–GMA was successfully prepared via free-radical polymerization, whereas the peroxide initiator abstracted a tertiary hydrogen from the PLA chain to form a macromolecular radical, as shown in Figure 1. Similar studies were done by Li et al.[18] and Burton et al.[19] The FTIR spectra of pure GMA, pure PLA, and PLA–GMA are given in Figure 2. Compared with the spectrum of pure PLA, a new peak appeared at 910 $cm^{-1}$ in the spectrum of PLA–GMA and was associated with the asymmetric stretching of the epoxy group. This showed that the GMA was successfully grafted onto the PLA chain. In addition, the disappearance of the peaks of C=C (1637 and 945 $cm^{-1}$) meant that the double bond of GMA vanished in the reaction. $^1$H-NMR spectra were also used to characterize the structure of the graft copolymer PLA–GMA. As shown in Figure 3, the signals of methyl protons and methylene protons of the PLA chain appeared at 1.574–1.592 and 5.140–5.193 ppm, respectively. On the other hand, the peaks at 2.638–2.844 and 3.238 ppm were attributed to the epoxy groups (—$OCH_2$ and —CH—, respectively). The results further indicate that the GMA was successfully grafted onto the PLA chain. The molecular weights of the pure PLA and PLA–GMA

**TABLE II**
**Detailed Thermal Property Values of the Nonisothermal Crystallization Process and Melting Process Obtained from the DSC Curves**

| Sample | $T_c$ (°C) | $T_m$ (°C) | $\Delta H_{cc}$ (J/g) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|---|---|---|---|---|---|
| Pure PLA | 96.33 | 169.06 | 30.09 | 31.83 | 1.86 |
| 20% BF/PLA | 101.01 | 169.15 | 14.26 | 30.18 | 21.26 |
| 1% PLA–GMA | 111.72 | 168.39 | 0.90 | 27.05 | 34.92 |
| 2% PLA–GMA | 109.41 | 169.18 | 1.95 | 26.30 | 32.51 |
| 5% PLA–GMA | 109.97 | 166.29 | 1.33 | 24.75 | 31.28 |
| 10% PLA–GMA | 107.39 | 166.90 | 6.4 | 23.03 | 22.21 |

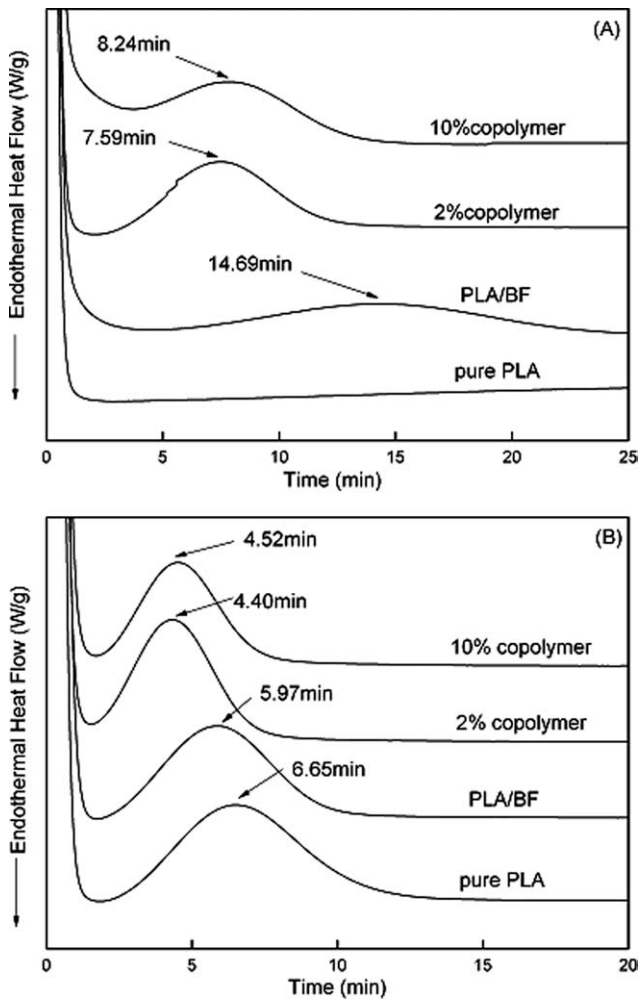


**Figure 7** DSC curves of the isothermal crystallization of the pure PLA and PLA/BF biocomposites at (A) 130 and (B) 110°C.

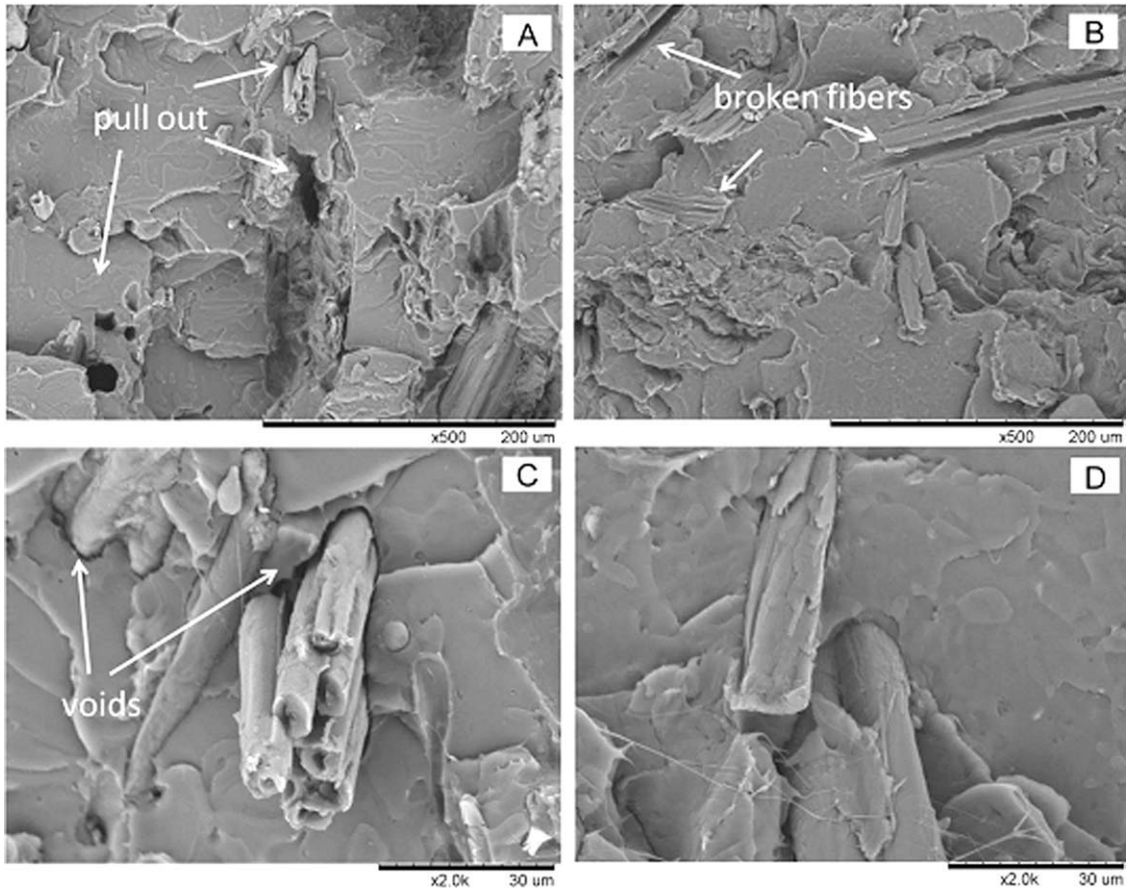


**Figure 8** SEM micrographs of the PLA/BF biocomposites: (A,C) nontreated biocomposites and (B, D) composites with added PLA–GMA.

were also measured by gel permeation chromatography. From Table I, one can see that the molecular weight and polydispersity of PLA–GMA increased compared with that of pure PLA. However, the increase of molecular weight was not so obvious. This may have been because the graft ratio of GMA was relatively low, and also, some PLA chains degraded during the reaction.

### Mechanical properties of the PLA/BF biocomposites

The epoxy groups in the graft copolymer PLA–GMA could react with the hydroxyl groups in the cellulose of BF, and the PLA chain of PLA–GMA had good compatibility with the PLA matrix. So, the graft copolymer PLA–GMA could be used as a coupling agent to improve the interfacial adhesion of the PLA/BF biocomposites. Figure 4 shows the effects of PLA–GMA content on the flexural properties of the PLA/BF biocomposites. The content of PLA–GMA was based on the total weight of the biocomposites. As shown in Figure 4, the addition of PLA–GMA greatly enhanced the flexural strength and flexural modulus of the PLA/BF biocomposites. As the PLA–GMA content increased to 10%, the flexural strength of the biocomposites increased from 90.05 to 109.46 MPa, whereas the flexural modulus increased from 4650 to 5043 MPa. This may have been because the PLA–GMA could improve the interfacial adhesion between the BF and PLA matrix and the stress transfer from PLA to BF was enhanced. The improvement of the interfacial adhesion is illustrated by SEM graphs later. The influence of the BF content on the flexural strength of the PLA/BF biocomposites with or without PLA–GMA was also investigated, and the results are given in Figure 5. The PLA–GMA content was set at 10 wt % on the basis of the weight of BF. For the PLA/BF biocomposites without PLA–GMA, the flexural strength of the biocomposites decreased with increasing BF content. This may have been due to the poor interfacial adhesion and increasing stress concentrators between the PLA matrix and BF. However, for the PLA/BF biocomposites with added PLA–GMA, the flexural strength increased from 98.74 to 108.02 MPa when the BF content was increased to 40 wt %. The enhancement in flexural strength with the addition of PLA–GMA was more obvious as the BF content was increased. All of the

results indicate that the addition of PLA–GMA improved the interfacial adhesion between the PLA matrix and BF.

### Crystallization behavior of the PLA/BF biocomposites

The poor crystallization of PLA is one of the drawbacks that limit its applications. Several methods have been used to improve the crystallization of PLA.[20] The influence of PLA–GMA on nonisothermal crystallization was researched by DSC, and the results are illustrated in Figure 6. Compared with the pure PLA, the PLA/BF biocomposite showed a larger crystallization peak in the cooling process and a smaller cold crystallization peak in the melting process. This suggested that the addition of BF improved the crystallization properties because of the heterogeneous nucleation of BF.[21,22] On the other hand, the crystallization peak shifted to a higher temperature when the PLA–GMA copolymer was added. This may have indicated that when the BF ws modified by the PLA–GMA copolymer, the bamboo fiber had better compatibility with the PLA chain, and the PLA chain was more liable to align and fold to crystallize on the surface of the BF. The detailed thermal properties data of the cooling crystallization and melting process were calculated and are listed in Table II. With the addition of 1% PLA–GMA, $X_c$ of PLA in the PLA/BF biocomposites increased from 21.26 to 34.92%. However, as the content of PLA–GMA increased, the crystallization temperature ($T_c$) moved to lower values, and $X_c$ decreased to 22.21%. Also, the melting temperature ($T_m$) decreased.

The isothermal crystallization behaviors of PLA and the biocomposites modified or not modified by PLA–GMA at 130 and 110°C were also investigated by DSC (Fig. 7). The crystallization rate of PLA in PLA/BF biocomposites increased obviously with the addition of 2% PLA–GMA. The times of the crystallization peak decreased from 14.69 to 7.59 min at 130°C and from 5.94 to 4.40 min at 110°C. Excess PLA–GMA slowed the crystallization of PLA. The time of crystallization peak of the PLA/BF biocomposites with a high content of PLA–GMA increased compared with that of the biocomposites with less PLA–GMA.

### Morphology characterization

SEM is an intuitive method for observing the interfacial adhesion between fibers and the polymer matrix. Figure 8 shows the micrographs of the fracture surfaces of 20% PLA/BF biocomposites modified and not modified by PLA–GMA. From the graphs of the untreated PLA/BF biocomposites [Fig. 8(A,C)], one can see that some fibers were pulled out from the polymer matrix, and gaping holes and voids between the fibers and matrix are visible. This indicates that the interfacial adhesion between the fibers and matrix was poor. Figure 8(B,D) shows the fracture surface of the biocomposite modified by PLA–GMA. A number of broken fibers were found, and the voids between the fibers and matrix disappeared; this indicated that the interfacial adhesion was improved by PLA–GMA.

## CONCLUSIONS

The grafting of GMA onto the PLA chain was achieved in solution via free-radical polymerization; this was confirmed by FTIR spectroscopy and $^1$H-NMR. Then, PLA–GMA as a coupling agent was added to the PLA/BF biocomposites. The flexural modulus and flexural strength of the PLA/BF biocomposites increased obviously as the content of PLA–GMA increased. The improvements were due to the improved interfacial adhesion between the bamboo fibers and the PLA matrix. The addition of PLA–GMA also enhanced the crystallization of the PLA.

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