Water Bamboo Husk Reinforced Poly(lactic acid) Green Composites

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Abstract

The water bamboo husk is one of major agricultural wastes in Taiwan. In this study, the powder obtained from the water bamboo husk was added to poly(lactic acid) (PLA) to form novel reinforced biodegradable composites. Morphologies, mechanical properties and heat resistance of these water bamboo powder reinforced composites were investigated. The results indicate that the char yields were increased as plant powder was incorporated to PLA. In addition, the mechanical properties were also enhanced due to the addition of powders. The increments of storage moduli of PLA were about 50 to 200%. Moreover, the increments of loss moduli of PLA were about 70 to 200%. On the other hand, the $T_g$ of PLA was slightly decreased by the addition of powder, and this may improve the brittle characteristics of PLA. Furthermore, this type of reinforced PLA would be more...
environmental friendly than the artificial additive-reinforced one.

*Keywords*: water bamboo, waste, poly(lactic acid), plant powder, composite.
Introduction

Water bamboo (Coba, Gausum) is a water plant that has a preference for warm, humid, and sunny environment. The peak production is during summer [1]. Despite that it is a highly popular vegetable, the water bamboo husk is one of the major agricultural wastes in Taiwan. Recently, plant-based fillers have attracted a great deal of interests for reinforcing plastics. Natural fillers have benefited from the perception that they are "green" or eco-friendly. Advantages of such fillers over man-made fills include low density, low cost, recyclability and biodegradability [2–4]. These advantages make plant-based fillers potential replacement for glass fibers in composite materials. Mechanical properties of natural fibers, especially flax, hemp, jute and sisal, are very good and may compete with glass fiber in specific strength and modulus [5-7]. Various researchers investigated the strengthening effects on the natural fillers containing polyolefins, polystyrene, polyester, polyurethane and epoxy resins, respectively [8-21]. Moreover, the plant fillers were further incorporated into biodegradable polymers (poly(lactic acid), starch product and polybutylene succinate) [22-29]. Mechanical properties and biodegradability of the plant filler containing biodegradable polymers were greatly enhanced as compared to the pristine biodegradable polymers. In our previous researches, it is also found that the mechanical and thermal properties of polybutylene succinate [30] and epoxy [31] were all promoted by the addition of water bamboo husk.
The development of biodegradable polymers has been a subject of great interest in materials science for both ecological and biomedical perspectives [32]. Increasing awareness of the environmental damage caused by plastic materials over the last few decades has led to research aimed at producing eco-friendly versions of those plastics. Aliphatic polyesters are among the most promising materials for the production of high-performance, environment-friendly biodegradable plastics [33-36]. One of the aliphatic polyesters is poly(lactic acid) (PLA) which is produced via the ring-opening polymerization of lactide (a cyclic dimer of lactic acid). PLA has a renewable source [33], with the lactic acid monomers used to produce it coming from the fermentation of corn, potato, sugar beet, and sugar cane [37, 38]. PLA is also well known for its degradability to natural products in a short period of time (0.5–2 years) in contrast to conventional plastics like PS, PE, etc. needed 500–1000 years [34, 39]. Moreover, PLA is a thermoplastic, high-strength, high-modulus polymer that can be used in either the industrial packaging field or the biocompatible/bioabsorbable medical device market. It is easily processed on standard equipment to yield molded parts, film, or fibers [40, 41]. However, the high brittleness and the quite high price of PLA currently limit its applications and considerable efforts have been made to improve these characteristics of the polymer [42-49]. In this study, the powder of water bamboo husk was screened to a very small size (~0.05 mm) to promote its compatibility with PLA. Then, the powder was incorporated into PLA, in order to enhance
the mechanical and thermal properties of the plastics. Furthermore, the production of such green composites will reduce the amount of agricultural wastes, and increase the economic value of the water bamboo, and lead to the cost down of PLA products.

2. Experimental

2.1 Materials

The husk of water bamboo grown in Nantou County, Taiwan was chopped and screened from 270 mesh (0.052 mm) to obtain the powder. The poly(lactic acid) (PLA, PLA2002D™) was supplied by Nature-Works LLC.

2.2 Preparation of the composites

The PLA, water bamboo powder were dried in an air oven at 100 °C for 4 hours under reduced pressure, until the moisture content was below 1.0 wt%. Immediately after drying, the PLA was melt blended with water bamboo powder in a counter-rotating internal mixer (Brabender PL2000, Duisburg, Germany) with a rotation speed of 60 rpm for 10 min at 180 °C. The amount of water bamboo powder was 5, 10, 15, 20 phr which was based on the weight of PLA, and the formulations of the samples were shown in Table 1. Samples for the investigations were prepared by compression molding (0.5 mm thick) at 185°C and then solidification by quenching to ambient temperature. The annealed samples was prepared
from the quenched samples by annealing at 130 °C for 1.5 h in order to allow the crystallization to complete.

2.3 Instruments

Thermal behavior was investigated using a Perkin-Elmer, TGA7 thermogravimetry analysis (TGA). All experiments were carried out under a nitrogen atmosphere at a purge rate of 100 ml/min. Samples of approximately 5mg were heated to 700 °C at a heating rate of 10 °C/min. Mechanical properties of samples were investigated using a Perkin-Elmer DMA 7e dynamic mechanical analysis (DMA) at frequency 1 Hz (heating rate of 3 °C/min). The specimen size is 0.5×0.5×0.3cm. X-ray diffractometry (XRD) measurements were carried out by using a Rigaku D/MAX-2200PC X-ray diffractometer (Cu Kα radiation, wavelength: λ = 0.154 nm) operated at 40 kV and 100 mA. Data were collected within the range of scattering angles (2θ) of 1.5~10°. X-ray diffractometry. Phase transition behavior was analyzed by differential scanning calorimeter (DSC; Seiko SII Model SSC5200). Moreover, the morphology was observed with a Carl Zeiss polarizing microscope, equipped with a Mettler Toledo hot-stage. The PLA samples were melted at 190 °C for 3 min and then cooled down to 110 °C at 5 °C min⁻¹, for isothermal crystallization to occur.

3. Results and discussion
3.1. TGA analysis

TGA thermograms of various samples under nitrogen are shown in Figure 1. The decomposition temperatures of powder-containing samples were all smaller than that of pristine PLA due to the nature of the plant. However, the char yields of powder-containing samples (Table 2) were all larger than that of pristine PLA. These results reveal that the addition of powder to PLA would effectively raise the char yields of the samples. As reported previously [50-52], the char yield is directly correlated to the potency of flame retardation for the polymers. Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and inhibit the thermal conductivity of the burning materials [53].

3.2. DSC analysis

Figure 2 shows the DSC thermograms for samples recorded during heating scan at the rate of 3 °C/min. These thermograms reveal the following: the glass transition (T_g), the cold crystallization exotherm (at T_c) and the main melting process characterized by two, more or less separated, endotherms (at Tm_1 and Tm_2). The endothermic maximum following the glass transition in powder-containing samples is generally ascribed to the enthalpic relaxation. The enthalpic relaxation is described in the literature using several names including stress relaxation, and volume relaxation [54, 55].
Table 3 shows that the values of $\Delta H_f$ were decreased with the addition of the powder, and the cold crystallization phenomenon was found at about 110°C for the powder-containing samples in Figure 2. This indicates that the powder may disrupt the crystallite formation of PLA, and lead to less ordered crystals and smaller crystallinity of the composites as compared with the pristine PLA [56]. Therefore, the cold crystallization was occurred in the powder-containing samples upon heating. Moreover, two $T_m$s were found for the composites in the thermograms. The temperature of first $T_m$ for the composites was much lower than that of pristine PLA. Most probably they are connected with a minute fraction of thinner and/or less perfect crystals formed during quenching of the films to room temperature after cold crystallization [45]. The temperature of second $T_m$ for the composites was similar to that of pristine PLA, and is more probable to refer to the melting point of the originally crystallized parts. Moreover, the $T_c$s and $\Delta H_c$ of the composites were decreased with the increasing content of the powder in the polymer matrix. This indicates that the cold crystallization phenomenon was more easily occurred at larger content of powder in PLA, nevertheless the crystallinity was smaller. Table 3 also shows that $T_g$s of composites were slightly smaller than that of pristine PLA. This results reveals that the powder of water bamboo husk may play a role of plasticizer.

3.3. POM analysis
To understand the crystallization behavior, POM was used to compare the crystal morphology of PLA and PLA/water bamboo husk composites and to determine linear growth rate $G$ of the spherulites. The optical micrographs of the crystalline growth at the crystallization temperature ($T_c$, 110°C) for the pristine PLA sample and powder-containing composite are shown in Figure 3-4. The spherulites were found in the matrices of pristine PLA (Figure 3). On the other hand, the smaller and less ordered crystals were found in the micrograph of the composite (Figure 4). These results revealed that the powder of bamboo husk acted as a nucleating agent to increase the number of the nuclei, causing the formation of smaller spherulites. The introduction of these powders would influence the morphological structures of the PLA crystal such as spherulite size, shape, and nucleation density. This agrees with the DSC study. The addition of powder decreased the size of the spherulites, whereas the shape of the spherulites became irregular. Moreover, linear growth rate $G$ of spherulites could be obtained from diameter of spherulite versus time for PLA and PLA/water bamboo husk composites and is shown in Figure 5 and Table 4. The value of parameter $G$ increases with increasing powder content and is probably because the powder of bamboo husk acted as a nucleating agent to increase the spherical growth. However, the value of parameter $G$ of PLA20 decreased is due to that the introduction of a great amount of powder into PLA causes a significant decrease in free volume and thus a decrease in molecular chain mobility, leading to a lower growth rate [57]. Moreover, the regression
factor of PLA20 for calculating the linear growth rate $G$ was much smaller than those of the other samples. This indicates that the powder in PLA20 was not dispersed well due to aggregative phenomenon occurs at high powder content.

### 3.4. WAXD analysis

Figure 6 shows that the powder of bamboo husk is low crystalline material since only a trace of crystallinity identified from the peaks close to $2\theta \approx 16^\circ$ and $22^\circ$. This is consistent with our previous study by solid NMR [30, 31, 58]. Figure 7 shows that the PLA matrices of the melt-quenched samples are amorphous since a scattered intensity distribution exhibits a broad peak around of $2\theta \approx 17.1^\circ$. Only the pristine PLA sample exhibits a trace of crystallinity identified from the broadened peak close to $2\theta \approx 17.1^\circ$. This agrees with the results of DSC analysis that the powder may disrupt the crystallite formation of PLA. Figure 8 shows the X-ray diffractograms of the annealed samples. PLA matrices of the all samples exhibit the crystalline peaks located at the same $2\theta$ position. A very strong reflection was found at $2\theta \approx 17.1^\circ$ due to diffraction from (200) and/or (110) planes and another reflection peak found at $2\theta \approx 19.5^\circ$ occurring from (203) plane. These profiles indicate that neat PLA crystals are the typical orthorhombic crystal [59-61]. No evidence of the formation of $\beta$-crystallographic form in those samples was found, similarly as it was reported for the neat PLA drawn slightly above $T_g$, which crystallized in $\alpha$-form [62].
XRD crystalline spectra indicates that in the samples only one crystalline modification is developed and the double melting peak seen in the DSC heating run reflects the melting of crystalline regions of various sizes and perfection.

3.5. DMA analysis

As shown in Figure 9, the storage moduli of powder-containing samples were all larger than that of pristine PLA. Moreover, the storage modulus of PLA15 was the largest among the samples. The storage modulus of PLA20 was smaller than that of PLA15, but was still larger than that of pristine PLA. Moreover, the loss moduli of powder-containing samples were all larger than that of pristine PLA (Figure 10), and PLA15 also exhibited the best result. Furthermore, the peak of PLA20 was not so smooth indicating the less homogeneity as compared with the other samples. This leads to the smaller storage and loss moduli. It is important to note that the $T_g$ of sample is slightly decreased by the addition of powder (Figure 10). This means that the powder of water bamboo husk may play the role of plasticizer, so the loss modulus of PLA was enhanced, and the brittleness of PLA was modified.

Conclusion

The addition of the powder obtained from water bamboo husks to PLA provides a vehicle to improve the mechanical or thermal properties. With the addition of the powders, the char yields of the composites were increased. Moreover, the maximum increment of the
storage and loss moduli of PLA was approximately 200% for the annealed sample. On the other hand, the $T_g$ of PLA was slightly decreased by the addition of powder. This means that the powder of water bamboo husk may play the role of plasticizer, so could improve the brittle characteristics of PLA. Furthermore, the innate biodegradability of water bamboo husks renders this type of reinforced PLA would be more environmental friendly than the artificial additive-reinforced one. The agricultural wastes and the cost of PLA products could be reduced through the usage as plastic reinforced additives.

ACKNOWLEDGEMENTS

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References


Figure captions

Figure 1  TGA thermograms of samples
Figure 2  DSC thermograms of samples
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Figure 4  POM micrograph of PLA10
Figure 5  Plots of radius of spherulite versus times for samples.
Figure 6  X-ray diffraction pattern of the powder obtained from water bamboo husk
Figure 7  X-ray diffraction patterns of un-annealed samples
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Figure 9  Temperature dependence of the storage moduli for samples
Figure 10 Temperature dependence of the loss moduli for samples
Table captions

Table 1  Formulations of samples (wt.)

Table 2  Char yields of samples at 600°C

Table 3  The results of DSC analysis

Table 4  The results of linear regression for calculating the linear growth rate $G$ of spherulites
Table 1  Formulations of samples (wt.)

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<th></th>
<th>PLA2002D</th>
<th>Water bamboo husk powder*</th>
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<tr>
<td>PLA</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>PLA05</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>PLA10</td>
<td>100</td>
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<td>PLA15</td>
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<td>PLA20</td>
<td>100</td>
<td>20</td>
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*: Which was dried in an air oven at 100°C for 4 hours under reduced pressure, until the moisture content was below 1.0 wt%.
Table 2  Char yields of samples at 600°C

<table>
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<tr>
<th>Char yield (%)</th>
<th>PLA</th>
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<tr>
<td>0.402</td>
<td>0.945</td>
<td>0.953</td>
<td>1.612</td>
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Table 3  The results of DSC analysis

<table>
<thead>
<tr>
<th></th>
<th>$T_m (^\circ C)$</th>
<th>$T_g (^\circ C)$</th>
<th>$T_c (^\circ C)$</th>
<th>$\triangle H_f$ (J·g$^{-1}$)</th>
<th>$\triangle H_c$ (J·g$^{-1}$)</th>
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<tr>
<td>PLA</td>
<td>154.52</td>
<td>59.62</td>
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<td>36.6</td>
<td>-</td>
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<tr>
<td>PLA05</td>
<td>152.25, 154.78</td>
<td>57.43</td>
<td>115.56</td>
<td>35.8</td>
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<tr>
<td>PLA10</td>
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<td>55.11</td>
<td>110.74</td>
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</tr>
<tr>
<td>PLA15</td>
<td>149.10, 155.89</td>
<td>55.00</td>
<td>105.69</td>
<td>31.9</td>
<td>-19.6</td>
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Table 4  The results of linear regression for calculating the linear growth rate $G$ of spherulites

<table>
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<th>Slope (linear growth rate $G$, $\mu m/s$)</th>
<th>Regression Factor</th>
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<tr>
<td>PLA</td>
<td>0.02258</td>
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<td>PLA15</td>
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</tr>
<tr>
<td>PLA20</td>
<td>0.01967</td>
<td>0.97931</td>
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