Chapter 6
Green Composites Based on Poly (Lactic Acid) and Bamboo Fiber: Flame Retardancy, Thermal, and Mechanical Properties

Yeng-Fong Shih and Zhong-Zhe Lai

Abstract A series of green composites composed of polylactic acid (PLA), bamboo fiber and halogen-free flame retardant (ammonium polyphosphate, APP) were prepared. Moreover, the APP was chemically modified with a silane coupling agent, 3-glycidoxypropyltrimethoxysilane to promote its compatibility with PLA. These green composites were prepared by melt-blending and its flame retardancy, thermal, and mechanical properties were investigated. The results reveal that the thermal degradation temperature and char yield of PLA were significantly elevated when modified APP was added. Furthermore, the storage and loss moduli of the composites can be enhanced effectively by the addition of bamboo fibers. This means that the addition of the bamboo fibers can reinforce both the rigidity and toughness of PLA. Moreover, scanning electron microscopy (SEM) analysis revealed that modified APP has better compatibility with PLA and bamboo fiber. According to the UL-94 analysis, the composite with modified APP and bamboo fiber can reach the highest retardant level V-0. These results indicate that modified APP can enhance the thermal resistance and flame retardant properties better than unmodified ones can. Moreover, the bamboo fibers can not only reinforce the mechanical properties of PLA, but also play an important role of synergistic flame retardancy with modified APP.

6.1 Introduction

Ammonium polyphosphate (APP) has attracted great attention because it is halogen-free and effective. The char produced protects underlying materials from heat and oxygen [1]. Recently, the development of biodegradable polymers has become a subject of great interest in materials science due to the environmental damage over the last few decades caused by plastic materials [2]. One of the biodegradable polymers is poly (lactic acid) (PLA), which is produced by a renewable source [3]. PLA is a

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thermoplastic, high-strength, high-modulus polymer and is easily processed using standard equipment to form molded parts, film or fibers [4]. However, the high brittleness and poor thermal stability of PLA currently limit its range of applications [5]. For wider applications of PLA, flame-retardant PLA composites have been widely studied [6–9]. In Shukor et al.'s study [10], PLA was blended with kenaf core fiber, polyethylene glycol and APP, respectively. It was found that APP was very effective in improving the flame-retardant properties with high limiting oxygen index (LOI) value and increased char residue at high temperatures. However, the compatibility between the PLA and kenaf fiber was poor, resulting in a significant reduction in the mechanical properties of the PLA composites.

Shaoa et al. [11] modified APP by ethylenediamine in order to reduce its hydrophilic property. It can be observed that when simply adding the unmodified APP into polypropylene (PP), the LOI of the composite is only increased from 18 to 20.9, and the flame retardant grade has no rating. This reveals that the addition of unmodified APP cannot achieve the flame retardant effect. After adding modified APP, the LOI of the composite increased from 18 to 32.5, and the flame retardant grade reached V-0, indicating that the modification of APP by ethylenediamine can not only reduce its hydrophilic property, but also improve the flame retardancy of the composite. Qin et al. [12] use vinyltrimethoxysilane (VTMS) to modify the surface of the APP. It can be observed that the flame retardancy of PP/dipentaerythritol (DPER)/APP composites has no rating. On the other hand, the flame retardancy of PP/DPER/modified APP composites can reach V-0 grade. It can be observed that the modification of APP is important in improving its flame retardant effect.

In this study, we incorporated bamboo fiber and flame retardant into PLA in order to prepare the flame retardant green composites with excellent mechanical and thermal properties. In addition, 3-glycidoxypropyltrimethoxysilane (GOPTS) was used to modify APP to improve its water resistance and enhance its interface compatibility with PLA. The flame retardancy, thermal, and mechanical properties of these green composites based on PLA and bamboo fiber were further investigated.

6.2 Experimental Procedures

6.2.1 Material

Polylactic acid (PLA) pellets (MW > 100,000) were purchased in 2003D grade from NatureWorks. The ammonium polyphosphate (APP) was provided by Parchem-fine & specialty chemicals. 3-glycidoxypropyltrimethoxysilane (GOPTS) was purchased from Echo Chemical.

6.2.2 Characterizations

Thermal behavior was determined using a TA Instruments' TGA Q50 thermogravimetric analyzer (TGA). A GT-HV 2000 analyzer was used to measure the heat deflection temperature (HDT) of the composites. Dynamic mechanical behaviors of the composites were measured by TA Instruments Q800. The UL-94 vertical tests were performed with an HVUL2 vertical burning tester (Atlas Technology Corp., Taiwan). A Hitachi scanning electron microscopy (SEM; model S-3000 N) was used to evaluate the morphologies and fractured surfaces of pure PLA and the composites.

6.2.3 Modification of APP

200 g APP, 4 g GOPTS and 200 mL ethanol were placed in a 500 mL three necked round-bottomed flask fitted with a stirrer and reflux condenser. The reaction was conducted for 1 h at 70 °C. The schematic diagram is shown as Fig. 6.1. Then the products were dried at 105 °C for 3 h in a vacuum oven.

6.2.4 Preparation of PLA Composite

The PLA, bamboo fiber, APP and modified APP had been dried in an oven at 100 °C for 4 h under reduced pressure until the moisture content was below 1.0 wt%. Immediately after drying, the PLA pellets were pre-melted at 175 °C in a counter-rotating internal mixer (Brabender PL2000, Duisburg, Germany) with a rotation speed of 50 rpm. Subsequently, the APP or modified APP were loaded into the mixer and blended with PLA for 5 min. Bamboo fiber was then further loaded into the mixer and blended with the mixture for another 10 min. Afterwards, the PLA composite was granulated. The sample was then processed by compression molding at 175 °C for 5 min (under 20 kgf/cm^2 or 50 kgf/cm^2), 3 min (under 75 kgf/cm^2) and 2 min (under 100 kgf/cm^2) in sequence. PLA contains 30% bamboo fiber named PF; PLA contains 20% APP named PA; PLA contains 30% bamboo fiber and 20% APP named PFA; PLA contains 20% modified APP named PEA; PLA contains 30% bamboo fiber and 20% modified APP named PFEA.

6.3 Results and Discussions

As can be seen from Table 6.1, whether or not a bamboo fiber is added, composites (PA and PFA) with unmodified APP, their 5 wt% degradation temperature (T_{d5}) and maximum degradation temperature (T_{dmax}) are all lower than those of composites

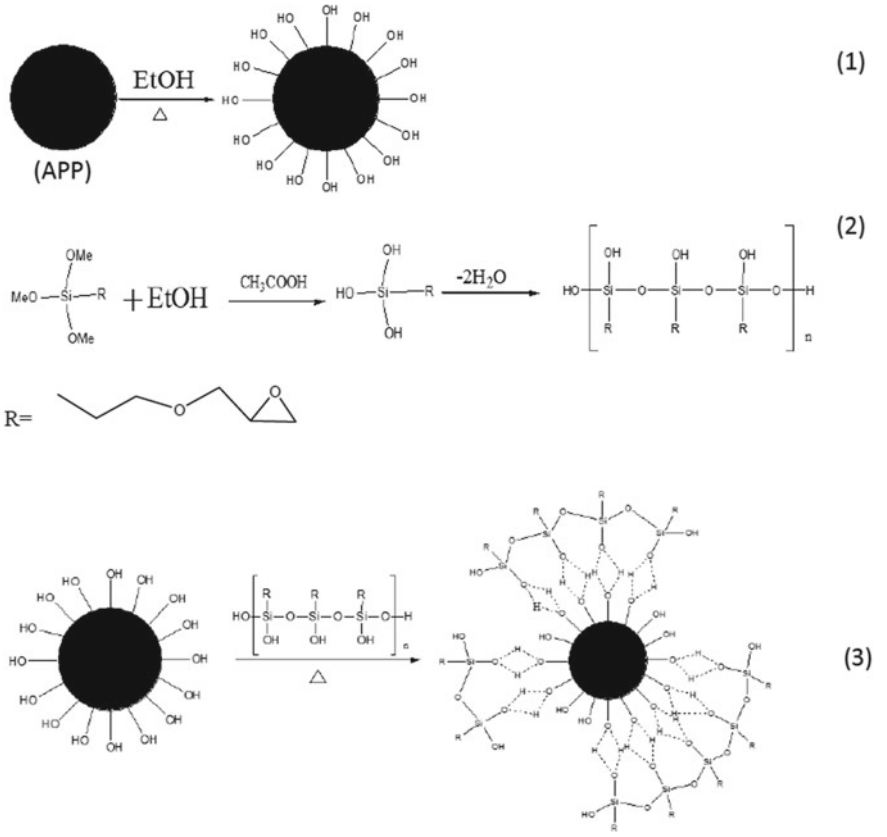

Fig. 6.1 Schematic diagram of APP modified by GOPTS

Table 6.1 TGA data of PLA and composites

Sample	T_{d5} (°C)	T_{dmax} (°C)	Char yield at 550 °C (%)
PLA	338.2	383.8	0.10
PF	308.2	364.1	7.60
PA	341.6	377.0	15.9
PFA	311.3	368.1	31.4
PEA	350.2	386.2	20.2
PFEA	311.7	371.5	30.8

(PEA and PFEA) with modified APP. Presumably, because the APP is modified by GOPTS, its surface layer is then coated with siloxane, and the siloxane also has the function of improving the heat resistance of the material, so the degradation temperature of the composites with modified APP is slightly improved. The 5 wt% and maximum degradation temperature (350.2 and 386.2 °C) of the composite containing

20% modified APP but no bamboo fiber (PEA) were the highest. However, in regard to the composites (PF, PFA and PFEA) containing bamboo fibers, the degradation temperature can be found to be lower because plant fibers usually begin to crack between 270 and 290 °C, resulting in an advance of the cracking temperature of the composites [13]. In addition, no matter whether adding APP or bamboo fiber, the char yield follows an increasing trend. Especially, the composite with the modified APP and bamboo fiber (PFEA) has the largest char yield of 30.8%, showing that the non-flammable ratio is effectively increased.

Table 6.2 shows the thermal deflection temperature (HDT) and dynamic mechanical properties of PLA and its composites. It can be observed that after simply adding APP or unmodified APP, the HDT is increased from 54.7 to 73.81 and 75.8 °C; after adding bamboo fiber, the HDT is significantly increased to 108.8 and 115.3 °C. This reveals that the rigidity and heat-resistant properties of the material can be effectively enhanced by adding bamboo fiber.

At the same time, it is found that the storage modulus of PLA was elevated by the addition of APP or bamboo fiber, representing that the rigidity of the material was enhanced, especially the bamboo fiber added ones. Among these, PFEA performed the best (4423 MPa). In addition, the storage moduli of PEA and PFEA (2051, 4423 MPa) were larger than those of unmodified APP containing ones—PA and PFA (1916, 2997 MPa). It is speculated that the modified APP can have better compatibility with PLA, so there is a better reinforcing effect. The proposed reaction mechanisms between modified APP and PLA are shown as Fig. 6.2.

From Table 6.2, it can be found that with the addition of bamboo fiber or APP to PLA, the loss moduli of composites have an increasing trend, representing that the toughness of the composites has been increased, especially the samples containing bamboo fibers (PF, PFA and PFEA). It is speculated that the hollow structure of the fiber can assist the PLA composites to absorb energy, so that the loss modulus of PLA can be improved.

Table 6.3 shows the results of the flame retardant analysis of PLA and its composites. It can be observed that the evaluation of pure PLA is not flame retardant (no rating), and still has no rating by the addition of bamboo fiber. It also did not achieve flame retardancy by the simple addition of flame retardant APP or modified APP (PA and PEA); the testing specimen produced a serious droplet phenomenon. The flame retardant grade can reach V-2 by adding bamboo fiber and APP (PFA) to the

Table 6.2 HDT and DMA data of PLA and composites

Sample	HDT (°C)	E′ (MPa)	E''_{max} (MPa)
PLA	54.7	1740	324.6
PF	58.4	2825	470.2
PA	73.1	1916	315.3
PFA	108.8	2997	469.5
PEA	75.8	2051	348.8
PFEA	115.3	4423	400.8

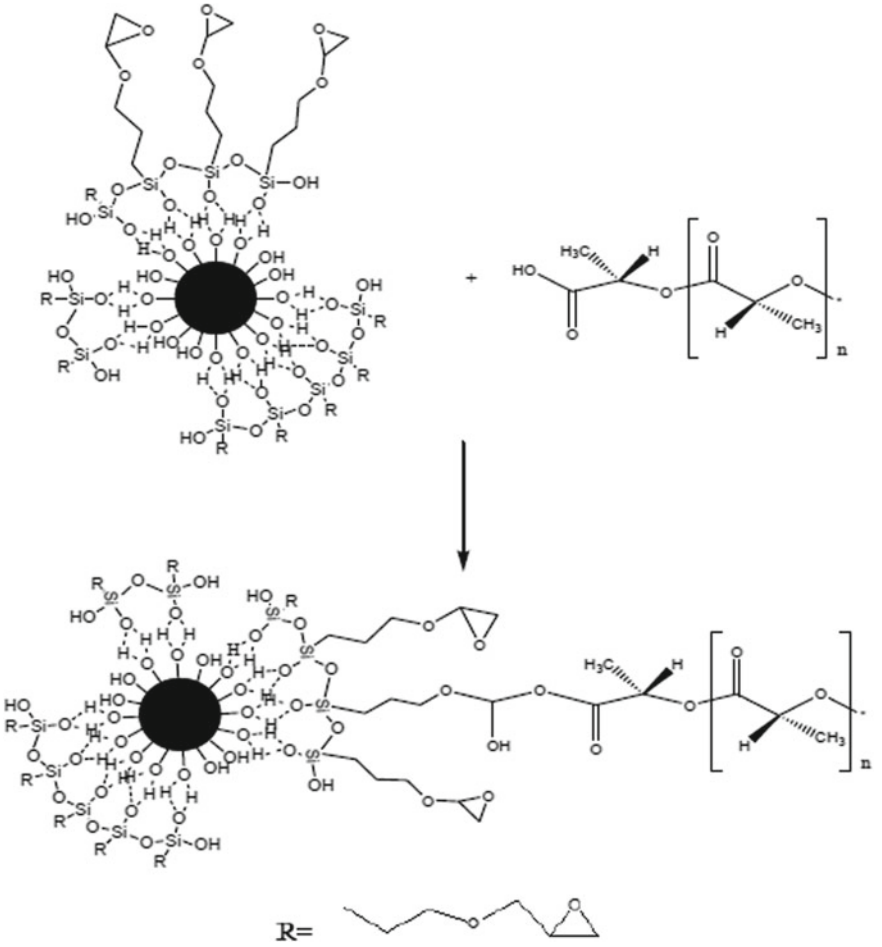

Fig. 6.2 Proposed reaction mechanisms between modified APP and PLA

Table 6.3 UL-94 test data of PLA and composites

	Flame retardancy
PLA	No rating
PF	No rating
PA	No rating
PFA	V-2
PEA	No rating
PFEA	V-0

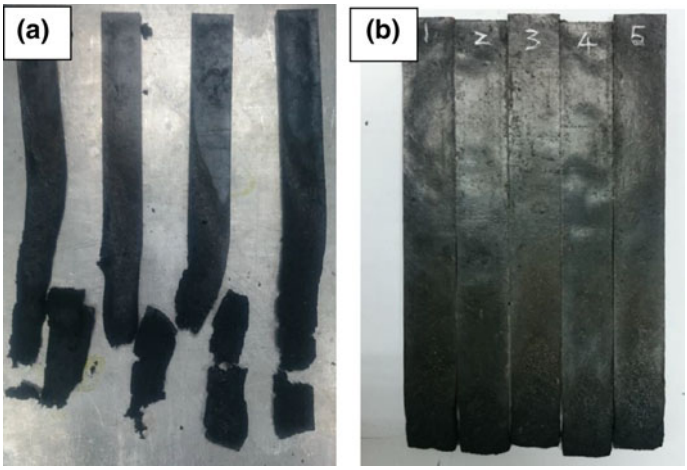

Fig. 6.3 Appearance of the **a** PFA and **b** PFEA test specimen after the UL-94 test

PLA. Moreover, the grade can reach the highest level of flame retardant V-0 with the addition of bamboo fiber and the modified APP (PFEA). It can be seen that the flame retardant effect of modified APP is better than that of APP. In addition, bamboo fiber can not only enhance the mechanical properties and heat resistance of PLA, but also produce synergistic flame retardant effects with flame retardants. Figure 6.3 is the appearance of the PFA and PFEA test specimen after the UL-94 test. It can be seen that the PFEA specimen is still very intact; however, the PFA specimen shows a little fragmentation phenomenon.

The SEM photographs of the fracture surface of PFA and PFEA are shown in Fig. 6.4. It is found from Fig. 6.4a that the compatibility of the unmodified APP and the PLA matrix is poor, as evidenced by the presence of voids and pull-out bamboo fibers on the fracture surface, which led to its weak thermal and mechanical properties. On the other hand, a densely knitted texture was found in Fig. 6.4b, indicating that the compatibility between modified APP and the PLA matrix is improved. This result corroborates the results of the thermal and mechanical analysis which determined that better adhesion in the additives/matrix increases both the HDT and the strength of the composite.

6.4 Conclusions

The green composite with the modified APP and bamboo fiber has a high non-flammable ratio with a char yield of 30.8%. The HDT and storage modulus of PLA can be significantly increased by the addition of both flame retardant and bamboo fiber.

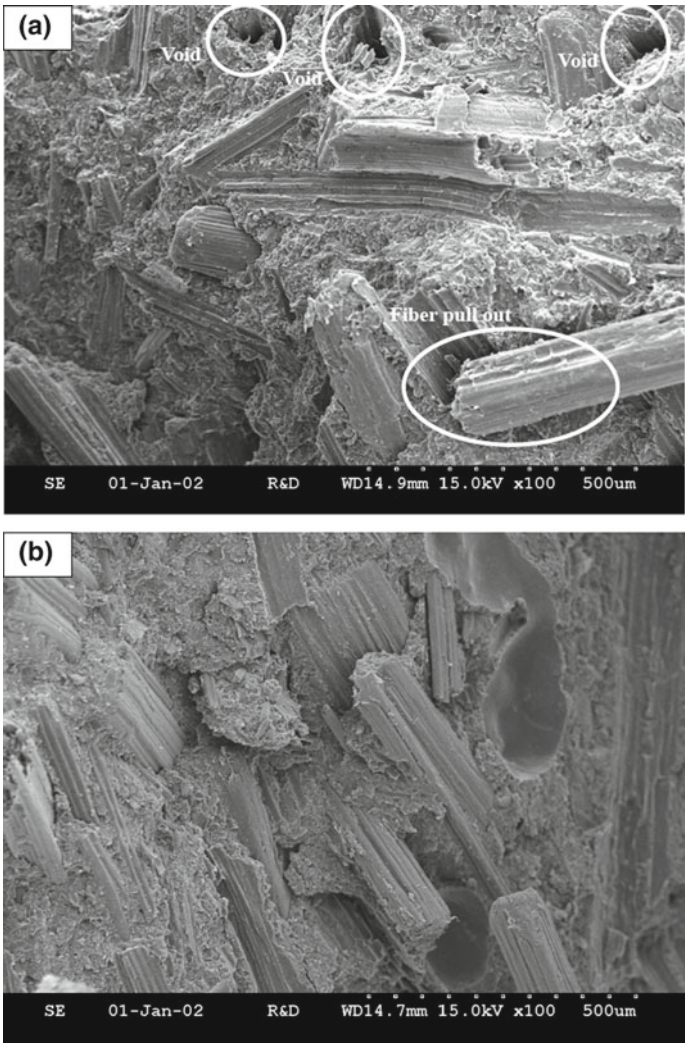

Fig. 6.4 SEM photographs of the fracture surface of **a** PFA and **b** PFEA

Moreover, the storage moduli of modified APP containing composites were larger than those of unmodified APP containing ones. It is speculated that the compatibility between the modified APP and PLA has improved, leading to a better reinforcing effect.

It also can be found that the loss moduli of composites were significantly increased by the addition of bamboo fiber due to its ability to absorb energy by the hollow structure of the fiber. Moreover, the flame retardant grade of PLA can reach the highest level of V-0 after the addition of both the bamboo fiber and the modified APP. It revealed that the flame retardant effect of modified APP is better than that of

APP. Moreover, bamboo fiber can not only enhance the mechanical properties and heat resistance of PLA, but also play an important role in synergistic flame retardancy with flame retardants.

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