

# Investigation on Flame Retardancy and Thermal Degradation of Flame Retardant Poly(butylene succinate)/Bamboo Fiber Biocomposites

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**ABSTRACT:** Poly(butylene succinate)/bamboo fiber (BBF) biocomposites were prepared by melt blending method. Microencapsulated ammonium polyphosphate (MCAPP) was used as flame retardants to prepare flame retardant BBF biocomposites. The thermal degradation and flame retardant properties of BBF biocomposites were investigated. The volatilized products of the thermal degradation of flame retardant BBF biocomposite are saturated hydrocarbons, unsaturated alkane, CO<sub>2</sub>, carboxylic acid, acid anhydride, aromatic compounds, NH<sub>3</sub>, and CH<sub>3</sub>OH. The peak of heat release rate (pHRR) and total heat release

(THR) of flame retardant BF biocomposites decrease substantially compared with that without MCAPP. The pHRR value of flame retardant BBF biocomposites decreases from 443.2 to 236.2 kW m<sup>-2</sup> and the THR value decreases from 62.0 to 36.1 kW m<sup>-2</sup>. Furthermore, MCAPP shows the best flame retardant property at the same loading, compared with other flame retardants such as Mg(OH)<sub>2</sub> and Al(OH)<sub>3</sub>. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** poly(butylene succinate); bamboo fiber; flame retardant; thermal degradation; biocomposite

## INTRODUCTION

Poly(butylene succinate) (PBS) has been regarded as an excellent biodegradable material to resolve the worldwide environmental problem of white pollution caused by nondegradable plastics.<sup>1,2</sup> PBS holds great promise for many end-use applications such as agricultural films, biomedical fields, packing materials, and so on due to its combined advantages of good biodegradable properties, thermal properties, and mechanical properties. Since the price of PBS is expensive, its use has been limited. Recently, PBS biocomposites from PBS and natural additives such as starch,<sup>3–5</sup> lignin,<sup>6,7</sup> and so on have attracted great interests in the composite science, because they can

decrease the cost of composites, and allow complete degradation in soil or by composting process and do not emit any toxic or noxious components.

Among the natural additives, bamboo fiber (BF) has numerous advantages, such as low cost, low density, high toughness, acceptable specific strength properties, ease of separation, and biodegradability. Compared with other natural additives such as starch and lignin, BF also has some unique advantages. The use of starch in preparation of PBS biocomposites increases the amount of non-grain starch and causes people to worry about food supply. The use of lignin also has some problems. The wood lumber needs a long period (about 10–20 years) to grow, and causes shortage of timber resources. However, bamboo growth cycle is short (about 2–3 years), and bamboo resources are relatively abundant. Further, more bamboo does not bring food crisis, and has natural anti-bacterial function.

Because of so many advantages of PBS and BF, the investigations on PBS/BF (BBF) biocomposites attract more and more attention. BBF biocomposites are prepared for various applications.<sup>8–12</sup> However, easy flammable properties limit its applications, so it is necessary to make these kind materials flame retardant to meet the necessary requirement. Until

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TABLE I  
Formulations of the Flame Retardant BBF Biocomposites

Sample	composition	UL-94
BBF1	PBS37.5 wt % + 62.5 wt % BF	Burning and dripping
BBF2	PBS55 wt % + 25 wt % BF + 20 wt % MCAPP	Burning and dripping
BBF3	PBS50 wt % + 30 wt % BF + 20 wt % MCAPP	V-2
BBF4	PBS40 wt % + 40 wt % BF + 20 wt % MCAPP	V-0
BBF5	PBS30 wt % + 50 wt % BF + 20 wt % MCAPP	V-0
BBF6	PBS30 wt % + 50 wt % BF + 20 wt % Mg(OH) <sub>2</sub>	Burning and dripping
BBF7	PBS30 wt % + 50 wt % BF + 20 wt % Al(OH) <sub>3</sub>	Burning and dripping

now, the study on flame retardant BBF biocomposites still lacks investigation.

In this work, BBF biocomposites were prepared by melt blending method. Microencapsulated ammonium polyphosphate (MCAPP) was selected as flame retardants to improve its flame retardant properties of BBF biocomposites. The flame retardant and thermal properties of flame retardant BBF biocomposites were studied by different methods.

## EXPERIMENT

### Materials

PBS ( $M_w = 190$  kDa, relative density = 1.26, melt-flow rate (190°C/2.16 kg) = 11 g/10 min) was purchased from Anqing Hexing Chemicals (Anhui, China). MCAPP which was microencapsulated by melamine-formaldehyde resin was kindly provided by KeYan (Anhui, China) and melamine formaldehyde: APP is 1 : 10 by weight. BF was obtained from Hangzhou Taiyi (Zhejiang, China).

### The preparation of samples

PBS, MCAPP, and BF were dried in a vacuum oven at 60°C overnight before use. Then PBS, MCAPP, and BF were melt-mixed in a twin-roller mill for 10 min, and the temperature of the mill was maintained at 140°C and the roller speed was 60 rpm. The samples are listed in Table I. The resulting biocomposites were hot-pressed into sheets with suitable thickness and size for vertical burning (UL-94) test, limiting oxygen index (LOI) test, and cone calorimeter test. The temperature, time, and pressure for hot-press process is 140°C, 10 min, and 10 MPa, respectively.

### Characterization

LOI was measured according to ASTM D2863, and the apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens dimensions used for test were 100 mm × 6.5 mm × 3 mm. The vertical burning test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China),

and the specimens dimension used for the test is 100 mm × 13 mm × 3 mm.

The combustion properties were evaluated using a cone calorimeter. All samples (100 mm × 100 mm × 3 mm) were exposed to a Stanton Redcroft cone calorimeter according to ISO-5660 standard procedures.

Thermogravimetric analyses (TG) were carried out using a TGA Q 5000IR (TA Instruments) thermo-analyzer instrument at a linear heating rate of 20 °C min<sup>-1</sup> under an air flow. Samples were measured in an alumina crucible with a mass of about 5.0 mg.

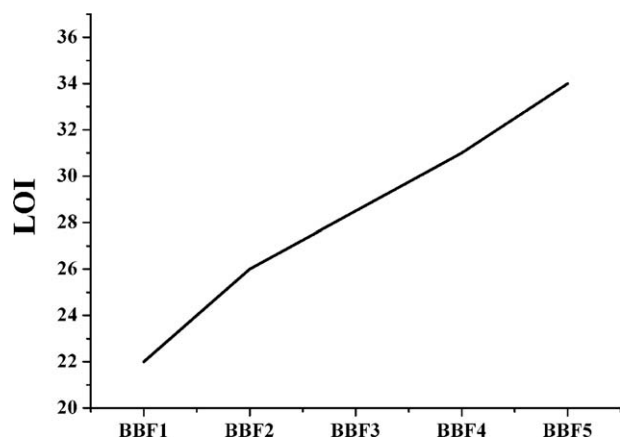
Thermogravimetric analysis-infrared spectrometry (TG-IR) was performed using the TGA Q5000 IR thermogravimetric analyzer that was linked to the Nicolet 6700 FTIR spectrophotometer. About 5.0 mg of the sample was put in an alumina crucible and heated from 30 to 600°C. The heating rate was 20 °C min<sup>-1</sup> (nitrogen atmosphere, flow rate of 60 mL min<sup>-1</sup>).

The scanning electron microscopy (SEM) image of the residue after the cone calorimetry experiment was taken using a DXS-10 scanning electron microscope produced by Shanghai Electron Optical Technology Institute. The char was placed on the copper-plate, and then coated with gold/palladium alloy ready for imaging.

## RESULTS AND DISCUSSION

### LOI and UL-94 analysis of flame retarded BBF biocomposites

The LOI results of flame retardant BBF biocomposites are shown in Figure 1. The LOI value of BBF1 is just 22.0. With the addition of 20 wt % MCAPP, the flame retardant properties of BBF biocomposites are greatly improved. The LOI value of BBF5 is as high as 34.0, increasing 50% compared with that without MCAPP. The flame retardant properties of BBF biocomposites are also influenced by the weight ratio of PBS to BF. Keeping 20 wt % MCAPP unchanged, with the weight ratio of BF to PBS increase, the LOI value also increases. With the ratio of BF to PBS increasing from 5 : 11 to 5 : 3, the LOI value increases from 26.0 to 34.0. The LOI results indicate that the higher the content of BF, the better flame retardant property can be obtained. BF is



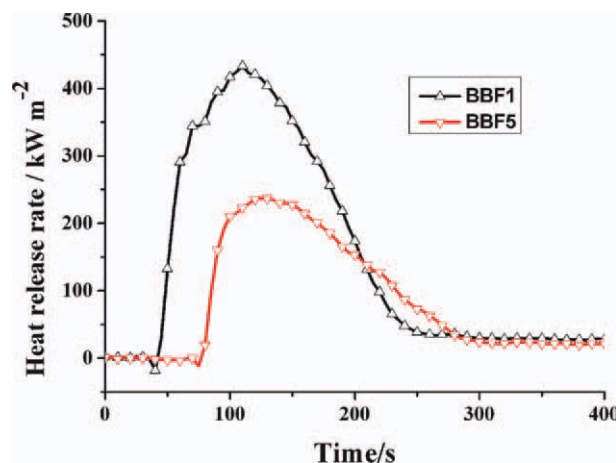
**Figure 1** The LOI results of flame retarded BBF biocomposites.

hydroxyl-containing compound, and can act as a carbon source. With addition of MCAPP acting as acid source and gas source, MCAPP and BF can form an intumescent system to protect the matrix from further burning, so the flame retardant properties of BBF biocomposites improve.

Table I shows results of UL-94 test for the various BBF biocomposites. Without addition of MCAPP, BBF1 is combustible, and burns seriously. With the addition of 20 wt % MCAPP, the samples PBS/50 wt % BF/20 wt % MCAPP and PBS/40 wt % BF/20 wt % MCAPP can reach V-0 rating. It should be noted that only with suitable ratio of PBS to BF, flame retardant BBF biocomposites can pass V-0 rating. Furthermore, MCAPP shows the best flame retardant property at the same loading, compared with other flame retardants such as  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ .

### Cone calorimeter test

Cone calorimetry provides much information on the combustion behavior and has good correlation with real fire disaster, so it is often used to evaluate the flame properties of materials. The heat release rate (HRR) and the total heat release (THR) are important parameters to estimate the developing, spreading, and intensity of fires.<sup>13</sup> The HRR curves of flame retardant BBF biocomposites is shown in Figure 2. The peak HRR (pHRR) of BBF1 biocomposite is  $443.2 \text{ kW m}^{-2}$ . With the addition of 20 wt % MCAPP, the pHRR value of BBF5 biocomposite decreases from 443.2 to  $236.2 \text{ kW m}^{-2}$  compared with that of BBF1. BF with MCAPP can form an intumescent char layer. With the presence of the efficient intumescent char layer, the amount of heat, oxygen transferred to the polymer matrix, and combustible gas escaping from the matrix decrease greatly, and further degradation of PBS is prevented, so the flame retardant properties of BBF biocomposites improves, and leads to a decrease of pHRR.

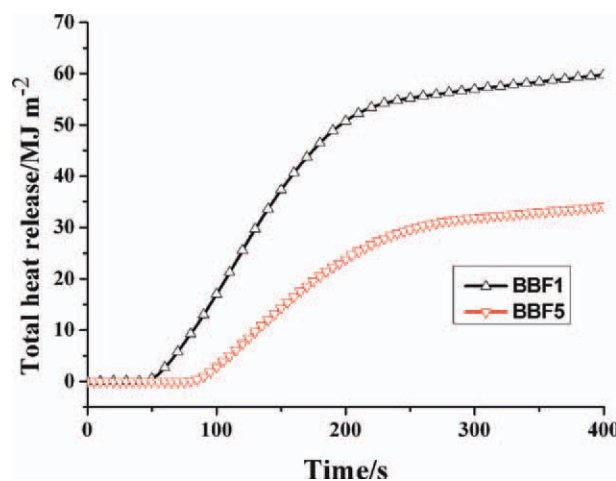


**Figure 2** HRR curves of flame retarded BBF biocomposite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

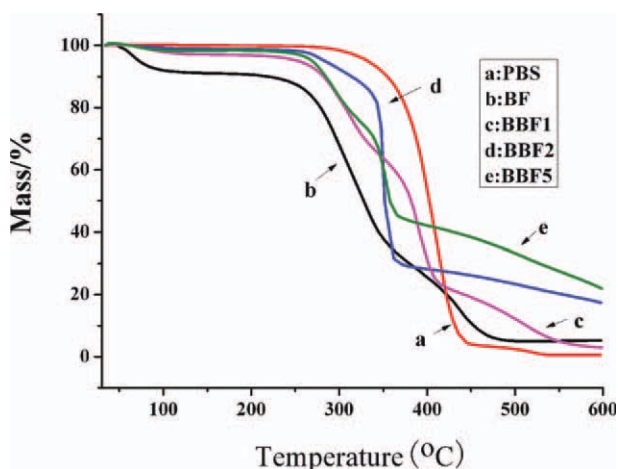
THR curves for flame retardant BBF biocomposite are shown in Figure 3. From this figure, it can be observed that the THR is decreased by the flame retardants. The THR value of BBF5 is  $36.1 \text{ MJ m}^{-2}$ , decreasing by 41.8% compared that of BBF1 ( $62.0 \text{ MJ m}^{-2}$ ).

### Thermal properties of BBF biocomposites

Figure 4 shows the TG results of flame retardant BBF biocomposites at a heating rate of  $20 \text{ °C min}^{-1}$ . Pure PBS has no char residue beyond the temperature of  $530 \text{ °C}$ , and shows one-step degradation of total weight loss in the range of  $300\text{--}450 \text{ °C}$ . Compared to pure PBS, the PBS/BF has poorer thermal stability below  $420 \text{ °C}$ , and the reason for this may be due to the poor thermal stability of BF. With the addition of MCAPP, the thermal stability of PBS obviously improves. Take BBF5 for example, the 10% weight loss temperature increases from  $283.8$  to



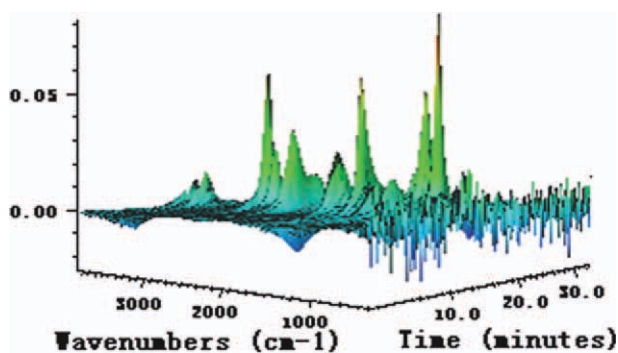
**Figure 3** THR curves for flame retarded BBF biocomposite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



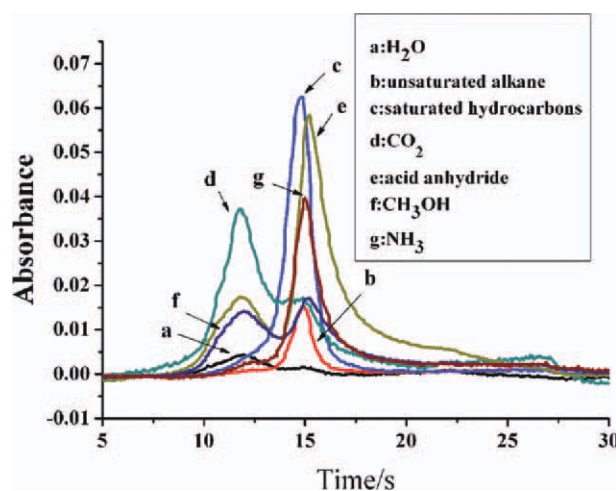
**Figure 4** The TG curves of flame retardant BBF biocomposite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

313.3°C, and the maximum decomposition temperature from 350.0 to 392.0°C, compared with those of BBF1. The ratio of PBS and BF also affects to the thermal behavior of the flame retarded BBF biocomposites. BBF5 shows lower thermal stability than that of BBF2 below 348.5°C, but has higher thermal stability above this temperature. The char residue of BBF5 at 600°C is about 22.0 wt %, much more than that (17.4 wt %) of BBF1.

TG-IR was used to further investigate the gas products during the thermal degradation of flame retardant BBF. Figure 5 shows the 3D TG-IR spectrum of the thermal degradation of BBF5 under nitrogen. All the volatile pyrolysis products can be identified from this figure by their characteristic absorbance. The peaks appearing at 3400–4000  $\text{cm}^{-1}$  correspond to the absorption bands of  $\text{H}_2\text{O}$ . The peak at 3076  $\text{cm}^{-1}$  is due to the unsaturated alkane group. The peaks at 2960 and 2920  $\text{cm}^{-1}$  attribute to the  $\text{CH}_2$  or  $\text{CH}_3$  asymmetric and symmet-



**Figure 5** The 3D TG-IR spectrum of the thermal degradation of BBF5 under nitrogen. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

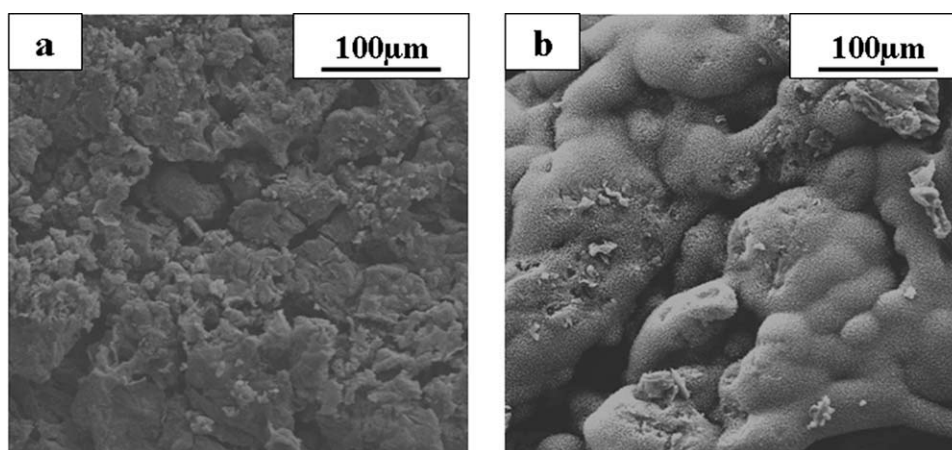


**Figure 6** The relationship between intensity of characteristic peak and temperature for the volatilized products. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ric vibration and the ones at 1460 and 1380  $\text{cm}^{-1}$  are assigned to the  $\text{CH}_2$  or  $\text{CH}_3$  deformation vibration. The band at 2381  $\text{cm}^{-1}$  belongs to the characteristic absorbance of  $\text{CO}_2$ . The peak at 1810  $\text{cm}^{-1}$  attributes to acid anhydride. The bands at 1050–1070  $\text{cm}^{-1}$  are assigned to  $\text{CH}_3\text{OH}$  group. The peak at 927  $\text{cm}^{-1}$  attributes to the  $\text{NH}_3$  group.<sup>14–16</sup> In order to clearly understand the changes of the formed products, the relationship between the intensity of the characteristic peaks and temperature for some of the volatilized products are plotted in Figure 6. It can be found from Figure 6 that at low temperature the small volatile gas such as  $\text{CO}_2$ ,  $\text{NH}_3$  acid anhydride, and  $\text{CH}_3\text{OH}$  appears due to the decomposition of MCAPP and BF. Associated with the analysis of TG result, the first-step decomposition of flame retardant BBF composites may be caused by the release of such small molecules. These small molecules are important for the formation of protective char layer and make the char layer to expand. Furthermore, these small molecules can dilute the oxygen and flammable gas during the burning. From Figure 6, it can be found that the characteristic peak for hydrocarbons appears at 14.9 min and then turns to a rapid decrease, and this step is assigned to the decomposition of PBS matrix. The volatilized products of the thermal degradation of flame retardant BBF biocomposites are saturated hydrocarbons, unsaturated alkane,  $\text{CO}_2$ , carboxylic acid, acid anhydride, aromatic compounds,  $\text{NH}_3$ , and  $\text{CH}_3\text{OH}$ .

#### SEM analysis of char residue after LOI test

Figure 7 shows SEM images of char residue after LOI test. The char residues play an important role in the flame retardant performance of the biocomposite, so



**Figure 7** SEM photographs of outer surface of the chars after LOI test: (a) BBF1, (b) BBF5.

the investigation of the morphology of the char is helpful to explain the differences in the flame retardancy among the flame retardant BBF systems. Without the addition of MCAPP, the char layer of BBF1 is swollen and has some big holes in it [Fig. 7(a)]. This char layer cannot provide a good protection for polymer matrix, so the flame retardant ability of BBF1 is poor. With the addition of MCAPP (BBF5), it can be found from Figure 7(b) that the coherent and dense char layer is formed. The char layer can prevent the heat, oxygen, and combustible gas transfer between the burning matrix and the flame zone, so the further burning of the matrix can be stopped.<sup>17</sup> So the flame retardant properties of BBF5 are much better than that of BBF1.

### CONCLUSION

PBS/BF biocomposites were prepared by melt blending method. MCAPP was selected as flame retardants to improve its flame retardant properties of BBF biocomposites. The results of cone calorimeter show that pHRR and THR of flame retardant BBF biocomposites decrease substantially compared with that without flame retardancy. The pHRR value decreases from 443.2 to 236.2 kW m<sup>-2</sup> and the THR value decreases from 62.0 to 36.1 MJ m<sup>-2</sup>. Furthermore, MCAPP shows the best flame retardant property at the same loading, compared with other flame

retardants such as Mg(OH)<sub>2</sub> and Al(OH)<sub>3</sub>. The SEM result indicates that the coherent and dense char layer is formed with the addition of MCAPP, which can prevent the heat, oxygen, and combustible gas transfer between the burning matrix and the flame zone.

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