Layer by layer deposition of polyethylenimine and bio-based polyphosphate on ammonium polyphosphate: A novel hybrid for simultaneously improving the flame retardancy and toughness of polylactic acid

Jian Jing\textsuperscript{a,b}, Yan Zhang\textsuperscript{b}, Xinlei Tang\textsuperscript{a}, Yang Zhou\textsuperscript{a}, Xiaoman Li\textsuperscript{b}, Baljinder K Kandola\textsuperscript{c}, Zhengping Fang\textsuperscript{a,b,*}

\textsuperscript{a} MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Institute of Polymer Composites, Zhejiang University, Hangzhou 310027, China

\textsuperscript{b} Laboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China

\textsuperscript{c} Centre for Materials Research and Innovation, University of Bolton, Deane Road, Bolton, BL3 5AB, UK

Abstract

In this study, a facile approach to fabricate a novel bio-based hybrid (BBH) with core/shell structure is presented by taking advantage of plant-derived resources. The BBH developed herein comprises of an inorganic core of ammonium polyphosphate (APP), covered with an organic shell that is constructed via layer-by-layer assembly of a novel bio-based polyelectrolyte (BPE) and branched polyethylene imine (bPEI). BBH can simultaneously enhance the flame retardancy and toughness of polylactic acid (PLA) with very high efficiency. The flame retardant PLA composite can pass UL94 V0 rating at the BBH loading content of 10 wt%. The efficient flame retardant performance is due to of its effectiveness in both gas and condensed phases. More importantly, the flame retardant PLA composite containing 10 wt% BBH exhibits ductile fracture with an elongation at break of 27.3 %, which is much higher than that of neat PLA (8%). The debonding and plastic void deformation of the PLA matrix around the BBH are responsible for the enhanced toughness. This work provides
important hints for devising highly efficient multifunctional flame retardant and broadening the application field of renewable resources.

1 Introduction

As a bio-degradable thermoplastic, polylactic acid (PLA) derived from starches and sugars is stimulating unprecedented scientific and technological interest.\textsuperscript{1, 2} The past decade has witnessed an extensive expansion of its application in textiles, fibers, transparent packaging materials, electronic instruments and biomedical devices areas due to sustainable development issues.\textsuperscript{3} However, PLA, similar to its petroleum-derived counterparts, is highly flammable and must be flame retarded for further applications.

Seeking effective strategies to flame retard PLA is of considerable significance and various methods have been developed in the past decade, such as blending PLA with flame retardant additives and chemically modifying PLA with flame retardant element.\textsuperscript{4-7} The former approach is more preferred on the basis of cost, and feasibility to massive production, which comprises of PLA blending with nano-inorganic, phosphorus-containing, and intumescent flame retardants. As for nano-inorganic fillers, metal oxides,\textsuperscript{8} nanoclays,\textsuperscript{9} and carbon-based nanomaterials\textsuperscript{10} have been extensively studied to fabricate the flame retardant PLA composites. However, the resulting materials exhibit poor performance in terms of UL-94 test and limiting oxygen index (LOI). With regards to the phosphorus-containing FRs, normally, a high loading level of the additives (i.e., at times >20 wt% of flame retardant additive) is
required to achieve ideal flame retardant grade for PLA. Recently, some highly efficient flame retardants for PLA have been developed. For example, Wang et al. applied N, N0-Diallyl-P-phenylphosphonicdiamide into PLA and found that only 1 wt% dosage of such additives was enough to lead PLA to pass UL94 V-0 rating. We also synthesized a diphenolic acid based polyphosphonate (BPPT). Only 4 wt% incorporation of BPPT made a PLA matrix pass UL94 V-0 rating along with 33.7 % of the LOI value. Though highly efficient flame retardant PLA was realized in the above mentioned approaches, the resulting flame retardant PLA composites normally become more brittle than the virgin matrix.

Apart from being highly inflammable, PLA is a comparatively brittle and rigid polymer material with low deformation at break and its application in various end-use areas are impeded. Although, some highly efficient flame retardants have been developed, the deterioration on toughness of the resulting PLA composites is inevitable and in most cases the flame retardant additives seriously impair the toughness of PLA matrix. Hence, developing efficient flame retardant additive and simultaneously toughening PLA is of great significance but a tough work.

On the basis of the discussion mentioned above. Herein, a novel bio-based polyelectrolyte (BPE) was designed and synthesized in two steps using diphenolic acid (DPA) as raw material, which is a plant-derived compound widely used for synthesis of polyesters and polycarbonates. etc. The as-synthesized BPE exhibits a good char forming ability and has good compatibility with the PLA matrix.
Besides, the BPE contains abundant pendant carboxyl group, which is a polyanion in water. The negatively charged BPE and positively charged branched polyethylenimine (bPEI) were consecutively deposited on ammonium polyphosphate, which is a widely used flame retardant additive on its own or as an acid source in intumescent system, through electrostatic interactions via LbL method. The polycation bPEI can serve as both the polycation and the blowing agent source in a intumescent system. The as tailored organic-inorganic hybrid flame retardant would on one side bring enhanced flame retardant efficiency owing to the tunable formulation of individual component through adjusting the layer numbers and on the other serve as a shell to improve the compatibility between the flame retardant and the matrix resin. The influence of the BBH on the flame retardancy and tensile properties of PLA was studied.

2 Experimental

2.1 Materials

Ingeo 3052D polylactic acid (PLA) was obtained from NatureWorks LLC. Diphenolic acid (DPA) was purchased from J&K Scientific Co., Ltd (China). Phenylphosphonic dichloride (PPDC) was purchased from Acros Organics. Formaldehyde aqueous solution (37 wt%), dimethylamine aqueous solution (33 wt%) and 732-type cation-exchange resin (crosslinked styrene and butadiene copolymer with pendant -SO₃H groups) were purchased from Sinopharm Group Chemical Reagent Co., Ltd (China). Prior to use, 5 g 732-type cation exchange resin was treated with 50 mL of
1M NaOH and 1M HCl, respectively, equilibrating for 12 h under constant agitation. The resulting 732 hydrogen-form cation exchange resin was washed with deionized water and then packed in a 10 cm length of glass column (5.0 mm i.d.) and furnished with glass wool at both ends to retain the resin inside. Ammonium polyphosphate (APP, P%= 31.0~32.0 wt%, degree of polymerization (DP)> 1000) was purchased from Hangzhou JLS Flame Retardants Chemical Co., Ltd (China). Branched polyethyleneimine (bPEI) ($M_n$=10 000 g/mol) was purchased from Aladdin-reagent (China). All other materials were A. R. grade and used as received.

![Scheme 1. Synthesis route of BADA and BPE](image)

### 2.2 Synthesis of 2,2’-bimethylaminemethylene-4,4’-diphenolic acid (BADA)

The synthesis route of the monomer 2,2’-bimethylaminemethylene-4,4’-diphenolic acid (BADA) is depicted in Scheme 1 (a). A 250 mL round-bottomed flask with a mechanical stirrer, a nitrogen inlet and a reflux condenser device was equipped, into which DPA (14.3 g, 0.05 mol), ethanol (100 ml), aqueous solutions of dimethylamine (20.5 g, 33 wt%) and formaldehyde (16.2 g, 37 wt%) were added. The mixture was
stirred at 25 °C under N₂ atmosphere for 24 h. Then the solvent of the resultant was removed by rotary evaporation at reduced pressure. The crude product was dissolved in deionized water (100 mL) and purified by 732 cation exchange resin, followed by the evaporation of the water by rotary evaporation at reduced pressure. The solid was dried in a vacuum furnace at 80 °C for 8 h to obtain white powder (yield: 18.0 g, 90 wt%); ¹H NMR (500 MHz DMSO-d₆, ppm): δ 6.88 (4H, Ar-H), 6.64 (2H, Ar-H), 3.48 (4H, -CH₂-N-), 2.25-2.14 (14H, -CH₃-N, -CH₂-COOH), 1.92 (2H, -CH₂-CH₂-COOH), 1.47 (3H, CH₃-C-). ¹³C-NMR (126 MHz DMSO-d₆, ppm): δ 175.2, (154.5, 153.6), (139.3, 138.7), (127.6, 126.6), 126.8, 121.7, 114.6, 60.1, 59.1, 43.8, 36.6, 34.3, 27.3.

2.3 Synthesis of BPE

The BPE was prepared through the polycondensation between BADA and PPDC, as depicted in Scheme 1(b). To a flame-dried 250 mL round-bottom flask equipped with a nitrogen inlet, reflux condenser device and mechanical stirrer, a mixture of acetonitrile (120 mL), triethylamine (5.1 g) and BADA (20 g, 0.05 mol) was added. The reactants were heated to 40 °C under continuous flow of N₂. Then PPDC (9.75 g, 0.05 mol) in acetonitrile (20 ml) was slowly added into the flask in one batch. The mixture was heated to 80 °C within 10 min and maintained for 5 h. The precipitated solid was collected by filtration and washed with ethyl acetate (200 mL) twice prior to being dried in a vacuum furnace at 60 °C for 8h to obtain a yellow product (yield: 25.3 g, 85%). ¹H NMR (500 MHz, DMSO-d₆, ppm): δ 7.75-6.82 (m, Ar-H), 4.21 (dd, -CH₃-N), 2.67 (d, -CH₃-N), 2.37 (m, -CH₂-COOH), 2.11 (m, -CH₃-CH₂-COOH), 1.53
2.4 Fabrication of BBH

The process for fabricating the bio-based hybrid (BBH) via LbL assembly is presented in Scheme 2. 2.0 g APP powder was dispersed evenly in deionized water to form a suspension (5 wt %) by mechanical stirring. Then, 40 mL of the bPEI aqueous solution (pH 9) was added into the APP suspension, and the adsorption process was allowed to proceed for 2 min with constant stirring of the mixture. Then, the particles were isolated by centrifugation. In a washing step, 60 mL of deionized water was added. The particles underwent two centrifuge/wash cycles before the addition of the next layer. For absorption on another layer, 40 mL of the BPE aqueous solution (pH 3) was added, followed by the same washing protocol. The procedure was repeated until two bilayers of PEI/BPE were constructed.

Scheme 2. Schematic representation of constructing the BBH
2.5 Preparation of PLA composites

PLA was dried under vacuum at 80 °C for 12 h prior to use, desired amounts of BBH and PLA were blended at 170 °C in ThermoHaake rheomixer (Polylab, Germany) at a rotor speed of 60 r/min, and the mixing time was set as 8 min for all samples. For comparison, the specimens of neat PLA were prepared by the same procedure. The as-prepared PLA composites were denoted as xPLA/yBBH, while x and y denotes their weight percentage in the composites. For instance, 85PLA/15BBH means that the sample contains 85 wt% PLA and 15 wt% BBH in the resultant composites.

2.6 Measurements

\(^1\)H NMR and \(^{13}\)C NMR spectra were recorded on a Varian Unity Inova spectrometer (500 MHz) (Advance2B, Bruker, Germany). Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 field-emission scanning electron microscopy, operated at 3 kV. Prior to analysis, the specimens were gold-sputtered for 1.5 min under a high vacuum to increase the conductivity. X-Ray photoelectron spectroscopy (XPS) was carried out using a Thermo ESCALAB 250 spectrometer.

Limiting oxygen index (LOI) values were measured according to ASTM D2863 with the dimension of the sample sheets of 150 × 6 × 3 mm\(^3\), and the apparatus was an HC-2 Oxygen Index Instrument (Jiangning Analysis Instrument Company, China). Vertical burning test was performed on a CZF-III Vertical Burning Tester (Jiangning Analysis Instrument Company, China) according to UL94 test (ASTM D3801 standard), with the dimension of the sample sheets of 127 × 12.7 × 3 mm\(^3\). Cone
calorimetry was carried out on a FTT Cone Calorimeter with the dimension of the sample sheets of $100 \times 100 \times 3$ mm$^3$ at a heat flux of $35$ kW/m$^2$ according to ISO 5660 standard. Thermal gravimetric analysis (TGA) experiments were conducted on TGA 209 F1 (NETZSCH, Germany) at a heating rate of $20 \degree$C/min in N$_2$ from 50 to 600 $\degree$C. Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TG-FTIR) measurements were performed with a TGA 209 F1 instrument (NETZSCH, Germany), coupled with a Thermo Nicolet iS10 FTIR spectroscopy (Thermo Fisher, Germany). The TG instrument is linked to the heated gas cell of the FTIR instrument by means of a heated line, and the volatiles evolved from TG can be transferred into the gas cell of FTIR through the transfer line by a suitable gas flow. The sample mass for the test is fixed at 9 mg. The resolution of the spectra was $4$ cm$^{-1}$.

Tensile testing was performed using an electronic universal mechanical testing machine (Model RTW10, Shenzhen Reger Instrument Co. Ltd., China). Dumbbell specimens with a $25 \times 4 \times 2$ mm$^3$ neck were used. Tests were performed at room temperature at a constant crosshead speed of $3$ mm/min. At least eight samples were tested to obtain the average values of tensile properties for neat PLA and PLA/BBH composites. Differential scanning calorimetry (DSC) measurements were carried out under N$_2$ flow of $25$ mL/min using a DSC 200 PC (NETZSCH, Germany) at a heating rate of $5$ $\degree$C/min. The samples were taken from the tensile test specimens, aiming to evaluate the effects of crystallinity of the specimens on the mechanical properties. The DSC heat flow curve during the first heating scan was used to examine the initial
crystalline state of the PLA matrix phase by determining the cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), enthalpy of cold crystallization ($\Delta H_{cc}$) and enthalpy of melting ($\Delta H_m$). The crystallinity, $X_c$ of PLA was determined using eq 1 as follows:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{w_f \Delta H_m^0}$$  \hspace{1cm} (1)

where $w_f$ is the mass fraction of PLA in the composites, and $\Delta H_m^0$ is the enthalpy of fusion for the 100% crystalline PLA, taking the value of 93.7 J/g from the literature.  

### 3 Results and Discussion

#### 3.1 Synthesis and Characterization of BADA and BPE

The novel monomer BADA was prepared using DPA, formaldehyde, and dimethylamine via Mannich reaction. The tailored BADA structure on one hand increases the solubility of the target BPE in water due to the interaction between the pendant carboxyl group and amine $^1$H NMR and $^{13}$C NMR spectra of BADA are shown in Fig. 1 (a) and (b), respectively. Compared with the $^1$H NMR spectra of DPA shown in Fig. 1 (a’), the new peak appeared at 3.48 ppm was assigned to the methene hydrogen (H$^d$, -CH$_2$-N). The hydrogen (H$^e$, CH$_3$-N) and (H$^h$, -CH$_2$-COOH) overlapped and appeared as multiplet in the range of 2.25-2.14 ppm. Furthermore, the intensity ratio of (H$^e$, H$^h$), H$^g$ and H$^f$ was close to 14 : 2 : 3, as expected for the composition of the target molecule. With regards to $^{13}$C NMR, all the carbons can be attributed to the expected signals. The absorptions in the range of 154.5-114.6 ppm
were assigned to the aromatic carbons. Notably, the C² (154.5, 153.6), C⁵ (139.3, 138.7) and C⁶ (127.6, 126.6) displayed as double adjacent peaks. We attribute this to the steric hindrance effect caused by the incorporation of the two large-volume pendant group, which leads to a stereoisomer. Peaks appeared at 60.1 and 59.1 ppm were corresponding to the carbons (C⁸ and C⁹) attached to the nitrogen. The results confirm that the BADA is a single pure substance.

Fig. 1 (a) ¹H NMR and (b) ¹³C NMR spectra of BADA, (a’) ¹H NMR and (b’) ¹³C NMR spectra of DPA in DMSO-d6

Fig. 2(a) shows the ¹H NMR spectrum of the BPE, All aromatic hydrogen from the BADA subunit and PPDC subunit are magnetically dissimilar, but are difficult to resolve owing to their occurrence in a relatively narrow range and some heteronuclei coupling with phosphorus. The broad multiplet peaks appeared at 4.21 (H₄) ppm and 2.67 (H₅) were assigned to the hydrogen in the methylene and methyl attached to the nitrogen atom. The methylene hydrogen (H₆, H₇) and methyl hydrogen (H₁) in the DPDA subunit appeared at 2.37, 2.11 and 1.53 ppm, respectively.

See from the ³¹P NMR spectrum of BPE shown in Fig. 2 (b), the peaks appearing at
16.13 ppm could be assigned to the chemical shifts of phosphorus in the repeated unit of BPE. And the peaks at 13.47 ppm were attributed to the phosphorus in the terminal groups. Moreover, the integral area ratio of these peaks (16.13:13.47) was 5.6:1, indicating the polymerization degree of BPE is 5-6.

![Fig. 2. (a) ^1H NMR and (b) ^31P NMR spectra of BPE in D_{2}O](image)

In this section, the thermal stability of BPE was studied by TG performed in N_{2} atmosphere, and the released gas products of BPE during thermal degradation under N_{2} atmosphere were characterized by TG-FTIR technique as well. Fig. 3 (a) lists the TG and DTG curves of the BPE. It could be observed that there are three degradation steps for BPE, represented by three DTG peaks with maxima at 291, 390 and 490 °C, respectively. The BPE exhibits a residue of 42.8 wt% at 600 °C indicating a good char forming ability. Moreover, the evolved gaseous products of BPE during thermal degradation was collected and investigated by means of FTIR technique. Fig. 3 (b) shows the FTIR spectra of evolved gas product at different temperature during thermal decomposition. Based on the curves listed in Fig. 3 (b), the decomposition products of BPE involved H_{2}O (3670 cm\(^{-1}\)), hydrocarbons (3060-2950 cm\(^{-1}\)), CO\(_{2}\)
(2360 cm\(^{-1}\)), carbonyl compounds (1780 cm\(^{-1}\)) and compounds containing structure of C-N (1380 cm\(^{-1}\)), P=O (1256 cm\(^{-1}\)), C-O stretching (1170 cm\(^{-1}\)), P-O-C stretching (1103 cm\(^{-1}\)). The phosphorus containing compound is deemed to interfere in the flame action in vapor phase.

![Graph](image)

Fig. 3(a) TG and DTG curves of BPE under N\(_2\), (b) FTIR spectra of evolved gaseous products from thermal decomposition of BPE at different temperatures

### 3.2 Fabrication and characterization of BBH

![SEM photographs](image)

Fig. 4 SEM photographs of APP (a) and BBH (b)

The microscopic features of the surface morphologies of the neat APP and BBH were investigated by SEM, as shown in Fig. 4. Notably, the surface of the unmodified APP
was quite smooth. An obvious change after constructing an organic shell on APP was observed. The BBH displays a relative rough surface. Because of the organic modification, intermolecular or interparticles interactions between BBH were formed.

The XPS spectra of APP and BBH are shown in Fig. 5. The peaks located at 134.7 and 190.9 eV are attributed to P$_{2p}$ and P$_{2s}$ of origin APP.$^{22}$ The intensities of peaks abovementioned for BBH decrease sharply. At the same time, the intensities of the C$_{1s}$ peak centered at 284.7 eV of BBH increases significantly. Furthermore, the surface elemental content of BBH and APP particles inserted in Fig. 5 confirm that the P, N, and O atom content of BBH are 8.38, 8.38, and 25.29%, respectively, which are much lower than those of APP (18.11, 13.68, and 56.97%). But the C atom content of BBH is 53.66%, much higher than that of APP (11.23%). The changes of the related peaks and elemental compositions are due to the coverage of the outside APP particles with the organic layer generated via LbL assembly method.

![Figure 5 XPS spectra of APP and BBH. The insert is the surface element content of](image)
3.3 Flame retardant properties

In this section, vertical burning rate (UL-94), limiting oxygen index (LOI) test and cone calorimetry were performed to investigate the influence of BBH on flame retardant performance of PLA. The results are shown in Table 1.

Table 1 Results of cone calorimetry, UL-94 and LOI tests for PLA/BBH

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>UL94 Rating</th>
<th>Dripping</th>
<th>Dripping AFT* (s)</th>
<th>LOI (%)</th>
<th>Cone calorimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TTI (s)</td>
</tr>
<tr>
<td>PLA</td>
<td>NR</td>
<td>Yes heavily</td>
<td>Burns</td>
<td>20.0</td>
<td>68 ± 1</td>
</tr>
<tr>
<td>95PLA/5BBH</td>
<td>V2</td>
<td>Yes heavily</td>
<td>5/3</td>
<td>27.2</td>
<td>68 ± 2</td>
</tr>
<tr>
<td>90PLA/10BBH</td>
<td>V0</td>
<td>Yes slightly</td>
<td>0.3/0.2</td>
<td>27.5</td>
<td>73 ± 2</td>
</tr>
<tr>
<td>85PLA/15BBH</td>
<td>V0</td>
<td>Yes slightly</td>
<td>0.1/0.1</td>
<td>30.2</td>
<td>72 ± 1</td>
</tr>
</tbody>
</table>

aAverage flaming time after the first and the second ignition.
bResidual Mass after cone calorimetry test.

Neat PLA burns completely with serious dripping and receives no rating in UL-94 test. The inclusion of BBH induced great impact on the vertical burning behaviors of PLA in the UL 94 test. The 95PLA/5BBH could self extinguish within 5 s after removing the igniter, but the drippings ignited the underlying cotton, thus, UL-94 V-2 rating was assigned for 95PLA/5BBH. Notably, 90PLA/10BBH and 85PLA/15BBH, self extinguished instantly after removing the ignitor. Additionally, the dripping is suppressed immensely and cannot ignite the underlying cotton. Consequently, V0 rating was achieved for 90PLA/10BBH and 85PLA/15BBH. Overall, BBH endowed efficient flame retardancy to PLA which was illustrated by the increase of oxygen sensitivity and self-extinguishment ability. The videos of neat PLA and its flame retardant composites during UL94 test are given in the supporting.
The LOI value for neat PLA was only 20.0, while the values for 95PLA/5BBH, 90PLA/10BBH and 85PLA/15BBH were 27.2, 27.5 and 30.2, respectively, indicating that the incorporation of BBH considerably increased the LOI values for PLA. Based on the images after LOI test shown in Fig. 6, it was observed that negligible char layer was formed for 95PLA/5BBH and 90PLA/10BBH after the LOI test, suggesting that the gas phase mechanism may be mainly responsible for the increased LOI values. As for 85PLA/15BBH, abundant foam-like char layer was formed on the surface of the specimen, which acts as barrier to slow down the heat and fuel transfer. Thus, obviously increased LOI value for 85PLA/15BBH was attributed to the cooperation of both condensed phase and gas phase flame retardant mechanism.

![Fig. 6 Images of PLA and PLA/BBH composites after LOI test. Percentage values refer to the weight percent of BBH in PLA.](image)

Cone calorimetric test performed at the heat flux of 35 Kw/m² was used to further investigate the effect of BBH on the combustion behaviors of PLA. The main parameters: time to ignition (TTI), peak of heat release rate (pHRR) and total heat release (THR) and residue mass (RM) for PLA and PLA/BBH composites are listed in Table 1. It is noted that the TTI for PLA blends were prolonged compared with that for pure PLA. With regards to pHRR and THR, The heat release rate (HRR) and the
total heat release (THR) curves as function of time for pure PLA and PLA/BBH composites are shown in supporting information. A gradual decrease in both pHRR and THR values was observed for PLA/BBH composites with the increased BBH loading content, e.g. 85PLA/15BBH displays a pHRR and THR values of 301 kW/m² and 49 MJ/m², respectively, which decreased by 28% and 31% compared with those of neat PLA. Additionally, the reduction in the THR means that more PLA chains participate in the carbonization process catalyzed by BBH, which resulted a residue mass of 21.9 wt%. The phenomenon is similar to the typically phosphorus-based flame retardants deposit significant char when acting through condensed phase reactions.²³,²⁴

Moreover, the CO/CO₂ ratio as a function of time during cone calorimetry experiments is an indicative parameters to reveal the flame retardant mechanism.²⁵ Relevant data is shown in Fig. 7. More interesting still, the results manifest that CO/CO₂ ratios of PLA/BBH composites are improved significantly with the increased BBH loading content over neat PLA. Such increment in CO/CO₂ yield is a typically demonstration of the incomplete combustion. Thus, the gas phase mechanism is an indispensable aspect to achieve the efficient flame retardant performance.
3.4 Thermal degradation behavior of PLA and PLA/BBH

The effect of BBH on the thermal degradation behaviors of PLA was studied by means of TGA and TG-FTIR techniques. Fig.9 presents the TG and DTG curves of neat PLA and its flame retardant composites with different BBH loadings. The temperature at 5% mass loss ($T_{\text{onset}}$), maximum decomposition temperature ($T_{\text{max}}$) and the char residual weight at 600 °C are shown in Table 2.

It can be observed that neat PLA shows $T_{\text{onset}}$ at 344 °C, as for flame retardant PLA, the $T_{\text{onset}}$s decrease gradually with increased loadings of BBH, which is ascribed to the earlier thermal degradation of the BBH. Based on the DTG curves, no obvious change for the $T_{\text{max}}$ between neat PLA and PLA/BBH composites is observed. While, the degradation rate is depressed with increased loading content of BBH in PLA matrix as
evidenced by the DTG curves. The formed char is responsible for the decreased weight loss rate through barrier effect, e.g., the 85PLA/15BBH displays a residue weight of 11.2 wt%, indicating the enhanced char-forming ability by the inclusion of BBH.

Fig. 8 TG and DTG curves of neat PLA and its flame retardant composites

Table 2. Results of thermogravimetric analysis of neat PLA and PLA/BBH composites in N₂ at a heating rate of 20 °C/min

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>Residue at 600 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>344</td>
<td>379</td>
<td>1.72</td>
</tr>
<tr>
<td>95PLA/5BBH</td>
<td>338</td>
<td>379</td>
<td>4.82</td>
</tr>
<tr>
<td>90PLA/10BBH</td>
<td>334</td>
<td>379</td>
<td>8.26</td>
</tr>
<tr>
<td>85PLA/15BBH</td>
<td>328</td>
<td>378</td>
<td>11.12</td>
</tr>
</tbody>
</table>

To further study the influence of BBH on thermal degradation action for PLA, TG-FTIR technique was employed to study the evolved gas product of PLA and 85PLA/15BBH during thermal decomposition process. Fig.9 (a) and (b) present the 3D images of evolved gaseous products of PLA and 85PLA/15BBH, respectively, during the TGA test in N₂. It is obvious that the main degradation products for 85PLA/15BBH did not change too much compared with those of neat PLA. However,
there is a significant decrease of the peak appeared at 1242 cm\(^{-1}\) (C-O stretching) for PLA after the BBH was incorporated. To compare quantificationally, the intensities of total IR absorbance and peak at 1242 cm\(^{-1}\) versus temperature were separately shown in Fig. 9 (c) and (d). The remarkable decrease of this peak in the gas phase indicating that most of C=O containing component participate in the char formation. In this process, the amounts of carbonyl compounds (shown in Fig. 9 (e)) and carbon monoxide (shown in Fig. 9 (f)) increased whereas the amounts of ether compounds decreased.

Fig.9. 3D image of TGA-FTIR results of PLA (a) and 85PLA/15BBH (b); Total absorption curves vs temperature of PLA and 85PLA/15BBH (c); Absorbance at 1242
cm_1 vs temperature curves of PLA and 85PLA/15BBH (d); Absorbance of carbonyl compound vs temperature curves of PLA and 85PLA/15BBH (e). Absorbance of CO vs temperature curves of PLA and 85PLA/15BBH (f).

3.5 Mechanical properties

The typical stress-strain curves for PLA and PLA/BBH composites are presented in Fig. 10. And the detail data of the measured tensile properties are provided in Table 3. Neat PLA is a rigid material that deforms in a brittle fashion. No obvious yield can be observed during tensile test and the elongation at break is only about 8.5%, consistent with the results reported in the literatures.26 Interestingly, the incorporation of BBH at contents of 5 wt% and 10 wt% induced a distinct yielding and stable necking development of the PLA matrix. The elongations at break for 95PLA/5BBH and 90PLA/10BBH reach 24.3% and 28.2%, respectively. With further increase of BBH loading content to 15 wt%, the fracture of the composites happens earlier during tensile deformation with the elongation at break dropping to 8.5%. It is seen that elongation at break increases immensely with BBH content first and then drops with excess BBH, which gives an optimum BBH content, that is, 10 wt %. The Young’s modulus and tensile strength of the composites suffer reductions with increasing BBH content, nevertheless, the merits of rigidity of PLA matrix are not impaired insignificantly by the inclusion of BBH. For instance, the Young’s modulus for 90PLA/10BBH decreases to 1.3 GPa (1.5 GPa for neat PLA) and tensile strength decreases to 41.7 MPa (47.1 MPa for neat PLA), the impaired mechanical properties
is minimal enough.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>1.5 ± 0.3</td>
<td>47.1 ± 0.8</td>
<td>8.5 ± 1.5</td>
</tr>
<tr>
<td>95PLA/5BBH</td>
<td>1.3 ± 0.2</td>
<td>41.7 ± 1.1</td>
<td>24.2 ± 2.5</td>
</tr>
<tr>
<td>90PLA/10BBH</td>
<td>1.3 ± 0.1</td>
<td>36.3 ± 2.1</td>
<td>28.3 ± 2.9</td>
</tr>
<tr>
<td>85PLA/15BBH</td>
<td>1.1 ± 0.1</td>
<td>33.5 ± 0.6</td>
<td>8.5 ± 0.4</td>
</tr>
</tbody>
</table>

Fig. 10 Strain-stress curves of neat PLA and PLA/BBH composites

Notched impact strength is also increased for flame retardant PLA composites, as shown in Table 3. For instance, the impact strength is increased from 3.0 kJ/m² for neat PLA to 5.1 kJ/m² for 90PLA/10BBH. As incorporation of BBH into PLA matrix dissipates more energy relative to neat PLA. However, the toughening performance of impact tests is not as efficient as the tensile tests. This phenomenon is similar to the reported work 27, which shows superior toughness in tensile tests, however, relative moderate behavior in notched impact tests. Because the dynamic fracture toughness obtained from different tests modes differs from each other greatly.
3.6 Toughening mechanism

The crystallization behaviors of the polymer matrix and compatibility between the multiphases in the solid state are crucial factors that determine the mechanical and thermal properties of semi-crystal polymer. Thus, DSC measurement was performed to study the crystallization behaviors of the PLA in the composites and compatibility with the BBH particles. The DSC curves are shown in Fig. 1, and Table 4 tabulates the detail data. An exothermic peak, attributed to the cold crystallization during heating scan, is observed for neat PLA and the flame retardant composites. As compared with neat PLA, the $T_{cc}$ of PLA in the composites shifts to much higher temperatures. The double endothermic peaks ranging from 140 to 160 °C are assigned to the melting of PLA crystals in the composites, with respect to the lower temperature melting peak ($T_{m1}$), relating to melting of less perfect PLA lamellar crystals, appears at higher temperature compared with that of neat PLA. And the principle melting peak, $T_{m2}$ to melting of more perfect PLA lamellar crystals is unaffected. Moreover, PLA in the composites shows relatively lower values of cold crystallization enthalpy, $\Delta H_c$ and the corresponding melting enthalpy, $\Delta H_m$ than those in neat PLA. Besides, the $T_g$ of all flame retardant PLA shift to high temperature relative to the neat PLA. These results suggest that the incorporation of BBH in the composites suppresses the chain mobility and crystallization of PLA component is depressed in a little degree.
Table 4 DSC results of neat PLA and PLA/BBH composites with different BBH loadings

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$\Delta H_{cc}$ (J/g)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>59</td>
<td>100</td>
<td>147.1</td>
<td>153.2</td>
<td>19.2</td>
<td>20.1</td>
<td>0.96</td>
</tr>
<tr>
<td>95PLA/5BBH</td>
<td>59</td>
<td>102</td>
<td>148.2</td>
<td>153.2</td>
<td>18.6</td>
<td>19.3</td>
<td>0.86</td>
</tr>
<tr>
<td>90PLA/10BBH</td>
<td>60</td>
<td>103</td>
<td>148.1</td>
<td>153.3</td>
<td>16.4</td>
<td>17.2</td>
<td>0.73</td>
</tr>
<tr>
<td>85PLA/15BBH</td>
<td>61</td>
<td>103</td>
<td>148.1</td>
<td>153.2</td>
<td>15.5</td>
<td>16.1</td>
<td>0.70</td>
</tr>
</tbody>
</table>

In view of molecular structure of BPE, in which abundant carboxyl (-COOH) exist in the pendant group. The large amounts of carbonyl group on the shell of BBH may react with the terminal group of the PLA or absorb the PLA molecule to the surface of the hybrid through hydrogen bonding during the melt process.\(^{29,30}\) Consequently, a hydrogen-bond induced cross-linked network is formed around the BBH particles.
which restrain the chain movement activity of PLA nearby the BBH particles.

It is widely recognized that a strong interfacial interaction between the fillers and polymer matrix normally leads to low toughness because the stress cannot be relieved via interfacial debonding\textsuperscript{31}. However, low interfacial adhesion inducing immiscibility or totally phase segregation is not favor for the tensile strength. In this work, improved toughness was achieved, and the tensile strength was not seriously deteriorated at the same time. Accordingly, an ideally good interfacial adhesion between PLA and BBH is mainly responsible for the good balance of the mechanical properties of the composites. Previous research suggested that the brittleness of PLA is due to the low entanglement density as amorphous PLA deforms in a brittle fashion because of the lack of energy-absorbing events during the crack propagation\textsuperscript{32}. As for PLA composites containing 5 wt\% and 10 wt\% BBH, inclusion of the BBH in the PLA matrix has shown great toughness, because the BBH induced network could also supply many sacrificial bonds that could break and dissipate a significant amount of energy\textsuperscript{33,34}. Notably, these composites display an initial strain softening after yielding and then underwent considerable cold drawing. During this process, there exists a competition between craze formation and shear yielding. There is a drop in stress with increasing strain beyond the yield point of 6\% strain. After the strain of 12\%, only cold drawing dominates with constant stress. This phenomenon suggests an occurrence of large energy dissipation, similar to the work using hyperbranched polymer\textsuperscript{35} and PLA graft-copolymers\textsuperscript{36} to tough PLA. During the cold drawing
process, the plastic yielding of the PLA molecule around particles and subsequent void formation, as well as the interference of the BBH particles during crack propagation. Such crack deflection and crack pinning are responsible for the improved ductility. So both the debonding of BBH induced networks and increased craze plasticity around the particle, leading to decrease in brittleness. Nevertheless, 85PLA/15BBH shows a brittle behavior in the tensile test. Wu first proposed that there is a minimum confinement length governing the onset of ductility of polymer composites. The confinement is usually characterized by a critical distance between neighboring dispersed particles known as the critical matrix ligament thickness. It is stated that if the average matrix ligament thickness is below the critical value, the blend could be tough, and if it is above the critical value, the blend could be brittle. In case of 85PLA/15BBH, as more additive is added, the ligament thickness may be above the critical value.

The schematic illustration of the debonding and void formation mechanism during the drawing process for PLA/BBH composites is shown in Fig. 12. To further study the tough mechanism, the fracture surface of the tensile specimens were studied by SEM. Fig. 13 displays the SEM images of the tensile fractured surfaces of neat PLA and 90PLA/10BBH composites, respectively. The surface of neat PLA was extremely flat, indicating the brittle failure of PLA during tensile test. However, the BBH containing PLA has significantly different surface characteristic after deformation. The 90PLA/10BBH composites exhibited considerable ductile tearing and surface roughness. The increased surface area of fractured surface of the PLA/BBH composites suggested
that the crack paths were highly bifurcated, and crack propagation absorbed considerable strain energy before failure. This was instrumental in improving the toughness of PLA.

Fig. 12. Schematic illustration of the debonding and void formation mechanism during the drawing process for PLA/BBH composites.
In conclusion, a bio-based polyelectrolyte (BPE) was synthesized utilizing diphenolic acid. Using so obtained BPE, bPEI and APP, we have developed a useful method to fabricate a core/shell flame retardants via LbL assembly method. The flame retardant was efficient enough to achieve UL94 V0 rating for PLA at a loading content of 10 wt%. Cone calorimeter and TG-FTIR indicate that the flame retardant performance was ascribed to joint effect of gas and condensed phase mechanism. More interestingly, the flame retardant PLA shows improved toughness relative to the neat PLA. So far, undoubtedly, this should be a pioneering work and green approach for preparing flame retardant PLA with enhanced toughness.
Acknowledgements

The authors acknowledge the financial support from the Ningbo Science and Technology Innovation Team (No. 2015B11005) and natural science foundation of Ningbo (2016A610209).

References


