Phosphorus-containing diacid and its application in jute/poly(lactic acid) composites: Mechanical, thermal and flammability properties

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ABSTRACT

Phosphorous-based flame retardant was demonstrated excellent fire resistance for polymers and their composites, but the mechanical properties were always deteriorated. In this work, a phosphorous-containing diacid derivative (DOPO-MA) was synthesized by the reaction between 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and maleic acid (MA). The chemical structure of DOPO-MA was confirmed by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). DOPO-MA had been incorporated into short jute/poly(lactic acid) (PLA) composites to study the influence of DOPO-MA on the mechanical, thermal and flammability properties of jute/PLA composites. Compared to DOPO, slight enhancements in tensile, flexural and impact strength were observed with DOPO-MA loading. The thermal degradation behaviour and flammability of the composites with different DOPO and DOPO-MA loading were investigated by thermogravimetric analysis (TGA), UL94 test, limiting oxygen index (LOI) measurements and microscale combustion calorimetry (MCC). The results showed that DOPO-MA imparted the better flame retardancy to the composites than DOPO.

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1. Introduction

Nowadays, polymer-matrix composites (PMCs) have been widely used in automotive parts, sporting goods and marine applications [1–3]. However, the petroleum-based resins, synthetic fibers and their composites have caused serious environmental problems due to their non-biodegradability [4,5]. With the enhancing concern on environmental protection, the biodegradable composites made by natural fibers and bio-based polymers have extensively studied to replace the synthetic fiber reinforced composites due to their acceptable mechanical properties and environmental benefits such as biodegradability, less greenhouse gas emissions, and renewability [6,7]. Ramie, jute, hemp, sisal, kenaf and flax are some common plant fibers which can be obtained from the different parts of plant such as leaves, stems and roots of the plants [8,9]. As a naturally growing material, they possess many advantages such as low price, low density, high specific strength and modulus, good sound absorption, no health risks, easy availability in some countries and environmental friendly [10–12]. Poly(lactic acid) (PLA) as a biodegradable thermoplastic polymer provides good aesthetics and easy processability in most equipment [13,14]. The composites made by natural fibers and PLA have been good candidate to be used in electronics, transportation or construction due to cost saving treatment and disposal after service [15,16]. However, the inherent flammability and high smoke emission restrict their applications.

Several works have been reported on improving the flame retardancy of plant fiber reinforced PLA composites. Yang et al. [17] reported that aluminium hypophosphite (AHP) was used for the flame retardancy of basalt fiber/PLA composites. For PLA/BF containing 19 wt% AHP and 1 wt% modified carbon nanotube (m-CNT), it achieved a V-0 classification in UL 94 testing with a high LOI (31%). The limiting oxygen index (LOI) could be raised to 44% for the PLA composite with 29% Aluminum trihydroxide (ATH) and 1% hyperbranched polymers (HBP6) [18]. However, there were relatively large amount of addition of this kind of flame retardants leading to the deterioration of mechanical properties. Ammonium polyphosphate (APP) was proved to be very effective in improving flame retardancy of hemp/epoxy composites [19], flax reinforced PLA/thermoplastic starch (TPS) composites [20] and ramie/PLA composites according UL94 test and LOI measurements [21]. Unfortunately, APP is not permanent due to the weak water resistance and poor compatibility of APP in the composites. Montmorillonite clays (C30B) can improve flame retardancy of sisal reinforce
epoxy/unsaturated polyester (UP) composites, but the composites only achieved UL 94 V-1 rate [22]. 9,10-Dihydro-9-oxa-10-phos phaphenanthrene-10-oxide (DOPO) as a highly effective phosphorus-based intumescent flame retardant has received con siderable attention due to its high thermal stability, good oxidation and water resistance. DOPO group is rigid and bulky which con tains an ultra-thermally stable P—O—C bond, and it can protect O=P—O group by phenylene groups [23,24]. However, the polar fibers have inherently lower compatibility with less polar PLA matrix, the addition of DOPO may further weaken the interfacial adhesion between plant fiber and PLA matrix. Phosphorus-containing monomers containing reactive function groups, such as hydroxyl and carboxyl, can form hydrogen bonds between flame retardant and plant fiber/PLA, which could be a good solution for solving the problem.

In this work, DOPO with diacid (DOPO-MA) was synthesized by the reaction between DOPO and maleic acid, and the structure of DOPO-MA was characterized by Fourier transform infrared spectroscopy (FTIR). Flame retardant jute/PLA composites were prepared by twin-screw extruder with DOPO-MA as flame retardant additive agent. The mechanical properties, thermal stability and flame retardancy of jute/PLA composites were investigated.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) (NatureWorks® 4032D, M_w = 140,000, M_w/M_n = 1.7, D stereo-isomer content of about 1.5%) was pur chased by NatureWorks Co. Ltd. Jute fiber yarn was supplied by Shanghai Qiancong Jute fiber Co. Ltd., China. DOPO, commercial grade, was obtained from Huizhou Sunstar Technology Co. Ltd., China. Maleic acid (MA), toluene and tetrahydrofuran (THF) were purchased by NatureWorks Co. Ltd., China. DOPO group is rigid and bulky which contains an ultra-thermally stable P—O—C bond, and it can protect O=P—O group by phenylene groups [23,24]. However, the polar fibers have inherently lower compatibility with less polar PLA matrix, the addition of DOPO may further weaken the interfacial adhesion between plant fiber and PLA matrix. Phosphorus-containing monomers containing reactive function groups, such as hydroxyl and carboxyl, can form hydrogen bonds between flame retardant and plant fiber/PLA, which could be a good solution for solving the problem.

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2.2. Synthesis DOPO-MA

DOPO was dried to remove water at 100 °C for 2 h before use, sine a certain amount of hydrated DOPO was usually found in the reagent. 162 g of dried DOPO was added in 200 ml mixture of toluene and THF with a ratio of 1:1 in a 500 ml three-necked flask equipped with condenser. The flask was heated to 95 °C and stirred with a mechanical stirrer. After the complete dissolution of DOPO, 87 g of MA was added in 1 h. Then the mixture was stirred and maintained at 95 °C for 20 h, keeping in N_2 atmosphere. After cooling down to room temperature, the obtained products were filtered and washed with THF until the unreacted DOPO and MA were removed. Finally, the produced DOPO-MA was dried under vacuum at 100 °C for 12 h. The yield of DOPO-MA is about 80%, and 85% MA chemically attached to DOPO. The synthesis route of DOPO-MA is illustrated in Fig. 1.

2.3. Preparation of jute/PLA composites with DOPO-MA

Before processing, PLA and jute yarn were dried at 60 °C in vacuum for 24 h. The dried PLA and DOPO-MA were firstly well mixed by a high speed mixer. And then the mixture and jute yarn were blended in a co-rotating twin-screw extruder (20 mm, L/D = 40; Nanjing jieya, China) at 80 rpm with the operating temperatures profile 155/160/165/170/160 °C. Jute yarn was cut by the screw into about 1 mm in average length, and the diameter of jute fiber was 5–10 μm. The extrude was cooled in a water bath and cut into granules. And then the granules were collected and dried in a vacuum oven at 60 °C for 24 h before further processing. The formulations of the composites are presented in Table 1. Test specimens for the mechanical properties testing were obtained in the injection moulding machine (Wuxi Haitian Machinery Co. Ltd., China) according to the standard. The specimens were prepared by the following processing conditions: barrel temperature 170 °C, mould temperature 30 °C, back pressure 4 MPa, and injection pressure 12 MPa.

2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on an EQUINOX 55 spectrometer (Bruker, Germany) using compression molded film samples at a range of 400–4000 cm⁻¹. Differential scanning calorimetry (DSC) measurement was carried out by a Q 20 thermal analysis system (TA, USA). The scanning temperature was ranging from 20 to 200 °C with a heating rate of 10 °C/min in N_2 atmosphere. A STA 449 C thermogravimetric analyzer (NETZSCH, Germany) was used to study the thermal stability of the composites with 5 mg samples scanned from ambient to 800 °C at a heating rate of 20 °C/min under N_2 atmosphere with the flow rate of 80 ml/min. Tensile and flexural properties were carried out with a computer controlled mechanical instrument (ETM-5040, Shenzhen electromechanical universal testing instrument Co. Ltd., China) according to GB 13022-91 and GB 1449-83 respectively. A crosshead speed of 2 mm/min was used. The test of Izod impact was performed by Notched Izod impact instrument (ZBC-1400-2 test machine, Shenzhen Sans test Instruments Ltd., China) according to GB 1451-83. At least five specimens were used for each test. The fracture surface of the composites was sputter-coated with gold layer before examination, and the morphologies of the composites were obtained by using FEI Quanta200 SEM (Holand), and the accelerating voltage was 20 kV. Limiting oxygen index (LOI) values were measured with an LOI instrument
3. Results and discussion

3.1. Characterization of DOPO-MA

FTIR was carried out to confirm the information of DOPO-MA, and the results were presented in Fig. 2A. In the spectrum of DOPO, the absorption peak at 2385 cm\(^{-1}\) assigned to P–H stretching vibration, the absorption peak at 956 and 1149 cm\(^{-1}\) assigned to P–O–Ph vibration, the absorption peak at 1585 and 1450 cm\(^{-1}\) assigned to P–Ph stretching vibration, and the absorption peak at 1209 cm\(^{-1}\) assigned to P=O stretching vibration. The band at 3345 cm\(^{-1}\) was attributed to the presence of hydroxyl groups introduced by atmospheric moisture. Comparing with the FTIR spectrum of DOPO, it was found that the absorption peaks at 2385 cm\(^{-1}\) for P–H stretching vibration and 3345 cm\(^{-1}\) for hydroxyl groups disappeared from the spectrum of DOPO-MA, and new absorption peaks at 2910 cm\(^{-1}\) for C–H stretching vibration and 3440 cm\(^{-1}\) for carboxyl groups appeared, which indicated that DOPO-MA was successfully produced.

Furthermore, thermal properties of DOPO and DOPO-MA were determined by DSC, and the results are shown in Fig. 2B. The melting point (\(T_m\)) of DOPO was 119 °C, and the \(T_m\) of DOPO-MA was higher than that of DOPO, which could reach 214 °C. The results of FTIR and DSC indicated that DOPO-MA was successfully synthesized.

Thermal stability of DOPO and DOPO-MA was measured by TGA under N\(_2\) atmosphere, and the results are presented in Fig. 3. The initial decomposition temperature (\(T_i\)) and solid residue left at 600 °C were obtained from the TG curve, and the temperature of the maximum mass loss rate (\(T_{\text{max}}\)) of the samples was also obtained from the derivative thermogravimetric (DTG) curve. DOPO showed good stability with a strong DTG peak at 300 °C.
and remained about 6.5% mass residue after thermal degradation. For DOPO-MA, \( T_f \) shifted to the high temperature, and 17.4 wt% residue char left at the end of the test, exhibiting a better charring performance than that of DOPO.

3.2. Mechanical properties of the composites

The tensile properties of jute/PLA composites with different loading of DOPO and DOPO-MA are shown in Fig. 4A. As can be seen, the composites showed gradual decrease in tensile strength with increasing DOPO and DOPO-MA loading. The similar results were reported by Brehme et al. [25]. The decrease in tensile strength as the flame retardant agent acted as a matrix discontinuity and stress was concentrated in this region, leading to premature failure. Moreover, the well-dispersed states of the fillers in polymer matrix and the good interfacial interaction between two components were key factors in order to prepare polymer composites with good mechanical properties [26]. Note that tensile strength of the composites with DOPO-MA was higher than that of the composites with DOPO at the same weight loading. Simultaneously, Young’s modulus of the composites reduced with increasing DOPO loading level. In contrast, the composites showed nearly unchanged modulus with increasing DOPO-MA loading level. The higher tensile strength and Young’s modulus were mainly due to the well disperse of flame retardant agent and the well interface between two components.

Fig. 4B presents the flexural properties data for jute/PLA composites with different loading of DOPO and DOPO-MA. Flexural strength of the composites was found to decrease with the increased DOPO and DOPO-MA loading, and that the extent of reduction was greater for the composites with DOPO. No significant reduction in flexural modulus were observed for the composites with DOPO-MA. These results were consistent with the tensile properties described previously.

The interfacial adhesion, fiber pullout and mechanism to absorb energy are some of the important parameters in determining the impact strength of short fiber reinforced composites. Fig. 4C shows the effect of the DOPO and DOPO-MA loading on the impact strength of jute/PLA composites. Similar to tensile strength, it can be seen that the impact strength of the composites decreased with the increased DOPO and DOPO-MA loading, and that the extent of decrease for the composites with DOPO was greater with the same weight loading. It was due to that DOPO after modification provided effective resistance to crack propagation during impact test because of improvement of interfacial adhesion.

3.3. Morphologies of the composites

The representative fractured surface morphologies of jute/PLA composites with 7 wt% DOPO and DOPO-MA were imaged by using SEM for direct comparison and shown in Fig. 5. DOPO and DOPO-MA were well dispersed in the composites, and no large agglomerations.

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Fig. 4. Mechanical properties of jute/PLA composites without and with different content DOPO or DOPO-MA: (a) Tensile properties, (b) Flexural properties, (c) Impact strength. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
ates of DOPO and DOPO-MA were observed in Fig. 5. However, DOPO coated on the surface of jute fiber or blended in PLA matrix had an influence on the interface between matrix and fiber. For the composites with DOPO, gaps and cavitations were observed in Fig. 5A, the gaps acted as stress concentrators in the composites resulted in lower strength. Besides, many fibers were pulled out from the matrix with the voids thereby being created, which suggested that the interface between matrix and fiber was very weak. Poor adhesion of the fiber to the matrix and the fiber breakages are some of the major factors that have been reported to be the main cause of failure in fiber reinforced composites [27]. For the composites with DOPO-MA, the gaps between the fiber and the matrix became small. It was also observed that the layers of matrix were pulled out together with the fiber during impact fracture, which further substantiated adhesion between the fiber and the matrix. These observations indicated that after loading DOPO-MA, PLA and jute were compatible and formed good fiber-matrix adhesion, which were translated in the high tensile strength value of the composite. The improved interface between jute and PLA could be attributed to the formation of hydrogen bonds between the hydroxyl groups of jute or PLA and the terminal carboxylic groups of DOPO. The possible mechanism of enhancement in the interface of jute and PLA by using DOPO-MA. Therefore, it seemed reasonable to conclude that the increase in impact strength observed with the addition of DOPO-MA to the jute/PLA composite was the result of the improvement in interfacial adhesion between jute and PLA matrix.

3.4. Thermal stability of the composites

Fig. 6 presents the representative TGA curves of jute/PLA composites without and with 7 wt% DOPO and DOPO-MA under nitrogen atmosphere. All the samples showed a single-step degradation progress, which was consistent with the results reported in the lit-

![Fig. 5. SEM micrographs of fracture surface (a) Jute/PLA/7-DOPO, (b) Jute/PLA/7DOPO-MA, (c) The mechanism of enhancement in the interface of jute and PLA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 6. TGA curves of Jute/PLA, Jute/PLA/7-DOPO and Jute/PLA/7DOPO-MA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)
Table 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>LOI (%)</th>
<th>Dripping</th>
<th>UL-94</th>
<th>PHRR (W/g)</th>
<th>Tmax (°C)</th>
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</thead>
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<tr>
<td>Jute/PLA</td>
<td>21.6</td>
<td>Y</td>
<td>NC</td>
<td>315</td>
<td>380</td>
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<tr>
<td>Jute/PLA/3DOPO</td>
<td>25.2</td>
<td>Y</td>
<td>V-1</td>
<td>252</td>
<td>387</td>
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<tr>
<td>Jute/PLA/5DOPO</td>
<td>27.3</td>
<td>Y</td>
<td>V-0</td>
<td>240</td>
<td>390</td>
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<tr>
<td>Jute/PLA/7DOPO</td>
<td>28.1</td>
<td>Y</td>
<td>V-0</td>
<td>222</td>
<td>391</td>
</tr>
<tr>
<td>Jute/PLA/3DOPO-MA</td>
<td>26</td>
<td>Y</td>
<td>V-1</td>
<td>247</td>
<td>385</td>
</tr>
<tr>
<td>Jute/PLA/5DOPO-MA</td>
<td>27.1</td>
<td>Y</td>
<td>V-0</td>
<td>236</td>
<td>392</td>
</tr>
<tr>
<td>Jute/PLA/7DOPO-MA</td>
<td>29.3</td>
<td>Y</td>
<td>V-0</td>
<td>219</td>
<td>390</td>
</tr>
</tbody>
</table>

* Fire not extinguished after ignition.

The assessment of the flammability properties for the composites without and with DOPO and DOPO-MA was provided by LOI and UL94 tested, and the results obtained from the two tests are summarized in Table 2. Jute/PLA is a flammable polymeric composite with a LOI 21.6%. It can be observed that the LOI value increased gradually to 28.1% and 29.3% with increasing DOPO and DOPO-MA content, respectively. The LOI value of the composites with DOPO was lower than that of the composites with DOPO-MA at the same weight loading, revealing that DOPO-MA has a better flame retardant efficiency than DOPO.

Since jute and PLA are flammable materials, jute/PLA composites without flame retardant agent were completely consumed with serious dripping and failed in UL 94 testing. When the mass fraction of DOPO and DOPO-MA was 3%, the composites can extinguish after the first application of the flame within a short time, and the burning time was less than 20 s after the second application of the flame. Moreover, the samples showed little dripping, and the dripping did not ignite the cotton. Therefore, the composites with 3% DOPO and DOPO-MA could achieve the V-1 classification testing. When the mass fraction of DOPO and DOPO-MA increased to 5% and 7%, the composites can pass the V-0 classification testing. Furthermore, the composites with 7 wt% DOPO-MA achieved a V-0 rating with shorter burning time in comparison with other composites. All these results demonstrated that DOPO-MA could significantly improve the flame retardancy of jute/PLA composites.

The flammability properties of jute/PLA composites without and with DOPO DOPO-MA were assessed by using MCC that directly measures the heat of combustion of the gases evolved during controlled heating of milligram-sized samples, the detailed heat release rate data are listed in Table 2. The PHRR values of the composites were shown to decrease with increasing weight loading of DOPO and DOPO-MA, demonstrating that the flame retardancy increased with the added DOPO and DOPO-MA. Furthermore, incorporating DOPO-MA into the composites exhibited the lowered PHRR value than that of the composites with DOPO. The mechanism of DOPO-MA in reducing the flammability of the composites was probably attributed to that the better interface between flame retardant agent and fiber or matrix created a barrier which could slow down the heat and mass transfer between gas and condensed phases, and prevent the underlying materials from further combustion.

The images of residue char from the representative jute/PLA composites with DOPO and DOPO-MA after LOI test were recorded, which are shown in Fig. 7. The coherent carbonaceous charring layer as a protective shield and thermal barrier could be found on the surfaces of the composites with DOPO and DOPO-MA, respectively. Compared to the composites with DOPO, the dripping of the composites with DOPO-MA were lightened, which was due to the char. Char served as a physical barrier for heat flux from the flame to the matrix or the fiber surface, as well as a diffusion barrier for gas transport to the flame. DOPO-MA was easily reacted with PLA or fiber to form the charring layer. The interactions increased the viscosity of the melt through the formation of a jammed network structure, which limited flame propagation through the inhibition of dripping and the decrease in the rate of release of combustible gases. Therefore, DOPO-MA imparted the better flame retardant properties to the composites than DOPO.
4. Conclusions

DOPO was functionalized and incorporated in short jute/PLA composites by using twin-screw extruder. The functionalization of DOPO provided the active sites linked between DOPO and PLA or jute, which ensured the good interface. With the incorporation of DOPO-MA, the improvement in tensile, flexural and impact strength was observed compared to that of DOPO. Simultaneously, the enhancement in thermal stability was achieved, and the flammability of the composites had also been reduced, indicating that the addition of DOPO-MA lead to the formation of the char layer to protect the inner composites from further burning. The approach described herein could provide a promising solution in the development of an efficient flame retardant which can improve the flame retardancy and lighten the influence on the mechanical properties of jute/PLA composites.

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