EFFECT OF PHOSPHORUS-BASED COMPOUNDS ON THE FLAME RETARDANCY AND MECHACNICAL 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, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) as phosphorous-based flame retardant was modified, and a series of DOPO-based compounds (DOPO-ICN and DOPO-MA) were obtained. The chemical structure of DOPO-ICN and DOPO-MA were confirmed by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). DOPO, DOPO-ICN and DOPO-MA had been incorporated into short jute/poly(lactic acid) (PLA) composites to study the influence of different flame retardant 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-ICN and DOPO-MA loading. The thermal degradation behaviour and flammability of the composites with different DOPO and DOPO-ICN 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-ICN and DOPO-MA imparted the better flame retardancy to the composites than DOPO. The approach described herein could provide a promising solution in the development of an efficient flame retardant which can enhance the mechanical properties and the flame retardancy of jute/PLA composites simultaneously.

1 INTRODUCTION

Recently, the materials extracted from natural resources such as biopolymers and plant fibers have shown considerable potential to replace traditional synthetic fiber and polymer and use in automotive components and aerospace industry etc. The most commonly preferred plant fiber, that is, jute fiber possesses good sound absorption, low density, no health risks and is inexpensive, commercially available in the required form and has higher strength and modulus than plastic[1, 2]. Poly(lactic acid) (PLA) is a versatile thermoplastic produced from a lactic acid monomer mainly deriving from the fermentation of corn, sugar beets etc[3, 4]. However, the inherent flammability and high smoke emission of plant fibers and polymers restrict their applications.

The methods to reduce the flammability of PLA have been attempted recently. The eco-friendly flame retardant including nano inorganic, phosphorus-based, intumescent flame retardants and new effective flame retardant system have been utilized as flame retardant agent for PLA[12-16]. Furthermore, several works have been reported on improving the flame retardancy of plant fiber reinforced PLA composites. Woo et al. found that the flame retardancy of kenaf/PLA composites could obtain the improvement of 66% by using aluminum trihydroxide (ATH) as flame retardant[17].

However, there were relatively large amount of addition of this kind of flame retardants leading to the deterioration of mechanical properties.

For plant fiber/PLA composites, the polar fibers have inherently lower compatibility with less polar PLA matrix, and the incompatibility may influence the composites processing and the properties of the composites. Therefore, it is a challenge to improve the flame retardancy and the mechanical properties simultaneously. Phosphorus-containing monomers containing reactive function groups, such as hydroxyl and carboxyl, adhered or grafted on the fiber and molecular chain of polymer matrix which could be a good solution for solving the problem.

In this work, DOPO with hydroxyl group (DOPO-OH) and diacid (DOPO-MA) were synthesized respectively. And the structures of DOPO-OH and DOPO-MA were characterized by Fourier transform infrared spectroscopy (FTIR). Since isocyanates can react with hydroxyl or carboxyl groups to form the stable chemical bond, the isoyanate group of diisocyanate reacted with free hydroxyl group of DOPO-OH, resulting in the in situ formation of isocyanate group on DOPO. Free isocyanate group can then react with the hydroxyl end group of jute or PLA, and produce urethane bonds. Flame retardant jute/PLA composites were prepared by twin-screw extruder with two methods. In the first method, DOPO-OH was added as flame retardant additive agent with 1,6-hexane diisocyanate (HDI) as compaibilizer. In the other method, DOPO-MA was added as flame retardant additive agent. The mechanical properties and flame retardancy of flame retardant 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 purchased 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. 1,6-hexane diisocyanate (HDI), ethanol, formaldehyde, maleic acid (MA), toluene and tetrahydrofuran (THF) were analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2 Synthesis DOPO-OH

DOPO was dried to remove water at 100 ℃ for 2 h before use, sine a certain amount of hydrated DOPO was usually found in the reagent. DOPO and ethanol were placed in a four-necked round bottom flask equipped with a stirrer. The solvent was heated to 70 ℃, and formaldehyde was added slowly while stirring refluxed at 70 ℃ for 24 h. After reaction, the remained DOPO-OH was filtered and dried in vacuum at 50 ℃ overnight.

2.3 Synthesis DOPO-MA

DOPO was dried to remove water at 100 ℃ 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 ℃ 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 ℃ for 20h, keeping in N2 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 ℃ for 12h. The yield of DOPO-MA is about 80%, and 85% MA chemically attached to DOPO.

2.4 Preparation of jute/PLA composites with DOPO-MA

Before processing, PLA, jute yarn, DOPO-OH and DOPO-MA were dried at 60 ℃ in vacuum for 24h. The dried PLA and DOPO-MA (or DOPO-OH) 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 ℃. For DOPO-OH, HDI should be added with jute yarn at same time. 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 extrudate was cooled in a water bath and cut into granules. And then the granules were collected and dried in a vacuum oven at 60 ℃ 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 ℃, mould temperature 30 ℃, back pressure 4 MPa, and injection pressure 12 MPa.

Samples ID	PLA (wt%)	Jute (wt%)	DOPO (wt%)	HDI (wt%)	DOPO-OH (wt%)	DOPO-MA(wt%)
Jute/PLA	85	15	-	-	-	-
Jute/PLA/DOPO	78	15	7	-	-	-
Jute/PLA/DOPO-ICN	77	15	-	1	7	-
Jute/PLA/DOPO-MA	78	15	-	-	-	7

Table 1: Formulations of jute/PLA composites

2.5 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}. 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℃ at a heating rate of 20℃ /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 2mm/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) accordance 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 (HC-3 Analytical Instrument Factory, China) according to GB2406-82 (China) with test specimen bars (100×6.5×3 mm). The UL-94 vertical burning test was used to test the ease of the ignition of polymeric materials using small burner. All of the bar specimens (125×13×3 mm) were tested by vertical burning test instrument (WC 5400) (Kunshan Wancheng Analytical Instrument Co., China) according to ASTMD 3801 UL-94 standard.

3 RESULTS AND DISCUSSION

3.1 FTIR results

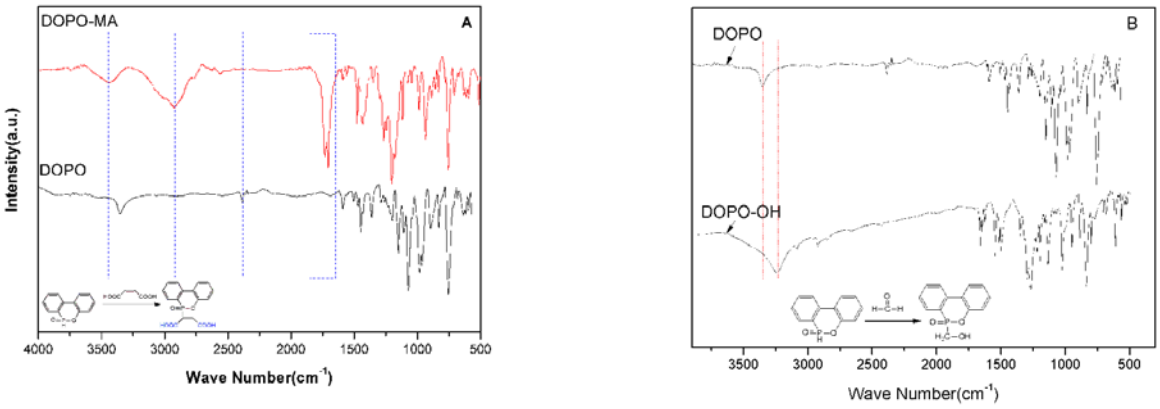

Figure 1: FTIR spectra of DOPO, DOPO-MA and DOPO-OH

FTIR analysis of DOPO, DOPO-MA and DOPO-OH were presented in Figure 1. In the spectrum of DOPO, the characteristic absorption peak of DOPO at 2385 cm^{-1} (P-H stretching vibration), 956 and 1149 cm^{-1} (P-O-Ph vibration), 1585 and 1450 cm^{-1} (P-Ph stretching vibration), and at 1209 cm^{-1} (P=O stretching vibration) were found. Furthermore, the band at 3345 cm^{-1} was attributed to the presence of hydroxyl groups introduced by atmospheric moisture. After reaction, it was found that the absorption peak at 2385 cm^{-1} for P-H stretching vibration disappeared from the spectra of DOPO-MA and DOPO-OH. 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. Also, the new absorption peak at 2892 cm^{-1} for C-H stretching vibration appeared, which clearly indicated that DOPO-OH was achieved.

3.2 Mechanical properties of the composites

Author’s name should include first name, middle initial (if desired) and surname, and be written centred, in 11pt Times New Roman, 11 pt below the title.

3.3 Thermal stability of the composites

Author's affiliation should be written centered, in 11 pt Times, 11 pt below the list of authors. A 11pt space should separate two different affiliations.

3.4 Flammability of the composites

A maximum of five keywords (beginning with **Keywords:** boldfaced) should be added, separated by a comma, and written centred, in 11 pt Times New Roman, a capital being used for the first letter of each keyword. Leave one 11pt space after title, author(s), affiliation(s) and keywords.

4 CONCLUSIONS

The normal text should be written single-spaced, justified, using 11pt Times in one column. The first line of each paragraph must be indented 0.5cm.

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