Journal of Engineering Science, Vol. 10, 9–18, 2014

Flammability and Mechanical Properties of Ramie Reinforced Poly(lactic Acid) Composites by Using DOPO

Tao Yu, Yan Li* and Yonglong Wang

School of Aerospace Engineering and Applied Mechanics, Tongji University, 1239 Siping Road, Shanghai, 200092, People's Republic of China

*Corresponding author: liyan@tongji.edu.cn

Abstact: *Ramie reinforced poly(lactic acid)(PLA) composites have been receiving a lot of research attention due to their excellent biodegradability. However, poor flammability of the composites limits their application in a few areas such as automobile and aircraft interior. In the present study, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) as flame retardant was incorporated into the ramie fibre reinforced composites to render the environment friendly character of the biocomposites in flame-retarded composition. Flame retardancy of the composites was greatly improved according to the UL94 vertical test and limiting oxygen index (LOI) measurements. The composites could achieve a UL94 V-0 rating and LOI value increases from 21.6 for ramie/PLA to 27.5 for the flame-retarded ramie/PLA. Enhanced char yield at higher temperatures was observed according to the thermogravimetric analysis (TGA) results. The influence of DOPO on the mechanical properties of the composites was also studied. DOPO can influence the mechanical properties of the composites. Observation can be made directly from scanning electron microscope (SEM) image that the compatibility between PLA and ramie fibre is disturbed by DOPO introduced into the composites. Not a lot of research has been done on the flame retardancy of natural fibre reinforced PLA composites. Therefore, this study offers benefits for future research on composites flame retarding.*

Keywords: Ramie, poly(lactic acid), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), composite flammability, mechanical properties, biodegradability studies

1. INTRODUCTION

Biodegradable materials have received a lot of research attention due to the increasing pressure on the world's resources and concerns about the disposal of materials. In the past decade, poly(lactic acid) (PLA) with high strength and modulus has been identified as a perfect eco-material for many studies for its potential in renewable engineering materials. PLA exhibits good aesthetics and easy processability in a lot of equipment. In manufacturing and processing, the price and inherent brittleness are the most limitation for its wide practical applications.[1,2] Natural fibres are obtained from the leaves or the stems of plants. As a naturally growing material, they sell at low price, possess low density and high specific strength and modulus, poses no health risks, are easily available in some countries, and environmental friendly.[3] By adding fibres including sisal, wood, bamboo, ramie and recycled newspaper, etc., or other filler material including nano-calcium carbonate, nano-titanium dioxide and multi-walled carbon nanotube, etc., the mechanical properties, biodegradability and thermal stability of the PLA based composites can be significantly improved and the price of PLA products can be lowered.[4,5] However, similar to other polyester resins, PLA and natural fibre have a very poor resistance to fire due to their molecular structure and intrinsic chemical composition, hence the modification of flame retardancy is indispensable.

Throughout the past decade, a number of methods have been performed to synthesise flame-retardant biocomposites. These include using halogen-free flame-retardants to obtain biocomposites with non-toxic and smoke-suppression properties, surface treatment, and flame-retardant compatibilisation and miniaturisation. Nanotechnology has also been used to produce biocomposites with good mechanical properties. Additionally, flame-retardant synergism is used to improve the flame-retardant efficiency of biocomposites.

Low cost and high efficiency are the development directions for flame-retardant biocomposites.[6,7] A lot of halogen-free flame retardants that contain phosphorus/nitrogen have been thoroughly researched and reviewed for their low toxicity and high efficiency. At high temperature, most organophosphorus flame retardants form phosphoric acid and prevent the substrate burning via a condensed phase mechanism. In our previous work, APP was added into ramie/PLA biocomposites, and the flammability of the composites was improved. However, the blossoming of transference phenomenon of APP can be found which could influence the flammability of the composites.[8, 9]

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a type of cyclic phosphate exhibiting a diphenyl structure (Figure 1). It possesses high thermal stability, and good oxidation and resistance. DOPO exhibits excellent flame-retarding properties. Thereby DOPO can either act only in the gas phase by flame inhibition, or in the gas phase and in the condensed phase (by char formation) at the same time.[10,11]

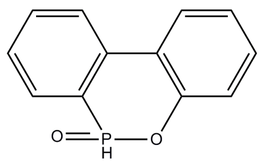

Figure 1: Structure of DOPO.

In the present study, DOPO was used to induce flame retardancy to ramie/PLA biocomposites. The flammability of the composites was thoroughly investigated via UL94, limiting oxygen index (LOI) and thermogravimetric analysis (TGA) measurement. The compatibility among PLA, ramie fibres and DOPO was observed with scanning electron microscope (SEM). Additionally, the influence of DOPO and formulation process on the mechanical properties were investigated. The experimental results obtained may contribute to the design of biocomposites with flame retardancy for various engineering applications.

2. EXPERIMENTAL

2.1 Materials

PLA (NatureWorks® 4032D, having T_g of 52–58°C, T_m of 150°C and M_w of 140,000) was purchased from NatureWorks Co. Ltd. Ramie yarn was supplied by Shanghai Qian-Cong Ramie Products Co. Ltd. (China). DOPO was obtained from Jiangyin Hanfeng Science & Technology Co. Ltd (China).

2.2 Preparation of Flame Retardant Ramie/PLA Composites

Ramie yarn, PLA resin and DOPO were dried at 50°C in a vacuum for 10 h, respectively. Then the dried PLA and DOPO were well mixed. Next, the PLA, DOPO and ramie yarn were blended in a co-rotating twin-screw extruder (F = 20 mm, L/D = 40; Jieya Nanjing, China) at operating temperature between 155°C and 175°C. The extrudate was later quenched in a water bath, cut into pellets and dried in a vacuum oven at 50°C for 8 h. The composite compositions are tabulated in Table 1. The biocomposites obtained were then molded into sheets by hot pressing at 170°C and 20 MPa for 4 min. This was followed by cooling to room temperature at 5 MPa. The sheets were made ready for structure characterisation and property measurements.

Table 1: Compositions of the composites.

Sample	Ramie /wt%	PLA /wt%	DOPO /wt%
F0	15	85	0
F1	15	80	5
F2	15	77	8
F3	15	75	10
F4	15	72	13
F5	15	70	15

2.3 Characterisation

LOI values were measured with an LOI instrument (HC-3 Analytical Instrument Factory, China) according to Chinese Standard GB 2406-82 with test specimen bars (100 × 6.5 × 3 mm^3). All of the specimens (125 × 13 × 3 mm^3) were tested by vertical burn test instrument WC 5400 (Kunshan Wancheng Analytical Instrument Co., China) according to ASTM D 3801 UL-94 standard. TGA was performed on a STA 449 C thermogravimetric analyser (NETZSCH, Germany) at a heating rate of 20°C min^{-1}. Samples were tested under flowing air (80 ml min^{-1}) over a temperature range from ambient to 600°C. Observation and analysis were done on the morphologies of the impact fractured surfaces of the composites using SEM (Quanta 200 FEG, FEI Company). This was done at room temperature. The samples were coated with gold using a vacuum sputter coater, and were viewed perpendicular to the fractured surface.

The composite specimens were tested for tensile strength according to GB 13022-91 standard using a CMT5105 Materials Testing Machine (Shenzhen Sansi Material Instruments Ltd., China). The composites were then tested for flexural strength under three point bending in a DXLL-5000 machine (Shanghai Jiedeng Instruments Ltd., China) in accordance with GB 1449-83.

3. RESULTS AND DISCUSSION

3.1 Combustion Performance

The flammability properties of ramie/PLA composites with different DOPO content were evaluated by UL-94 test and LOI measurement. The UL-94 results were shown in Table 2. Ramie/PLA composite without DOPO is highly combustible and it was not classified in the UL-94 test. The flame retardancy of ramie/PLA composite is clearly improved with loading of DOPO, and the self-extinguishing can be detected. Only 5 wt% DOPO was added to the composite, the UL-94 test results of the composites can achieve V-0 and serious melt dripping appeared during burning.

Although flame retardancy of the composite was not improved with the increasing content of DOPO, melt dripping was lightened. This can be observed from Figure 2. The effects of different content of DOPO on the LOI value of the composites are presented in Figure 3. When 5 wt% DOPO was added to ramie/PLA composite, the LOI values are levelled up from 21.6% to 32.5%. The LOI values of the composites showed a slight increase with increasing DOPO content. It is suggested that DOPO can improve flame retardancy of the composites sharply.

Table 2: Flame retardancy of the composites.

Specimens	t_1(s)	t_2(s)	UL-94	Dripping
F0	> 30	–	NR	Yes
F1	0.4	0.6	V-0	Yes
F2	0.3	0.4	V-0	Yes
F3	0.4	0.5	V-0	Yes
F4	0.4	0.3	V-0	Yes
F5	0.4	0.4	V-0	Yes

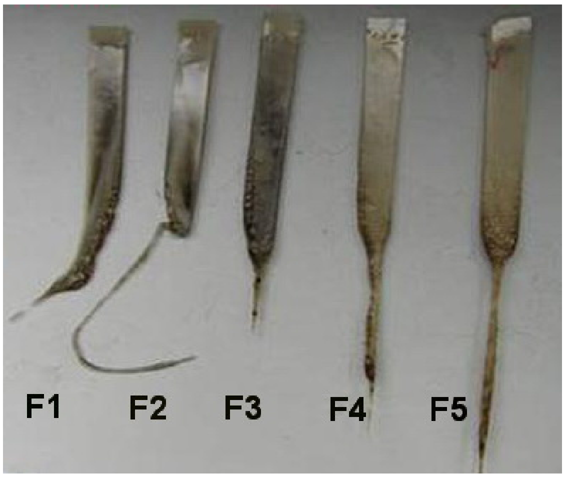

Figure 2: Specimens after UL94 Test.

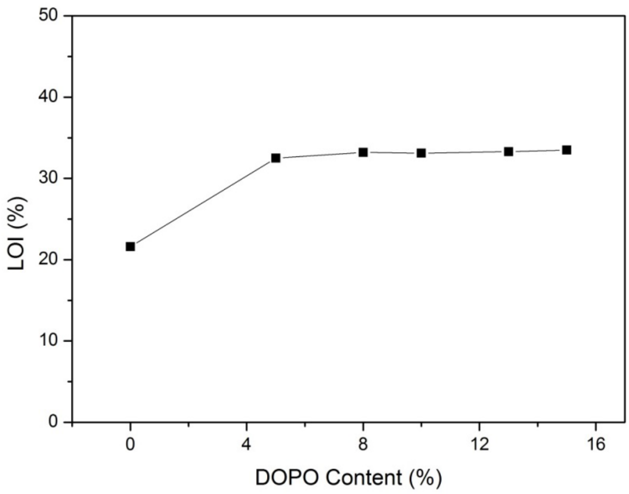

Figure 3: LOI value of the composites.

3.2 Thermal Stability

The thermal stability of the ramie/PLA composite without and with DOPO was investigated by TGA, and the results are presented in Figure 4. Thermal degradation of ramie/PLA without DOPO showed completely in a single stage and occurred at 335.1°C. The T_{onset} of F2 is similar to that of F0. It shows that the improvement of thermal stability of the composites can be negligible with the addition of DOPO. When the temperature increased above 400°C, the matrix and the flame retardant began to fully develop a bonded char structure. During formation of the char, the heat and the burning amount of the volatile products were drastically reduced, and thermally stable char in high temperature contributed to the thermal and flame protection to matrix. Moreover, it can be observed that the residue left at 600°C increased significantly with the addition of DOPO. The results can explain the improvement of flame retardancy of the composites.

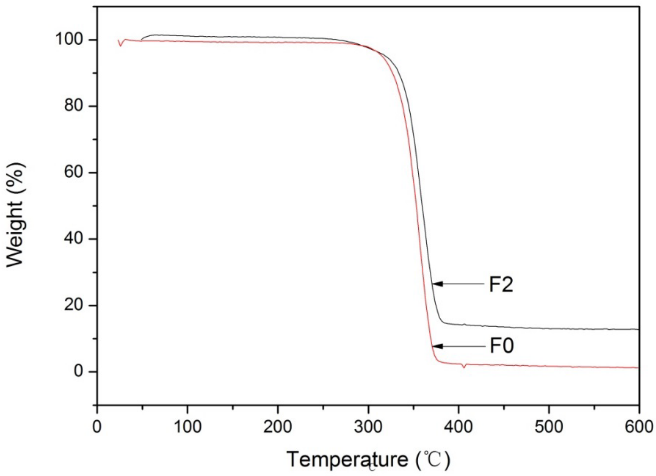

Figure 4: TGA curve of the composites.

3.3 Mechanical Properties

The composites with different content of DOPO were further evaluated by tensile and flexural testing. Data related to the tensile properties are shown in Figure 5. It can be seen that the tensile strength and tensile modulus of ramie/PLA composite without DOPO were 32.09 MPa and 1.61 GPa respectively. The tensile strength and tensile modulus have slightly increased with the addition of DOPO. For example, after adding 8 wt% DOPO, the tensile strength and tensile modulus reached 38.76 MPa and 2.25 GPa respectively. It shows that DOPO acts as reinforcing filler in the composites in some way.

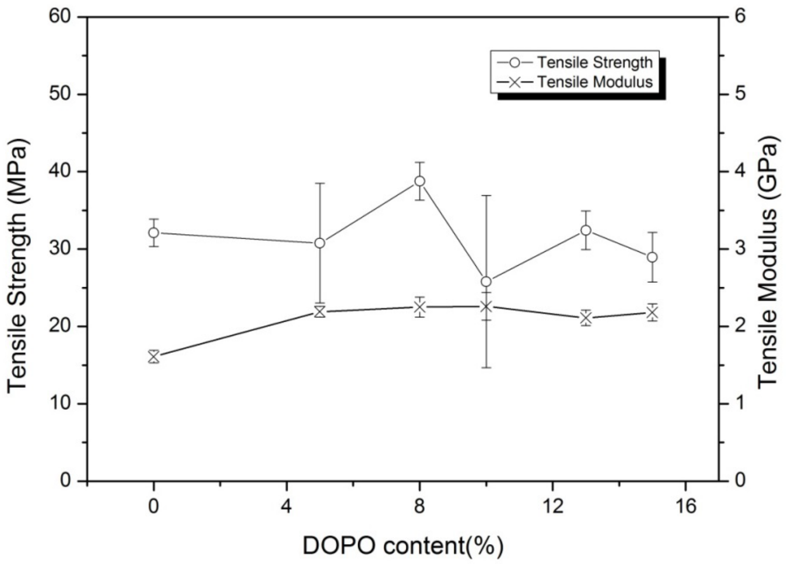

Figure 5: Tensile properties of the composites.

Moreover, the tensile strength of the composites decreased when the adding content of DOPO increased to over 8%. Figure 6 shows the flexural properties of the composites with different content of DOPO. The flexural strength and flexural modulus of the composites sharply decreased with the addition of DOPO. When adding 8% DOPO to the composites, the flexural strength and flexural modulus decreased from 95.23 MPa to 36.36 MPa and 5.35 GPa to 4.31 GPa respectively. This may be due to the fact that high loading of DOPO influenced the bonding of PLA and ramie fibres.

The compatibility between fibres and PLA is poor. The mechanical properties of fibre-reinforced composites are greatly influenced by the interfacial bond strength. The compatibility between the polymer matrix and the ramie fibres was made worse by hindering interaction at the polymer/fillers interface. The results indicate that the addition of DOPO to the ramie fibres reinforced PLA composites decreases the composite mechanical properties.

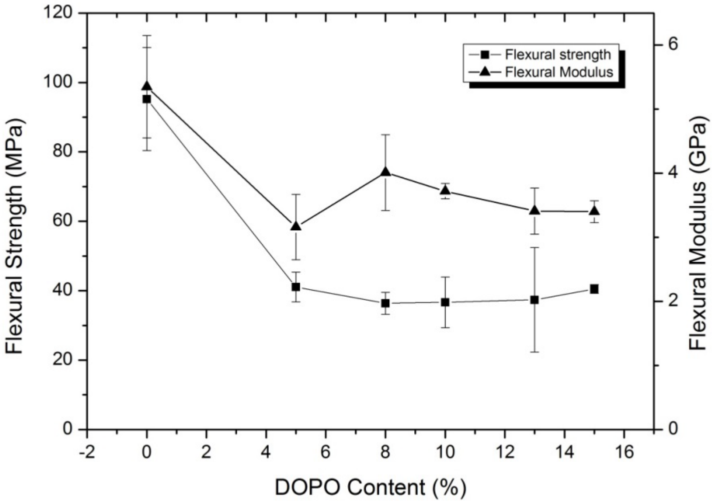

Figure 6: Flexural properties of the composites.

3.4 Morphology Analysis

SEM micrographs of the impact fracture surfaces of the samples are represented in Figure 7. As shown in the figure (illustration A), the ramie fibres dispersed in the form of a separated fibre. The DOPO is well dispersed in the PLA/ramie composites (B). No large agglomerates of the DOPO and good adhesion between the matrix and DOPO have been observed. This should play an important role towards improving flame retardancy. DOPO adsorbed on the surface of ramie fibres or blended in PLA matrix influenced the interfacing between ramie fibres. It can be seen from Figure 7 that there are obvious voids between the fibres and PLA. This observation indicates that there is weak interfacial adhesion between PLA and nature fibres.

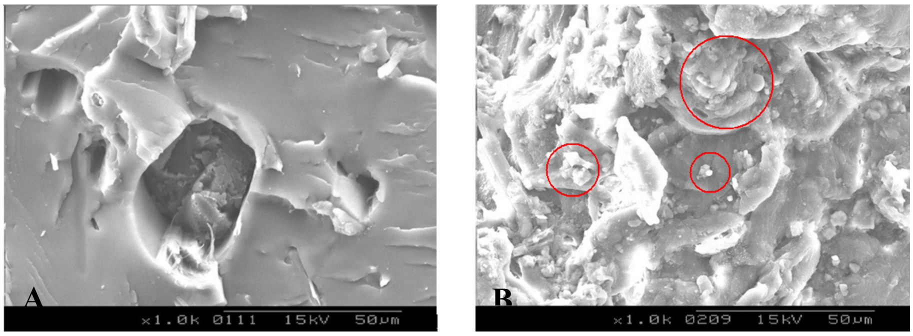

Figure 7: SEM micrographs of the composites (A = F0, B = F2).

4. CONCLUSION

The flammability and mechanical properties of ramie/PLA composites were explored using DOPO. The composite can achieve UL 94 V-0 rating with the addition of DOPO. According to the TGA results, DOPO can effectively increase char residue at high temperature, which results in the improvement of flame retardancy. From SEM image, it can be directly observed that DOPO introduced into the composites disturbs the compatibility between PLA and ramie fibres. DOPO can influence the mechanical properties of the composites.

5. ACKNOWLEDGEMENT

The authors would like to thank the support of the National Basic Research Program of China (973 Program, No. 2010CB631105) and Natural Science Foundation of China (No. 51103108 and No. 11172212).

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