Study on Flame Retardancy of Polylactic Acid Composites

Shaoyu Wang, Lei Zhou, Wenyan Feng and Dongze Li

ABSTRACT

Based on poly lactic acid (PLA) as the main body, we have selected the phosphorus flame retardant and montmorillonite as auxiliary materials. Prepared PLA composites by Huck torque rheometer, through limiting oxygen index determination, MCC test, UL-94 flame test, we have known the effect of flame-retardant material and discussed its flame retardant mechanism. In addition, through measuring tensile strength, impact strength, flexural strength and elongation at break of poly lactic acid composite, we discuss the change of mechanical properties after adding flame retardants. Combustion performance tests show, phosphorus flame retardant and montmorillonite retardant system for poly lactic acid efficiency is very high. Adding a small amount of flame retardants can greatly improve the limiting oxygen index value, the vertical burning poly lactic acid level increased from NR level becomes V-0 level. Mechanics test research shows that a small amount of montmorillonite on composite materials tensile strength, impact strength and static bending strength has obvious promotion effect.

INTRODUCTION

Poly lactic acid is a novel biodegradable materials. From the viewpoint of environmental protection, PLA is the best choice to replace the traditional petroleum-based material[1-3]. In fact, PLA has been used in various applications such as medical applications and plastics[4-5]. However, PLA is easily combustible and does not meet the safety requirements in many cases, which consequently restricts its potential application. Society and academia face with frequent occurrence of fire and a lot of unnecessary loss. We should not only strengthen
awareness, but also pay attention to the study of materials and flame retardant properties.

Phosphorus flame retardant is one of the most important environmentally friendly flame retardants. Formed of high viscosity melt glassy or a dense touch carbonaceous by the combustion. Because it will be decomposed into phosphoric acid or poly phosphoric acid, which use of a solid form of the matrix isolated from heat and oxygen. DOPO(10-(isopropyl-2-ol)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) is a new intermediate. DOPO and its derivatives due to the molecular structure containing biphenyl ring and phenanthrene ring structure. Thermal stability and chemical stability are high than general organic phosphates[6-8].

"Nanotechnology" appears and rise in the 1980s, Japanese scholars Fujiwara apply for to nanoclay flame retardant nylon patent opened research hotspot. Giannelis[9-10] found melt blending methods can be prepared PLSN without use of organic solvents. Since then, PLSN nanocomposites preparation, characterization and explore the mechanism, for applications such as automotive industry and fire-retardant materials has become an enthusiasm. PLSN flame retardancy mechanism have three factor. The barrier mechanism[11-12] show layered silicate dispersing in nanoscale and limited chain segment movement to improve the heat resistance of the polymer. The catalytic charing[13-14] show the organic montmorillonite produced acidic point by Hofmann degradation reaction with burning polymer. Acidic points help polymer degradation into carbon lead to improve the flame retardancy. The radical scavenging[15] show clay contains a small amount of paramagnetic impurities capture living radical polymerization in the thermal degradation process.

In the present study, we consider synergistic flame retardant effect of montmorillonite and the new phosphorus flame retardant on combustion property of polylactic acid.

**EXPERIMENTAL**

**Matierials**

Poly lactide (PLA 4032D) was obtained commercially from Nature Works. Montmorillonite was purchased from Feng Hong (Zhejiang, China) Co. The new phosphorus flame retardant in this study were synthesized in our laboratory. 10-(isopropyl-2-ol) -9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was purchased from Ming Shan (Shandong, China) Chemical Co., Ltd.

**Synthesis of the New Phosphorus Flame Retardant Method[16]**

DOPO (43.2 g) and diethanolamine (21 g) were dissolved in 100ml of distilled water in a three-neck flask equipped with a reflux condenser, a thermometer, and an addition funnel. The reaction mixture was heated to 80 °C. Paraformaldehyde (3.10
g) was added in a drop wise manner during a period of 5 min. This reaction mixture was heated under reflux for 1 hour. Using a vacuum rotary evaporator and the solution was evaporated by heating, and finally concentrated to a white solid. The solid was washed repeatedly with ethanol to remove reactants and then dried, and the remaining product was treated at 120 °C vacuum for 3 hours to give a clear gum finally.

**Preparation of PLA Composites**

Mixed 50 g samples as a component. The formulations of samples were listed in Table 1. The samples were melt-mixed in HAAKE torque rheometer at 30 rpm for 10 min under 190 °C. The samples were pulverized and dried. Injection of a standard samples.

**Characterization**

The Fourier transform infrared spectra (FTIR) were measured over the wavenumber range of 400-4000 cm⁻¹. The powdered samples were mixed with KBr and pressed in the form of pellets for the measurement of FTIR analysis. Samples (5 mg) were tested with a Govmark MCC-2 microcombustion calorimeter at 1 °C/s heating rate under nitrogen from 100°C to 600 °C. The instrument was capable of recording heat release capacity (HRC), total heat release (THR), peak heat release temperature (HRR). Limiting oxygen index (LOI) values were determined using a HC900-2 oxygen index meter (Jiangning, China) with sheet dimensions of 130 mm×6.5 mm×3 mm. The UL-94 vertical test was performed according to the ANSI/UL 94-2013 testing standard. Use electronic universal testing machine tested in accordance with GB/T 1040.2-2006 and GB/T 9341-2008, stretching rate is 50 mm/min. All of samples need to be placed in the climatic chamber for 24 h.

**RESULTS AND DISCUSSION**

**Characterization of The New Phosphorus Flame Retardant**

In the FT-IR spectrum, the structure of the synthesized the new phosphorus flame retardant is confirmed with characteristic absorption at 2956 cm⁻¹ and 2880 cm⁻¹ (-CH₂- characteristic absorption peaks), 1030 cm⁻¹ (-C-N- stretching vibration peaks). In addition, 2387 cm⁻¹ (-P-H-characteristic absorption peaks) completely disappeared, indicating that the active hydrogen on the reaction was complete.

**Mechanical Properties of PLA Composites**

As shown in table 2, PLA composites with various the new phosphorus flame retardant contents. Tensile strength, notched impact strength and flexural strength
begins to decrease with increasing of the new phosphorus flame retardant contents. Its due to poor compatibility between phosphorus flame retardant and PLA. Compared PLA4 and PLA6 data, we find that add montmorillonite improve the mechanical properties of materials.

**Flammability Properties of PLA Composites**

Figure 2 show that pure PLA limiting oxygen index is only 20 %, is very easy to burn, but after adding the new phosphorus flame retardants, limiting oxygen index was significantly improved. The results suggests that LOI increased to 24,25,26, and 28 with the addition of 0.5,1,1.5 and 2 wt% of the new phosphorus flame retardant. PLA composites become a flame retardant materials. When adding montmorillonite the limiting oxygen index does not changes. Description montmorillonite have a little effect on the oxygen index of the material.

Through vertical flame test results (Table.4) can be seen, pure PLA burn time is the longest, melt droplets can ignite cotton. Add phosphorus flame retardant can be shorten the combustion time. After adding montmorillonite the burn time is further shorten. Although the results improving the flame retardancy, flame retardant levels reached UL-94 V2. The phosphorus flame retardants cannot let the material reaches UL-94 V0.

**Burning Behaviors of PLA Composites**

“Microscale combustion Calorimeter (MCC) measures the flammability of materials on milligram quantities and is based on the principle of oxygen consumption as well as cone calorimeter to measure the rate and amount of heat during combustion. MCC is a small-scale flammability testing technique to screen polymer flammability prior to scale-up and is a convenient and relatively new technique, developed in recent years. It was regarded as one of the most effective methods for investigating the combustion properties of polymer materials”.[17] From the figure HRR of three materials are only one peak. PHRR value of pure PLA is 485 W/g. The PHRR value of PLA4 and PLA6 are lower than pure PLA, decreased 1.2 % and 9.1 %. Total heat release and heat release rate also reduced. It can be considered as significant improvement in flame resistance. In addition, the montmorillonite have a greater contribution to improving flame retardancy of PLA. Compare PLA4 and PLA6 show the synergy (Table.5).

**CONCLUSIONS**

A flame retarded PLA nanocomposite were prepared by HAAKE torque rheometer. Limiting oxygen index of PLA nanocomposite increased to 28, flame retardant levels reached UL-94 V2. The fire retardant mechanism observed in the microscale combustion calorimetry is char formation, slowing the initial
decomposition, and increasing the final char yield. PLA6 have the lowest heat release rate show the synergistic effects. Its show that phosphorus flame retardants and montmorillonite can collaborate flame retardant polylactic acid.

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