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Synergistic effect between expandable graphite and ammonium polyphosphate on flame retarded polylactide

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ABSTRACT

Synergistic effect was observed between expandable graphite (EG) and ammonium polyphosphate (APP) on flame retarded polylactide (PLA) in this paper using limiting oxygen index (LOI), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray spectroscopy (XPS) and cone calorimeter tests etc. In the experiments, PLA composites with 15 wt% of APP/EG(1:3) combinations showed a LOI value of 36.5 and V-0 rating in UL-94 tests, greatly improved flame retardant properties from composites with APP or EG alone. Results from TGA and cone calorimeter demonstrated that APP/EG combination could retard the degradation of polymeric materials above the temperature of 520 °C by promoting the formation of a compact char layer. This char layer protects the matrix effectively from heat penetrating inside and prevents its further degradation, resulting in lower weight loss rate and better flame retarded performance.

1. Introduction

Polylactide, as one of bio-based and bio-degradable polymers, has good biocompatibility, biodegradation, mechanical properties, thermal plasticity, high degree of transparency and gas permeability. Being the first bio-based plastic produced on a large-scale, PLA has name plate capacity 150 kt p.a in 2009. Based on company announcements, its worldwide capacity has an increasing tendency in the future. It has been widely utilized in packaging, textiles, cutlery, diaper and biomedical applications [1,2]. With the development of technology, the mechanical and physical properties of PLA have been improved greatly [3,4]. Recently, PLA is being further considered for applications in the areas of electrical/electronic devices, household goods, and automotive industries etc. [5]. However, there is a great limitation for PLA being applied in these areas because of its flammability and dripping combustion. Therefore, it is necessary to improve the flame retarded performance of PLA.

Intumescent flame retardant (IFR) systems have attracted great attention because they are halogen-free, environmental friendly and highly effective. An IFR system is usually composed of three elements, an acid source, a blowing agent and a carbonic source. The intumescent char produced from the synergistic interaction among these elements protected underlying materials from heat and oxygen. For example, the combination of APP and pentaerythritol (PER) system is a widely used IFR system for polymer. Reti et al. [6,7] has studied the efficiency of different intumescent formulations for PLA containing starch and lignin, and the formulation of the additives has been optimized to have less APP. Bourbigot et al. [10] showed that IFR reduced the dripping of PLA, but only achieved V-2 rating in his studies.

To further decrease the flammability of PLA for wider applications, there is a need to find additional effective IFR formulations with synergistic effects additives. Research efforts have been devoted to improve the efficiency of flame retarded PLA by designing and synthesizing novel carbonization agents or flame retardants. Triazine phosphamide synthesized by Hu et al. [8] exhibited high flame retarding efficiency in PLA. The limiting oxygen index (LOI) value could reach 33.5 with 15 wt% additives, but the samples failed in UL-94 testing. Ke et al. [9] combined hyperbranched charring agent with APP in PLA to improve the charring and flame retardant efficiency. Their material obtained a UL-94 V-0 rating with 15 wt% additives, but the LOI value was only 26.2. It seems that, although the efficiency of flame retarded PLA can be improved using conventional IFR, it is hard to obtain UL-94 V-0 rating and high LOI value simultaneously without dripping at low content of additives.

In our previous work, it was found that the fire-resisting efficiency of APP solely flame retarded PLA was very low. Thus, it is necessary to select a high efficient synergistic additive. Expandable

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Table 1
Formulation and fire test results of PLA and PLA composites.

Samples	PLA (wt%)	APP (wt%)	EG (wt%)	APP/EG	LOI	UL-94
PLA	100	0	0	/	22.0	F
PLA-1	70	30	0	/	33.0	V-2
PLA-2	70	18	12	3:2	49.0	V-0
PLA-3	80	5	15	1:3	47.5	V-0
PLA-4	90	2.5	7.5	1:3	26.2	V-2
PLA-5	85	15	0	/	27.1	V-2
PLA-6	85	11.25	3.75	3:1	26.4	V-2
PLA-7	85	7.5	7.5	1:1	29.2	V-2
PLA-8	85	5	10	1:2	31.8	V-2
PLA-9	85	3.75	11.25	1:3	36.5	V-0
PLA-10	85	3	12	1:4	39.7	V-2
PLA-11	85	2.5	12.5	1:5	40.7	V-2
PLA-12	85	0	15	/	41.0	F

graphite is a potential physical and inorganic IFR element [11–14,27]. And a number of studies have suggested that the combination of APP and EG presented great fire-resisting effect [15–21]. However, few report have been published about the synergistic effect of APP and EG in PLA system. In this work, we introduced APP and EG into PLA to improve its flame retardant properties and efficiency. The flammability of the materials was evaluated via UL-94 tests, LOI tests and Cone calorimeter experiments. Thermal degradation behavior and char structure were investigated using thermo gravimetric analysis, scanning electron microscope and X-ray spectroscopy.

2. Experimentation

2.1. Materials

PLA resin (2002D) was purchased from Natureworks company, Ammonium polyphosphate ($n > 1000$) is offered by Hangzhou JLS Flame Retardant Chemical Company. Expanded graphite (Kp50) is supplied by Qingdao Tianhe Graphite Company. All materials were dried in vacuum oven at 80 °C for 24 h before use.

2.2. Preparation of flame retardant PLA samples

The flame retardant PLA composites were prepared on a Brabender mixer at the temperature of 180 °C at a roller speed of 50 rpm for 8 min. After mixing, the samples were hot-pressed at about 190 °C under 10 MPa for 5 min into sheets in the dimensions of 100.0 mm × 100.0 mm × 3.0 mm and then cut into suitable sample bars for LOI and UL-94 testing. The formulations of PLA samples are presented in Table 1.

2.3. Measurements

2.3.1. Scanning electron microscopy (SEM)

The char formed after LOI testing was first sputter-coated with a conductive layer, and then its surface morphology was observed by a TM-1000 Tabletop Scanning electron microscopy with a 15 kV accelerated voltage. And electron beam energy of 15 kV was used for the EDS spectra and maps.

2.3.2. Thermal gravimetric analysis (TGA)

Samples were examined under air flow on a METTLER TOLEDO TGA/DSC1 Analyzer, in a range from 30 °C to 800 °C at a heating rate of 10 °C/min.

2.3.3. X-ray photoelectron spectroscopy (XPS)

An AXIS UTLTRADLD Multifunctional X-ray Photoelectron Spectroscope was employed to investigate element migrations and chemical bond on the surface of samples.

2.3.4. Cone calorimeter

The cone tests were carried out in an FTT cone meter according to ISQ5660 under a heat flux of 35 kW/m^2. The sheets for the test are 100.0 mm × 100.0 mm × 3.0 mm in dimension. The data of PLA-12 was missing because it is too brittle to obtain an intact sheet for the test.

2.3.5. Flame retardancy tests

The Limited Oxygen Index was measured by a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM D2863. The specimens used for the test were 100.0 mm × 6.5 mm × 3.0 mm in dimension.

The UL-94 vertical tests were performed on an AG5100B vertical burning tester (Zhuhai Angui Testing Equipment Company, China). The specimens used were of 100.0 mm × 12.5 mm × 3.0 mm specimens.

3. Results and discussions

3.1. Flammability of PLA/APP/EG composites

Table 1 summarized the LOI values and UL-94 rating for the samples. According to the results, virgin PLA has a LOI of 22 and is flammable in nature. The LOI value of PLA with 15 wt% APP is 27.1 while the LOI value of 15 wt% EG-based PLA reaches 41. EG is more effective than APP at improving the LOI value of PLA. The LOI values of PLA/APP/EG composites are between LOI value of PLA/APP composite and PLA/EG composite, and increase rapidly

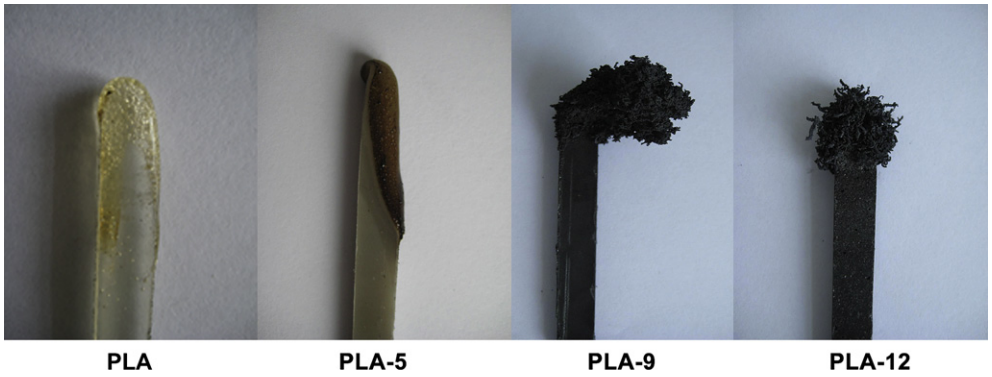

Fig. 1. Photographs of PLA specimens after LOI tests.