



Preparation of nucleotide-based microsphere and its application in intumescent flame retardant polypropylene



Zhijing Wang^{a,c}, Yinfeng Liu^c, Juan Li^{a,b,*}

^a Ningbo Key Laboratory of Polymer Materials, Institute of Materials Technology, Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, Ningbo, Zhejiang, 315201, PR China

^b University of Chinese Academy of Sciences, Beijing, 100049, PR China

^c School of Materials and Science Engineering, Shanghai University, Shanghai 200444, PR China

ARTICLE INFO

Article history:

Received 23 May 2016

Received in revised form 2 September 2016

Accepted 3 September 2016

Available online 4 September 2016

Keywords:

Nucleotide

Microsphere

Bio-based

Intumescent flame retardant

Polypropylene

ABSTRACT

The toxicity, environmental persistence and bio-accumulation of flame retardant additives have attracted a lot of attentions for several years. People try to develop perfect strategy to achieve green flame retardant materials. Bio-based flame retardants are one of the most environmentally friendly alternatives, but lots of natural resources are thermal unstable. Therefore, it is important and necessary to modify the performance of biological raw materials by using physical or chemical methods to meet the requirements of flame retardant materials. In this paper, biological element-nucleotide was embedded in the backbone of melamine formaldehyde resin to form a functional microsphere (MFA). The MFA was employed in polypropylene (PP)/intumescent flame retardant (IFR) system to modify its flame retardant performance. The flammability of PP composites was evaluated by using the limiting oxygen index (LOI) and UL-94 vertical burning tests etc. The results showed that PP composites containing 17 wt% IFR and 1 wt% MFA achieves a LOI value of 27.0 and passes the UL-94 V-0 rating, while no less than 25 wt% single IFR is needed to obtain the same UL-94 rating. Furthermore, the MFA delays the time to the peak heat release rate (PHRR) and decreases 65% for PHRR. This paper provides a novel approach for constructing a bio-based IFR system and opens another door for the applications of bio-resources in flame retardant materials meanwhile.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Flame retardant materials and technology was developed with the developing of polymer materials since the 1960s. Flame retardant additives, which contain halogen, phosphorus, nitrogen, silicon *etc.* were introduced into polymers by physical or chemical methods to modify their flammability. Nowadays, with the ever-increasing environmental protection awareness, some additives with potential pollution risk or secondary damage such as halogens and halogen derivatives are not welcomed to be applied in flame retardant materials for many fields. Because some of the current halogenated flame retardants have been proven to be persistent, bio-accumulative, carcinogenic and toxic for animals and humans [1–3].

With the deepening of the global green strategy, “from nature and to nature” is becoming one of the most necessary ways to achieve sustainable development of materials, so bio-based flame retardants is also becoming one of the best alternatives to realize the greenization of flame retardant materials. It is well known that the three elements of combustion are: flammable chemicals, combustion supporting materials and ignition source. Cutting off one or more than one elements will achieve flame retardancy of materials. It is based on this that all current flame retardants can work.

Among all flame retardants, intumescent flame retardant (IFR) is environmentally friendly and has caught the eye of researchers significantly [4–9]. Usually, the IFR system consists of three basic components: an acid source, a carbon source and a blowing agent. Only the three components of IFR react at a suitable time and temperature, can a consistent and intumescent char layer be formed, which could prevent the polymer matrix from combustion effectively. Therefore, the key factor for IFR is the char, including its porous structure, quality, forming speed *etc.* Researchers have developed novel IFR system, charring agent or using catalyst or synergist to improve the flame retardant efficiency and achieved great progress [10–13]. In fact, many natural resources, for

* Corresponding author at: Ningbo Key Laboratory of Polymer Materials, Institute of Materials Technology, Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, Ningbo, Zhejiang, 315201, PR China.

E-mail address: lijuan@nimte.ac.cn (J. Li).

example, polysaccharides [14], starch [15], chitin [16], cyclodextrin [17], etc., have been used as carbon source in IFR system due to their polyhydroxy structure which is easy to form char by dehydration during combustion. However, the natural materials that can be used as acid source and blowing agent are hard to be developed, only a limited kinds are tried such as phytic acid [18], casein [19] and deoxyribonucleic acid (DNA) [20]. Moreover, thermal stability of these natural resources is not good enough to be used in many fields. So they can only be used in limited fields that do not need process at high temperature, for example coating, adhesive etc.

DNA is an important bio-macromolecule in the life. It consists of phosphate group, pentose and nitrogen-containing bases. The phosphate can be used as acid source, pentose as carbon source and nitrogen-containing base as blowing agent of IFR. So DNA is a natural IFR which containing the three components in one molecule. Jenny Alongi et al., [21–24] used DNA as IFR to enhance the flame retardant properties of cotton fabrics and ethylene vinyl acetate copolymer. Rick D. Davis et al., [25] researched the flame retardant effect of blend of DNA, chitosan and clay on polyurethane. Improved flame retardancy for these materials was achieved. However, DNA is thermal unstable as most of the natural resources which has 10 wt% weight loss at 171 °C [20]. So it cannot meet the melt processing requirement of most polymer materials. Moreover, the price of DNA is so expensive, about 3 orders of magnitude higher than that of commercial IFR, that it is hard to be applied in common polymer materials.

It is well known that polymer materials obtained a boom because the synthetic technology overcame shortcomings of natural polymers. Maybe natural materials can become good flame retardants if they are modified by chemical methods. We focus on the nucleotide because it is not only the basic unit of DNA and ribonucleic acid (RNA) but also cheaper than DNA. Moreover, nucleotide contains amino or hydroxyl groups, which provide a broad space for subsequent modification. But as mentioned above its thermal performance is poor which must be modified firstly. Melamine formaldehyde (MF) resin is prepared via the reactions between amino of melamine and aldehyde group, and it has good flame retardancy itself. Then it is possible to combine nucleotide and MF into one molecular by using the reactions between amino or hydroxyl and MF, thus the covalent bond between MF and nucleotide can modify the thermal performance of nucleotide and turn it into a suitable flame retardant for polymers.

Based on the background, adenosine monophosphate (AMP) was chosen as a unit for IFR in this paper. It was embedded in the backbone of MF resin to form a functional microsphere (MFA). The MFA was used in polypropylene (PP) to improve its flame retardancy. Because the three components of IFR in MFA is fixed and the content of phosphate group in MFA is low, it was used with commercial IFRs to regulate the right ratio of acid, carbon and blowing source. The used IFR is a mixture of ammonium polyphosphate (APP) and pentaerythritol (PER) at a weight ratio 3/1. Thermogravimetric analysis (TGA), limiting oxygen index (LOI) and UL-94 vertical burning tests were carried out to assess the thermal properties and flame retardancy of PP composites. In addition, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy was used to observe the morphology of the MFA and the char layers. Moreover, cone calorimeter was carried out to study the combustion characteristics of PP composites.

2. Experimental section

2.1. Materials

APP ($n > 1500$, Preniphor TMEPFR-APP231) was provided by Pre-safer Phosphor Chemical Co. Ltd. PER was provided by Aladdin

Industrial Inc. (Shanghai, China). Melamine and formaldehyde were purchased from Sinopharm Chemical Reagent Co. Ltd. AMP was purchased from Hubei Jusheng Technology Co. Ltd. PP (F401) was provided by Yangzi Oil Co. Ltd with a melt index of 2.0 g/10 min. All reagents were used without further purification.

2.2. Preparation of MFA

0.2 mol melamine and 250 ml deionized water were injected into a three-neck flask equipped with a stirrer. The pH value of the solution was maintained to 8–9 by sodium hydroxide. Then the mixture was heated up to 70 °C and 0.6 mol formaldehyde aqueous solution (37 wt%) was added into the mixture. When the solution became transparent, the MF precondensate was obtained. 0.2 mol AMP and 150 ml deionized water were added into another three-neck flask equipped with a stirrer, condenser, and pressure funnel and 20 ml PVA solution (1 wt%) was added into the same flask. The solution was stirred at 80 °C for 2 h. Then, the MF precondensate was added dropwise to the AMP solution. The pH value of the solution was maintained to 4–5 by formic acid. Keep the mixtures stirring at 80 °C for 5 h. Then, the mixture was cooled to room temperature, filtered and washed with deionized water for 3 times. Then the MFA microsphere was obtained. The possible reactions are listed in Scheme 1, R can be R1 or R2, and the preparation process of MFA microsphere is shown in Scheme 2.

2.3. Preparation of flame retardant PP composites

All raw materials were dried in a vacuum oven at 80 °C for 12 h before using. The PP composites were prepared by melt-blending on a Brabender mixer at 200 °C with rotor speed of 50 rpm, and the processing time was 10 min. Then the PP composites were hot pressed into a 100 × 100 × 3.2 mm³ plate at 200 °C under 10 MPa for 5 min, and then cut into bars with suitable size for the LOI and UL-94 testing. The formulations of the composites are given in Table 1.

2.4. Characterization

Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded by a Nicolet 6700 FTIR spectrophotometer using the KBr disk.

TGA was carried by a TGA/DSC1 Analyzer (METTLER TOLEDO International Inc., Switzerland). About 3.0–5.0 mg sample was put in an alumina crucible at a heating rate of 10 °C/min in nitrogen or air atmosphere at the temperature range from 50 °C to 800 °C.

UL-94 vertical burning performance was measured on an AG5100 B vertical burning tester (Zhuhai Angui Testing Instrument Co. Ltd., China). The specimens dimension is 100 × 13 × 3.2 mm³ according to ASTM D3801.

LOI values were tested on a 5801 digital oxygen index analyzer (Kunshan Yangyi Testing Instrument Co. Ltd., China) according to ASTM D2863–97; the dimension of samples is 100 × 6.5 × 3.2 mm³.

Combustion behaviors were investigated by means of cone calorimeter (Fire Testing Technology Co. Ltd., U.K.). The samples with a dimension of 100 × 100 × 3.2 mm³ were placed on a holder and irradiated at a heat flux of 35 kW/m² in horizontal configuration.

Morphology of the residual char and MFA was observed by a SEM (S4800 Hitachi Corp., Japan) after being sputter-coated with a conductive gold layer. The element of MFA was measured by an EDX spectrometer.

Download English Version:

<https://daneshyari.com/en/article/5134742>

Download Persian Version:

<https://daneshyari.com/article/5134742>

[Daneshyari.com](https://daneshyari.com)