Journal of Analytical and Applied Pyrolysis xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Thermal degradation properties of biobased iron alginate film

Yun Liu [a,*], Jun-Sheng Wang [b], Ping Zhu [a,*], Jin-Chao Zhao [a], Chuan-Jie Zhang [a], Yi Guo [a], Li Cui [a]

[a] College of Chemistry and Chemical Engineering, Hubei Biomass Fibers and Eco-dyeing & Finishing Key Laboratory, State Key Laboratory of New Textile Materials and Advanced Processing Technologies, Wuhan Textile University, Wuhan 430073, China
[b] Tianjin Fire Research Institute of the Ministry of Public Security, Tianjin 300381, China

ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form 16 March 2016
Accepted 18 March 2016
Available online xxx

Keywords:
Iron alginate
MCC
Py-GC–MS
TG-FTIR–MS
Thermal degradation mechanism

ABSTRACT

The flame retardancy and pyrolysis behavior of iron alginate were investigated by a microscale combustion calorimeter (MCC), a thermogravimetric analyzer which was coupled with a Fourier transform infrared spectroscopy and a mass spectrometry (TGA-FTIR–MS), and a pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS), respectively. Large differences in the flame retardancy and pyrolysis behavior were observed from the MCC and Py-GC–MS results of iron alginate and sodium alginate. The MCC results showed that iron ions seriously reduced the value of peak heat release rate (PHRR) of alginate at lower temperature. TGA-FTIR–MS and Py-GC–MS results indicated that iron ions influenced the devolatilisation products upon pyrolysis process. The pyrolysis of iron alginate was found to yield much less gaseous products than sodium alginate. And it was suggested that the iron ions strongly catalyzed alginate to produce H_2O, CO_2 and other gaseous compounds which owned lower combustion heat values, resulting in the improvement of flame retardancy for iron alginate. On the basis of the results of TG-FTIR–MS and Py-GC–MS of iron alginate, the possible thermal degradation mechanism of iron alginate was proposed. The results obtained from this study might supply useful message for comprehending the flame retardant mechanism of alginates.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the last few decades, polysaccharides, a kind of biobased materials, have been thriving in popularity and increasing researchers are taking interest in them [1]. Cellulose and chitin, which are the most abundant polysaccharides, are not soluble in water and most of organic solvents [2]. While alginate, a kind of polysaccharide, is readily water-soluble and regarded as one of desirable candidates for wet spinning [2]. Alginate is derived from algae [3,4]. And it is a linear co-polymer, and comprised of α-1, 4-L-guluronate (G) and β-1, 4-D-mannuronate (M) repeating monomeric units, which arrange in an anomalous structure of changing proportions of MM, MG, GG and blocks [5–7]. The alginate has ion-exchanger roles [8]. Alginate gelation takes place when divalent or trivalent cations interact with blocks of G residues [9], producing the so-called "egg-box" structure [10,11]. Alginate has increasing industrial used fields, such as in the textile printing field, paper field, food field, drug formulations and wound dressings [12,13].

It has been known that alginate fibers and films have flame retardant properties without any addition of other flame ratardants [14–20]. Xia et al. [15,16] and Zhu et al. [17–21] have investigated the effects of divalent and trivalent metal cations on the flame retardant properties, thermal degradation properties and pyrolysis properties of alginate fibers and films. The results indicated that divalent and trivalent metal ions improved the flame retardancy of alginate fibers and films, and that the addition of divalent metal ions and aluminum ions reduced the type of pyrolysis products of alginates. However, the effect of Fe^{3+} on the thermal degradation mechanism of alginate was also not investigated in detail. Zaafarany [22] has studied the non-isothermal degradation of Fe, Cr and Al cross-linked trivalent metal-alginate complexes using thermogravimetry (TG) techniques in static air, and the results revealed the formation of metal hydroxide, oxalate and carbonate for Al^{3+}, Cr^{3+} and Fe^{3+}-alginate complexes, which were followed by degradation of these intermediate fragments to the corresponding metal oxides as the final products; however, Zaafarany did not investigate the effects of trivalent cations on the pyrolysis process of alginate.

* Corresponding authors.
E-mail addresses: liuyun0215@126.com (Y. Liu), pzhu99@163.com (P. Zhu).

http://dx.doi.org/10.1016/j.jaap.2016.03.014
0165-2370/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: Y. Liu, et al., Thermal degradation properties of biobased iron alginate film, J. Anal. Appl. Pyrol. (2016), http://dx.doi.org/10.1016/j.jaap.2016.03.014

Table 1
Data obtained from the MCC parameters of iron alginate.

Sample	$PHRR_1$ (W/g)	T_{PHRR1} (°C)	$PHRR_2$ (W/g)	T_{PHRR2} (°C)	Residues (%)
Iron alginate	15.5	135	29.6	219	28.2
Sodium alginate	105.0	230	31.4	453	47.4

In our previous work [20], the flame retardant properties, thermal degradation properties of trivalent metal-alginate films, including aluminum alginate and iron alginate, have been reported; however, the pyrolysis mechanism of iron alginate is not included. And in another our previous work [18], the pyrolysis behavior and mechanism of aluminum alginate have been reported. The results indicated that the addition of aluminum ions changed the thermal degradation process, producing fewer pyrolysis products. Does the addition of iron ions take the same effect on the pyrolysis properties? Understanding the effect of iron ions on the thermal degradation of alginate during pyrolysis is useful for well understanding the flame retardant mechanism of alginate. The purpose of this research is to extend the previous work to explore the effects of iron ions on the pyrolysis process and the pyrolysis mechanism of alginate, further to investigate the flame retardant mechanism of trivalent metal alginates.

In the present work, the flame retardant properties and pyrolysis behaviors of iron alginate were studied by microscale combustion calorimeter (MCC), a thermogravimetric analyzer which was coupled with a Fourier transform infrared spectroscopy and a mass spectrometry (TGA-FTIR–MS), and a pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS), and the effect of iron ions on the pyrolysis process and pyrolysis mechanism of iron alginate were proposed on the basis of the results of TG-FTIR-MS and Py-GC–MS.

2. Experimental

2.1. Materials

Sodium alginate powder (M_n = 357,475, M_n/M_w = 1.392, M/G = 0.32) was purchased from Qingdao Mingyue Co. Ltd (China), and used as-received. Iron chloride was supplied by Sinopharm Chemical Reagent Co., Ltd. (China), and was an analytical reagent.

2.2. Preparation of iron alginate

Sodium alginate aqueous solutions (5 wt%) were prepared in a beaker with a vigorous stirrer for 4 h. Then the obtained solution was cast into a sheet with suitable thickness and size, and dried under room temperature for 3 d. When they were dried, the films were removed and immersed in iron chloride aqueous solutions (5 mol/L) for 2 h. After coagulation, the films were washed in order to take the unreacted iron chloride away. And then the film was put into a vacuum drying for 24 h.

The limiting oxygen index (LOI) value of iron alginate film was 35.3%, and the UL-94 rating was V-0 rating [20].

2.3. Measurements

2.3.1. Microscale combustion calorimeter

The microscale combustion calorimeter (MCC) measurement was carried out by an micro-scale combustion calorimeter (Govmak MCC-2) on the basis of ASTM D7309-2007. 5 ± 0.1 mg of samples was heated to 750 °C in nitrogen with a flowing rate of 80 mL/min, and the heating rate was set to be 1 °C/s. The anaerobic and volatile pyrolysis products in the nitrogen gas stream were blended with a 20 mL/min stream of oxygen before entering a 900 °C combustor. Each sample was carried out in three replicates, and the reproducibility was ± 5%.

2.3.2. Thermogravimetric analyzer-Fourier transform infrared spectroscopy–mass spectrometry

A thermogravimetric analyzer (NETZSCH TG 449C, Germany) coupled with a Fourier transform infrared spectroscopy (Bruker Tensosr 27 FTIR, Germany) and a mass spectrometry (NETZSCH QMS 403C, Germany) (TG-FTIR–MS) was utilized to study the thermal stability of iron alginate and the formation of volatiles produced in the thermal degradation process. About 10 mg iron alginate was put into the furnace and heated with a heating rate of 10 °C/min from room temperature to 800 °C with a nitrogen flowing rate of 100 mL/min. The FTIR instrument was linked to the TG instrument through a stainless pipe and a flow cell. And the pipe and cell were preheated to 180 °C to prevent the evolved gases from condensing. Through the FTIR real-time tracking on the gases produced in the thermal degradation process, the spectra for volatile evolution during iron alginate thermal degradation process were recorded by the FTIR real-time tracking mode. The scanning range was from 4000 to 400 cm^{-1}. A mass spectrometer was connected to the thermobalance to detect the gaseous compounds produced during thermal degradation process. The gas ionization was carried out at 100 eV.

TGA of iron alginate was carried out in duplicate. The mass was reproducible to within ± 0.1%, and the temperature of the instrument was reproducible to within ± 1 °C.

2.3.3. Pyrolysis-gas chromatography–mass spectrometry

The fast pyrolysis analyzer (CDS5200) was connected with gas chromatography-mass spectrometry Systems (Py-GC–MS) (PerkinElmer Clarus680GC-SQ8MS) to study the formation of volatiles from iron alginate fast pyrolysis process against chemical reaction temperature, and the carrier gas was He, about 300 μg of iron alginate was placed into the pyrolysis tube. The pyrolysis temperature of the furnace was 700 °C, and the flash heating rate was 20 °C/ms. The remaining time for the sample was set to be 15 s, to make most of the solid sample pyrolyzed. The gaseous compounds produced in the pyrolysis process were identified by GC–MS. The conditions for GC–MS test were as follows: the chromatographic separation was carried out using a 0.25 mm HP-5 capillary column; the temperature of the chromatographic column was set to be from 40 °C (3 min) to 280 °C (5 min) with a heating rate of 10 °C/min; the injector temperature was maintained at 280 °C; the mass spectra were performed in electron ionization (EI) mode at 70 eV. The yields of the gaseous compounds were determined by means of the characterized GC–MS spectrums, on the basis of the database from NIST library.

3. Results and discussion

3.1. Microscale combustion calorimetry

Microscale combustion calorimetry (MCC), which is a kind of pyrolysis-combustion flow calorimetry, has dynamic capability to investigate heat release rate (HRR); what is more, MCC uses a few milligram sizes to avoid the samples preparation problems faced for cone calorimetry [23,24]. The HRR curve of iron alginate and sodium alginate as a function of temperature is shown in Fig. 1, and the data

Please cite this article in press as: Y. Liu, et al., Thermal degradation properties of biobased iron alginate film, J. Anal. Appl. Pyrol. (2016), http://dx.doi.org/10.1016/j.jaap.2016.03.014

Download English Version:

https://daneshyari.com/en/article/7606575

Download Persian Version:

https://daneshyari.com/article/7606575

Daneshyari.com