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Bio-based barium alginate film: Preparation, flame retardancy and thermal degradation behavior

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

[a] Hubei Biomass Fibers and Eco-dyeing & Finishing Key Laboratory, College of Chemistry and Chemical Engineering, State Key Laboratory of New Textile Materials and Advanced Processing Technologies, Wuhan Textile University, Fangzhi Road, 1, Wuhan 430073, China
[b] IMDEA Materials Institute, C/Eric Kandel, 2, Getafe, Madrid 28906, Spain

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ABSTRACT

A bio-based barium alginate film was prepared via a facile ionic exchange and casting approach. Its flammability, thermal degradation and pyrolysis behaviors, thermal degradation mechanism were studied systemically by limiting oxygen index (LOI), vertical burning (UL-94), microscale combustion calorimetry (MCC), thermogravimetric analysis (TGA) coupled with Fourier transform infrared analysis (FTIR) and pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS). It showed that barium alginate film had much higher LOI value (52.0%) than that of sodium alginate film (24.5%). Moreover, barium alginate film passed the UL-94 V-0 rating, while the sodium alginate film showed no classification. Importantly, peak of heat release rate (PHRR) of barium alginate film in MCC test was much lower than that of sodium alginate film, suggested that introduction of barium ion into alginate film significantly decreased release of combustible gases. TG-FTIR and Py-GC–MS results indicated that barium alginate produced much less flammable products than that of sodium alginate in whole thermal degradation procedure. Finally, a possible degradation mechanism of barium alginate had been proposed.

1. Introduction

The energy crisis and the increasing global warming have urged human beings to look for novel types of energy instead of petroleum-based energy (Li, Chen, Zhang, Ye, & Xing, 2011). Biomass is more sustainable than fossil-based materials, and the use of it can reduce the emission of CO_2 (Ross, Anastasakis, Kubachi, & Jones, 2009). Recent interest in alternative sources of biomass as a potential feedstock had included the development of alginate (Ross et al., 2011). Alginate is a kind of biomass extracted from algae (Pathak, Yun, Lee, Baek, & Paeng, 2009), and it is a linear copolymer of β-1,4-D-mannuronate (*M*) and α-1,4-L-guluronate (*G*) repeating monomeric units. Sodium alginate, a kind of alginic salt, is soluble in water, forming very viscous solution or jellies which depend on their physical properties (Tod, 1946; Chen, Wang, Sánchezsoto, & Schiraldi, 2012). Gelation of alginate may happen by the interaction between carboxylate groups and divalent or trivalent metal ion in aqueous solution, forming strong, rigid and ordered structures, the hydrogels (Papageorgiou et al., 2010; Atkins, Nieduszynski, Mackie, Parker, & Smolko, 1973). Alginate has many industrial uses in food industry, textile printing industry, paper industry, wound dressings and drug formulation (Ross et al., 2011; Qin, 2008).

Due to its water solubility, alginate was a desirable candidate for aqueous processing (Shen & Hsieh, 2014). Alginate fibers have been produced through wet-spinning process according to the gelation properties of alginate (Qin, 2008). Calcium alginate fibers, barium alginate fibers, copper alginate fibers and zinc alginate fibers owned good flame retardant properties without any addition of other flame retardants (Zhang, Zhang, Wang, & Zhu, 2011a; Zhang et al., 2011b; Zhang, Ji, Wang, Tan, & Xia, 2012; Kong et al., 2009). The effects of these divalent metal ion on the flame retardant properties, thermal properties of alginate fiber were investigated by Xia et al. (Zhang et al., 2011a, 2011b, 2012) and Zhu et al. (Zhang et al., 2011a, 2011b; Liu, Zhao, Zhang, Ji, & Zhu, 2014a). The results indicated that the addition of divalent metal ion improved the flame retardant properties of alginate fibers. However, flame retardancy of functional alginate film and its pyrolysis mechanism have not been investigated yet.

The aim of the present research is to extend our previous work to explore the effects of barium ion on the flame retardant properties, thermal stabilities, thermal oxidative degradation properties,

* Corresponding author. Tel.: +86 27 5936 7672.
** Corresponding author. Tel.: +34 917871888.
E-mail addresses: pzhu99@163.com (P. Zhu), deyi.wang@imdea.org (D.-Y. Wang).

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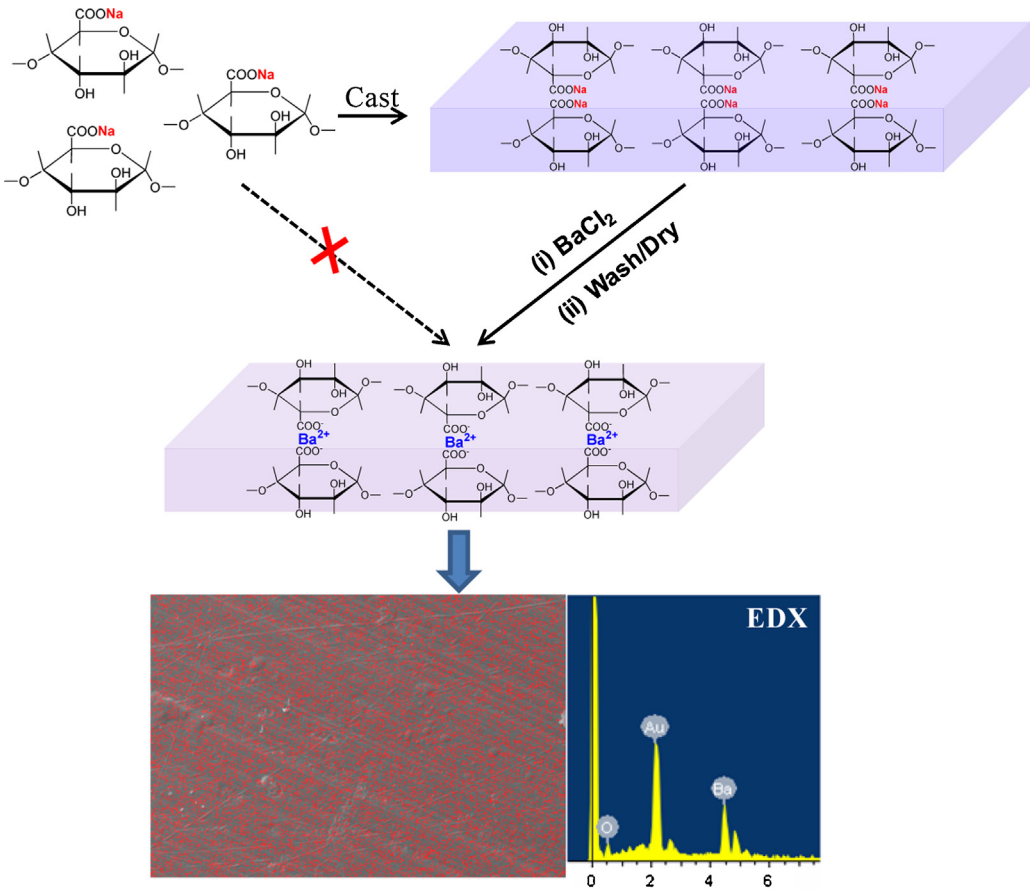

Scheme 1. Schematic illustration of preparation and characterization of barium alginate film.

pyrolysis properties and thermal degradation mechanism of alginate film in more detail, further to investigate the flame retardant mechanism of barium alginate. In the present work, the flame retardancy, thermal degradation, thermal oxidative degradation and pyrolysis properties of barium alginate film were studied by limiting oxygen index (LOI), vertical burning (UL-94), microscale combustion calorimetry (MCC), thermogravimetric analysis (TGA) coupled with Fourier transform infrared analysis (TG-FTIR) and pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS). The thermal degradation mechanism of barium alginate was proposed according to TG-FTIR and Py-GC–MS techniques. These results would be helpful to optimize the properties of alginate-based films and understand the fire behavior of alginates, leading to the development of high performance alginate-based materials. These high flame retardant performance alginate-based materials may be used in textile and packaging industry in the future.

2. Experiment section

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. (Qingdao, China), and used as received. Barium chloride was supplied by Sinopharm Chemical Reagent Co., Ltd (Wuhan, China), and was of analytical reagent.

2.2. Preparation and characterization of barium alginate film

The concentration of sodium alginate in aqueous solution was 5 wt% and the aqueous solution was stirred at room temperature for 4 h. Then the solution was cast into a sheet of suitable thickness and size according to LOI and UL-94 tests standard and air-dried at room temperature for over 3 d. After being dried, the film was immersed in 5 mol/L barium chloride aqueous solution for 2 h. After coagulation, the prepared film was washed using deionized water to remove the unreacted barium ion. And the obtained film was subjected to vacuum drying for 24 h before measurements. The thickness of the film was 2.0 ± 0.2 mm.

The preparation precess and energy dispersive X-ray spectroscopy (EDX) characterization of barium alginate film was shown in Scheme 1. The result of EDX indicated that barium ion was dispersed uniformly in the film, and barium alginate film could be prepared successfully through the facile ionic exchange and casting approach.

2.3. Measurements

2.3.1. LOI

The LOI value was carried out by an XZT-100A oxygen index meter (Chengde, China), and the sheet dimension of samples was 130 mm × 6.5 mm × 2.0 mm according to ASTM D2863-97.

2.3.2. UL-94

Vertical burning test was measured by a vertical burning test instrument (CZF-2-type) (Jiangning, China), and the sheet dimension of samples was 130 mm × 13 mm × 2.0 mm according to ASTM D3801.

2.3.3. TGA

Thermogravimetric analysis (TGA) was investigated on a SDTQ600 Instruments (TA Instruments Co., USA)