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Bio-based calcium alginate nonwoven fabrics: Flame retardant and thermal degradation properties

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ABSTRACT

Alginate fibers, which are bio-based fibers, are one of inherently flame retardant materials. What about flame retardancy of calcium alginate nonwoven fabric made from alginate fibers? In order to resolve this question, the flame retardancy and surface morphology of char residues for viscose nonwoven fabric and calcium alginate nonwoven fabric were performed by vertical burning (UL-94), cone calorimeter (cone), and scanning electron microscopy (SEM). Thermal degradation properties and thermal degradation mechanism were also explored by thermogravimetric analysis coupled with Fourier transform infrared analysis (TG-FTIR) and pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS). Compared with viscose nonwoven fabric, calcium alginate nonwoven fabric passed UL-94 V-0 rating. Importantly, peak heat release rate (PHRR) and total heat release (THR) of calcium alginate nonwoven fabric were much lower than those of viscose nonwoven fabric, suggesting calcium alginate nonwoven fabric has much better flame retardancy. Py-GC–MS and TG-FTIR results revealed that calcium alginate nonwoven fabric released much less flammable gaseous products. At the end, on the basis of TG-FTIR and Py-GC–MS results, a proposed thermal degradation mechanism of calcium alginate nonwoven fabric had been put forward. The results obtained in this study provided useful information for designing bio-based fabrics with excellent flame retardancies.

1. Introduction

During the past decades, increasing researchers have been taking interest in polysaccharides because of resources and oil crisis [1–3]. Alginate is one of water-soluble polysaccharides and recognized as a kind of preferable candidates for wet spinning [4–6]. Alginates can be used as spinning materials and alginate fibers are bio-based fibers produced by wet spinning of sodium alginate aqueous solution into calcium chloride coagulating bath. More and more researchers are focusing on the preparation and application of alginate fibers as textile materials, because of their excellent biocompatibility, degradation, non-toxicity and intrinsical flame retardancy [7–9]. What is more, the spinning process of alginate fiber is green and environmental.

In the last decade, many papers [10–22] have reported that alginate fibers, films and foams have intrinsical flame retardancy with no extra addition of flame retardants. Zhu et al. [14–21] and Xia et al. [10–13] have studied the influence of divalent and trivalent metal ions on flame retardant, thermal stability properties and pyrolysis properties of alginate fibers and films. Zaafarany [23] had investigated the non-isothermal degradation of trivalent metal-alginate complexes. The obtained results showed that some divalent and trivalent metal ions had enhanced the flame retardant properties, and that reduced the type of pyrolysis gaseous compounds of alginates, resulting in enhancement of flame retardant properties for alginates.

Xia et al. [10] had investigated flame retardant and pyrolysis properties of calcium alginate fiber; and the proposed thermal degradation mechanism of calcium alginate was put forward on the basis of the pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS) results obtained at different temperature. Calcium alginate fibers were one of intrinsically bio-based flame retardant materials. What about flame retardancy of calcium alginate nonwoven fabric? Thermogravimetric analysis coupled with Fourier transform infrared analysis (TG-FTIR) and Py-GC–MS are two out-

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standing means to explore thermal degradation characteristics and evolved products during pyrolysis process [24]. What is the constitution of gaseous products in the thermal degradation process of calcium alginate? And what is the possible thermal degradation mechanism of calcium alginate according to results of TG-FTIR and Py-GC–MS?

In order to solve these questions mentioned above, in this work, the flammability and surface morphology of char residues for viscose nonwoven fabric and calcium alginate nonwoven fabric were performed by scanning electron microscopy (SEM), cone calorimeter (cone) and vertical burning (UL-94). The thermal degradation properties and thermal degradation mechanism were explored by TG-FTIR and Py-GC–MS. And the influence of calcium ions on the pyrolysis process and thermal degradation mechanism of calcium alginate were put forward according to the results of TG-FTIR and Py-GC–MS. The aim of this study is to broaden the previous work to investigate the proposed thermal degradation mechanism of calcium alginate, further to explore the proposed flame retardant mechanism of calcium alginate.

2. Experimental

2.1. Materials

Calcium alginate nonwoven fabric and viscose nonwoven fabric were purchased from Qingdao Huajin Co. Ltd. (Qingdao, China).

2.2. Measurements

2.2.1. Cone calorimeter test

According to the procedures in ISO 5660-1, combustion properties of calcium alginate nonwoven fabric and viscose nonwoven fabric were examined by a cone calorimeter (Fire Testing Technology, UK). Specimens (100 mm × 100 mm × 12 mm) were laid into an aluminum foil and irradiated horizontally, and the heat flux was set to be 35 kW/m^2. Each sample was conducted in three times.

2.2.2. TG-FTIR

TG-FTIR test was carried out using a TG analyzer (Perkin-Elmer STA 6000), which was coupled with a Fourier transform infrared spectrometer (Perkin-Elmer Frontier FTIR), and FTIR was outfitted with a gas cell. Gaseous compounds formed during the thermal degradation process of calcium alginate nonwoven fabric were directly collected and analyzed immediately by the FTIR spectrometer. 10 ± 0.2 mg of calcium alginate nonwoven fabric was heated from room temperature to 700 °C in nitrogen atmosphere with a heating rate of 10 °C/min, and the flow rate of nitrogen was set to be 50 mL/min. The FTIR spectrometer and TG instrument were connected with a stainless pipe. Before doing the TG-FTIR test, the stainless steel pipe and gas cell were heated to 280 °C, minimizing secondary reactions and tar condensation. The spectral range and resolution factor of FTIR spectrometer were from 4000 to 450 cm^{-1} and 2 cm^{-1}, respectively.

2.2.3. SEM

Surface morphologies of viscose nonwoven fabric and calcium alginate nonwoven fabric before and after vertical burning test (UL-94) were studied by a scanning electron microscopy (SEM) (PHENOM-Pro, Holland), respectively. The sample surface was coated with a gold layer before SEM test.

2.2.4. Vertical burning (UL-94)

Vertical burning test (UL-94) was performed using a vertical burning test instrument (CZF-2-type) (Jiangning, China), and the sheet dimensions of the sample were 300 mm × 80 mm on the basis of GB/T 5455-1997 standard.

2.2.5. Pyrolysis-Gas Chromatography-Mass Spectrometry

A fast pyrolysis instrument (CDS5200) was coupled with a gas chromatography-mass spectrometry system (Py-GC–MS) (Perkin Elmer Clarus680GC-SQ8MS) to examine the volatiles formation of calcium alginate nonwoven fabric in the fast pyrolysis process. About 300 μg of calcium alginate nonwoven fabric was put into the pyrolysis tube, and the carrier gas was He. The pyrolysis temperature of the furnace was 700 °C, and the heating rate was 20 °C/ms. In order to make the solid sample completely pyrolyzed, the sample was stayed at 700 °C for 15 s after the furnace arrived at 700 °C. The pyrolysis volatiles were investigated by GC–MS. Experimental conditions were set as follows: the chromatographic separation was achieved by a 0.25 mm HP-5 capillary column; temperature of the chromatographic column was from room temperature (remaining for 3 min) to 280 °C (remaining for 5 min), and the heating rate was 10 °C/min; the injector temperature was 280 °C; the mass spectra were carried out in electron ionization (EI) mode at 70 eV. The structures and yields of the volatiles were obtained according to the database from NIST library.

2.2.6. LOI

Limiting oxygen index (LOI) test was carried out on a digital display oxygen index instrument (JF-3, Jiangning, China), and the sheet dimensions of the sample were 150 mm × 58 mm on the basis of GB/T 5454-1997.

3. Results and discussion

3.1. Flammability of calcium alginate nonwoven fabric

3.1.1. UL-94

In order to investigate flame retardant properties of calcium alginate nonwoven fabric, vertical burning (UL-94) and limiting oxygen index (LOI) tests were carried out; and flame retardant properties of viscose nonwoven fabric was also explored. UL-94 and LOI results are depicted in Table 1, and digital (a, b) and scanning electron microscopy (SEM) (A, B, C and D) photographs of calcium alginate nonwoven fabric (a, A and B) and viscose nonwoven fabric (b, C and D) before (A, C) and after (B, D) UL-94 test were presented in Fig. 1. It was noted that the LOI value of calcium alginate nonwoven fabric was 49.9, which was much higher than that of viscose nonwoven fabric, 20.9. The afterflame time and afterglow time of viscose nonwoven fabric were 34 and 105 s, respectively, until viscose nonwoven fabric burned out completely. UL-94 results indicated that viscose nonwoven fabric was totally destroyed. However, the afterflame time and afterglow time of calcium alginate nonwoven fabric were 0 and 8 s, respectively, and the damaged length was 25 mm, which was much shorter than that of viscose nonwoven fabric. The results mentioned above demonstrated that flame retardancy of calcium alginate nonwoven fabric was much better than that of viscose nonwoven fabric. From Fig. 1, it can be observed that there was almost no char residue left for viscose nonwoven fabric after burning, while there was more char residue remaining for calcium alginate nonwoven fabric. The shape of viscose fibers was kept after burning, while the diameter of viscose fibers was shorter than that before burning. And the shape of calcium alginate fibers was kept after burning, while the length of calcium alginate fibers was shorter than that before burning. This indicated that calcium alginate fibers were destroyed during combustion, and this may result from the fragile char residue formed in the burning process. The formed char residue contained organic