

Flame retardancy and thermal properties of lanthanum alginate

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Abstract: The lanthanum alginate (Alg-La) and sodium alginate (Alg-Na) film were prepared via wet coating and confirmed by FTIR. The flame retardancy and thermal degradation of films were investigated by microscale combustion calorimetry (MCC) and thermogravimetric analysis (TG). The MCC results indicated that the addition of rare earth ions mainly reduced the release of combustible gaseous products at lower temperatures and thus reduced the HRR values of Alg-La. The results of TG showed that the thermal stabilities of Alg-La were better than Alg-Na, and the weight of residual char was higher than Alg-Na at higher temperatures. Scanning electron microscopy (SEM) images of the residues indicated that the Alg-La film produced denser than Alg-Na film did. The La^{3+} exhibit a significant effect on the thermal degradation behavior of alginate. The results obtained from this study presented some beneficial message for comprehending the flame retardancy mechanism of alginate and designing biomaterials with better flame retardant properties.

Keywords Alg-La; Alg-Na; film; thermal degradation; flame retardancy

INTRODUCTION

Alginate is a kind of biological polysaccharides extracted from brown algae, which is a linear copolymer with the repeating monomeric units of β -1, 4-D-mannuronate (M) and α -1, 4-L-guluronate (G) [Ashby et al.]. It is an essential flame retardant material which can be applied in food industry, wound dressing and textile industry, because of its better flame retardancy, biocompatibility and non-toxicity. Noticeably, Xia et al. has proposed the flame retardancy mechanism of metal ion in biologic material (alginate, cellulose and chitosan) [Li et al., 2017, Shi et al., 2017, Zhang et al., 2011, Zhang et al., 2016].

Alginate gelation takes place when divalent or trivalent cations interact with blocks of G residues, producing the so-called “egg-box” structure. It was confirmed that alginate fibers with divalent or trivalent metal ion possess excellent flame retardancy [Liu et al., 2016, Liu et al., 2015, Yun et al., 2015, Zhang et al., 2012].

The rare earth metals, including 17 chemical elements, have excellent magnetic, optical, and electrical properties, which play an important role in improving product performance, increasing product variety and production efficiency. Since a very small amount can play a big role, they have become an important class of elements for improving product structure, increasing scientific and technological content, and promoting technological progress. They has been widely used in fields such as metallurgy, military, petrochemicals, advanced ceramic, agriculture and advanced materials. So it has been described as the vitamin of industry [Charalampides

et al., 2015, Garai and Karmakar, 2016, Verma et al., 2018].

In the previous research, rare earth metal ions being used to improve the flame retardancy of materials has been reported [Cai et al., 2013, Lili et al., 2012, Shen et al., 2012, Wei et al., 2013]. However, the flame retardancy and thermal pyrolysis properties of the rare earth metal ions crosslinked alginate film has not been investigated in detail. In this work, the flame retardancy and thermal properties of Alg-La film was studied by microscale combustion calorimeter (MCC) and thermogravimetric analysis (TG). This work aims to explore and propose the rare earth metal ions retardant mechanism in alginate film, and further to consummate the flame retardancy mechanism of metal alginate.

EXPERIMENTAL

Materials

Sodium alginate powder (G/M=1.4) were provided by Qingdao sea forest biological technology Co., Ltd. (Shandong, China) and used as received. Lanthanum chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$), was purchased from Aladdin and used directly without prior treatment. Absolute ethyl alcohol was obtained from Sinopharm Chemical Reagent Co., Ltd.

Film preparation

Based on the wet-spinning, the film preparation adopted wet-coating method. First of all, the sodium powder was added to deionized water to get 4 wt% aqueous solution. Secondly, 5 wt% of lanthanum chloride was prepared. And 200ml of the above salt

solution were poured into Petri dish as coagulation bath for later use. The last but not the least, 10ml of the transparent sodium alginate solution was poured into a glass plate of $10 \times 10 \text{ cm}^2$, then pressed on another glass plate and pulled slowly until separated, so that the solution is evenly coated on the surface of the two glass plates. After that the glass were put into a Petri dish with coagulation bath. 30 minutes later, transparent films were obtained. The crosslinked films were taken out, washed with deionized water and dipped in absolute ethyl alcohol for 20 minutes for dehydration. Finally, the films were air-dried at room temperature for 24 hours and then kept in sealed bag at room temperature.

Measurements

The thermal stability and flame retardancy of the film were related to the metal ion content. And the contents of metal ions in films were assessed by ICP-OES (Avio™200, PerkinElmer Co., Ltd. USA). Fourier transform infrared (FTIR) spectroscopy studies comparing the films of Alg-La and Alg-Na were performed on a Nicolet 5700 FTIR spectrometer (Thermo Fischer Scientific, USA). The heat release rate (HRR) was investigated by microscale combustion calorimetry (MCC-2). $5 \pm 0.5\text{mg}$ of the sample was heated to $700 \text{ }^\circ\text{C}$ at a flowing rate of 80 ml/min under nitrogen atmosphere and the heating rate was set on $1 \text{ }^\circ\text{C/s}$. The thermal degradation of Alg-La and Alg-Na films were mixed with the oxygen (flowing rate of 20 ml/min) in nitrogen stream, then entered the $900 \text{ }^\circ\text{C}$ combustor. The thermal stability of films was recorded by thermogravimetric analysis (TG), which was used to investigate the relationship between the mass loss of sample and different heating temperature. The thermogravimetric analysis was conduct with Netzsch TG 209 F1 Libra® (Netzsch, Germany). The text was performed from room temperature to $900 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C/min}$ under nitrogen atmosphere. The surface morphology of film residues which pyrolysis in Muffle furnace for one hour at $400 \text{ }^\circ\text{C}$ were analyzed by SEM (Hitachi TM-3000, Japan).

RESULTS AND DISCUSSION

ICP-OES analysis

Table 1 The metal ion contents of films

Sample	Alg-Na	Alg-La
Sodium content (wt.%)	9.8	<0.01
Lanthanum content (wt.%)	0	13.4

The contents of metal ion inside the films were evaluated by ICP and the results were summarized in Table 1. After calculation, we found that the sodium content of Alg-Na was 9.8 %, while the lanthanum content of Alg-La was 13.4 %. It can be seen that the cross-linking ability of lanthanum ions is higher than that of sodium ions. The Alg-La sample contained

minute amount of sodium ions, which we thought it have no influence on their flame retardant performance.

FTIR spectroscopic analysis

Bands at about 1607 and 1402 cm^{-1} were attributed to asymmetric stretching vibrations and symmetric stretching vibrations of the COO-groups, respectively. Bands at about 3300 cm^{-1} were assigned to stretching vibrations of the hydrogen bond of the hydroxyl groups. Bands at about 1017 cm^{-1} were attributed to stretching vibrations of the C-O-C groups, while bands at about 2917 cm^{-1} was assigned to stretching vibrations of kinds of C-H bonds. It was noted from Figure 1 that there did not exit differences among FTIR spectra of Alg-La and Alg-Na films. As mentioned above, it was made a conclusion that the different metal ions have no significant effect on the membrane structure.

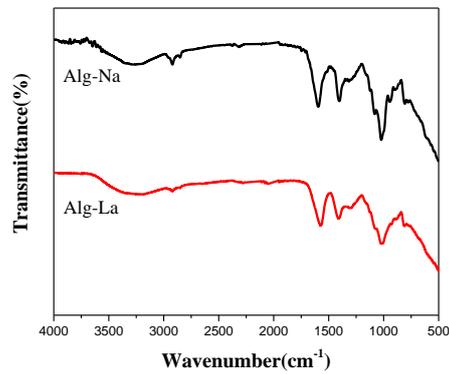


Figure 1 FTIR curves of Alg-La and Alg-Na films

MCC analysis

Microscale combustion calorimetry was widely used to estimate fire performance, and used fewer sample compared to Cone calorimetry that avoid the samples preparation problems encountered for testing. Heat release rate (HRR) plots of film different as a function of temperature were shown in Figure 2 and the relevant data obtained from MCC test were shown in Table 2. The Figure 2 and Table 2 showed that all the film showed the curves with two peaks and the combustion behaviour of Alg-La film was less intense than that of Alg-Na film. The first peak heat release rate (PHRR₁) of Alg-Na was 44.2 W/g at $247 \text{ }^\circ\text{C}$ and the second one (PHRR₂) was 15 W/g at $408 \text{ }^\circ\text{C}$. While the first peak heat release rate (PHRR) of Alg-La was 13.4 W/g at $239 \text{ }^\circ\text{C}$ and the second one was 11 W/g at $492 \text{ }^\circ\text{C}$. Compared with the curve of sodium alginate, there is a significant decrease in HRR values of Alg-La. This suggests that the addition of La^{3+} could promote the thermal degradation of alginate and catalyze alginate to form more amounts of combustible gases, such as CO_2 and H_2O , that reduce the release of combustible gases at lower temperature. Compared with the curve of sodium alginate, however, the PHRR₂ value of Alg-

La takes place at higher temperature, which suggested the addition of La³⁺ improved the flame retardancy of alginate. From the results of MCC, it showed the order of the flame retardancy properties of film: Alg-La > Alg-Na film.

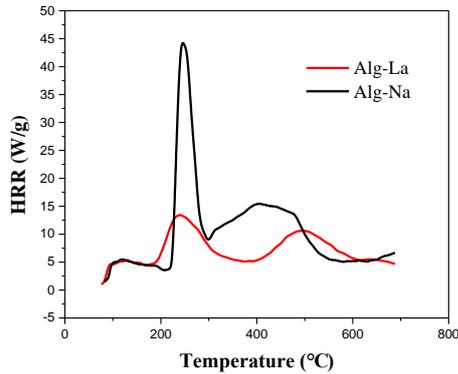


Figure 2 MCC curves of Alg-La and Alg-Na films

Table 2 Data obtained from MCC test

Sample	Alg-Na	Alg-La
THRR ₁ (W/g)	44.2	13.4
Reduction ₁ (%)	0	69.7
T ₁ (°C)	247	239
THRR ₂ (W/g)	15	11
Reduction ₂ (%)	0	26
T ₂ (°C)	408	492

TG analysis

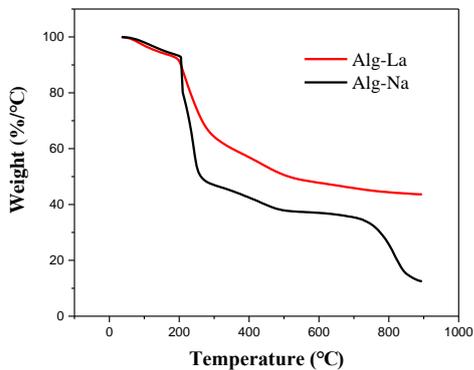


Figure 3 TG curves of Alg-La and Alg-Na films

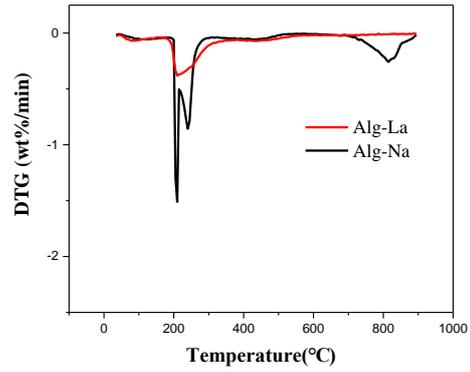


Figure 4 DTG curves of Alg-La and Alg-Na films

The thermogravimetric analysis (TG) and their differential thermogravimetric analysis (DTG) curves of films were shown in Figure. 3 and Figure 4. From Figure. 3 and Figure 4, it can be observed that the Alg-La had three steps of weight loss, while sodium alginate had four steps. The first step was from 30 to 203 °C for Alg-La and the sodium alginate was from 30 to 214 °C. The weight loss of steps was due to the physical loss of moisture evaporation from the samples and a small part of the glycosidic bonds breaks. The second step is the majority degradation of all process. It was from 203 to 315 °C for Alg-La, and from 214 to 272 °C for Alg-Na, resulted in the degradation of alginate during these steps, including the fracture of glycosidic bonds and ether bonds, dehydration, decarboxylation and decarbonylation of alginate and release CO₂, H₂O and other small molecular compounds. The last steps of Alg-La, was from 315 to 525 °C. The degradation of this step was due to the further degradation of the fragments formed in the second degradation steps. The third step of sodium alginate was from 272 to 626 °C and the decomposition products were similar with the last step of Alg-La. The final steps of sodium alginate appeared around 626 to 948 °C, which might be the further degradation of the fragments formed in the second and third degradation steps. From the results of data and curves, it showed the order of the flame retardancy properties of film: Alg-La> Alg-Na film.

SEM analysis of residues

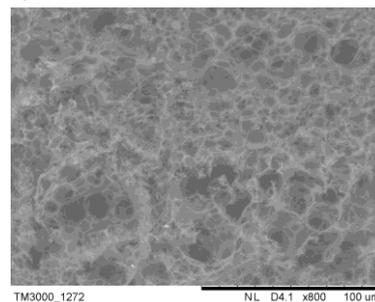


Figure 5 SEM images of Alg-Na film residues

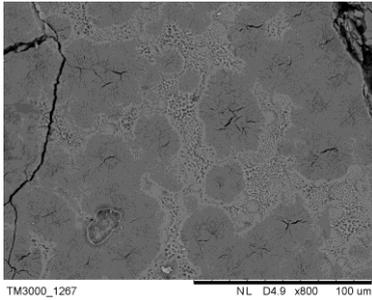


Figure 6 SEM images of Alg-La film residues

SEM images of the sample residues are shown in Figure 5 and Figure 6. It can be seen that the residue surface layer for the Alg-Na film was full of holes. The residue-layer structures of the Alg-La was different from Alg-Na film, that more dense, and the structures are retained very well. This char crust not only reduced the rates of formation of volatile gases, but also provided a barrier to heat and flame penetration to inner layers of the material, thus resisting the start and spreading of fire. This result indicates why Alg-La film have the better flame retardant properties.

CONCLUSION

The combustion performance and flame-retardancy mechanism of Alg-La and Alg-Na films were studied. Large differences in the flame retardancy and thermal degradation were observed from the lanthanum alginate and sodium alginate investigated by ICP, MCC, TG, and SEM. The results indicated that the addition of La^{3+} mainly reduced the release of combustible gaseous products at lower temperatures and thus reduced the HRR values of rare earth alginate. And the weight of residual char was higher than that of the sodium alginate at higher temperatures. As a result, La^{3+} ion in alginate decreases the quantity of heat released during combustion, and improves the flame retardancy of alginate.

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