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

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10

11 Abstract:

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

25

26 **Keywords:** Bio-based alginate film, Flame retardancy, Thermal properties, TG-FTIR, Py-GC-MS,
27 Thermal degradation mechanism

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30 1. Introduction

31 The energy crisis and the increasing global warming have urged human beings to look for novel
 32 types of energy instead of petroleum-based energy (Li, Chen, Zhang, Ye & Xing, 2011). Biomass is
 33 more sustainable than fossil-based materials, and the use of it can reduce the emission of CO₂ (Ross,
 34 Anastasakis, Kubachi & Jones, 2009). Recent interest in alternative sources of biomass as a
 35 potential feedstock had included the development of alginate (Ross et al., 2011). Alginate is a kind
 36 of biomass extracted from algae (Pathak, Yun, Lee, Baek & Paeng, 2009), and it is a linear
 37 copolymer of β -1, 4-D-mannuronate (M) and α -1, 4-L-guluronate (G) repeating monomeric units.
 38 Sodium alginate, a kind of alginic salt, is soluble in water, forming very viscous solution or jellies
 39 which depend on their physical properties (Tod, 1946; Chen, Wang, Sánchezsoto, Schiraldi, 2012).
 40 Gelation of alginate may happen by the interaction between carboxylate groups and divalent or
 41 trivalent metal ion in aqueous solution, forming strong, rigid and ordered structures, the hydrogels
 42 (Papageorgiou, 2010; Atkins, Nieduszynski, Mackie, Parker & Smolko, 1973). Alginate has many
 43 industrial uses in food industry, textile printing industry, paper industry, wound dressings and drug
 44 formulation (Ross et al., 2011; Qin, 2008).

45 Due to its water solubility, alginate was a desirable candidate for aqueous processing (Shen &
 46 Hsieh, 2014). Alginate fibers have been produced through wet-spinning process according to the
 47 gelation properties of alginate (Qin, 2008). Calcium alginate fibers, barium alginate fibers, copper
 48 alginate fibers and zinc alginate fibers owned good flame retardant properties without any addition
 49 of other flame retardants (Zhang et al., 2011; Zhang, Ji, Wang, Tan & Xia, 2012; Kong, Wang, Ji,
 50 Xia, Guo & Yu, 2009; Zhang, Zhang, Wang & Zhu, 2011). The effects of these divalent metal ion
 51 on the flame retardant properties, thermal properties of alginate fiber were investigated by Xia et al
 52 (Zhang et al., 2011; Zhang, Ji, Wang, Tan & Xia, 2012;) and Zhu et al (Zhang, Zhang, Wang & Zhu,
 53 2011; Liu, Zhao, Zhang, Ji & Zhu, 2014). The results indicated that the addition of divalent metal
 54 ion improved the flame retardant properties of alginate fibers. However, flame retardancy of
 55 functional alginate film and its pyrolysis mechanism have not been investigated yet.

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

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 process 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

86 dispersed uniformly in the film, and barium alginate film could be prepared successfully through
87 the facile ionic exchange and casting approach.

88

89 **2.3 Measurements**

90 **2.3.1 LOI**

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

93

94 **2.3.2 UL-94**

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

98

99 **2.3.3 TGA**

100 Thermogravimetric analysis (TGA) was investigated on a SDTQ600 Instruments (TA Instruments
101 Co., USA) thermogravimetric analyzer. 4-6 mg of the sample was examined at a heating rate of 10
102 °C /min with a flowing rate of 50 cm³/min under air and N₂, respectively, from room temperature to
103 700 °C.

104

105 **2.3.4 ICP**

106 0.2 g barium alginate was held in air in a muffle oven at 800 °C for 3 h, and then cooled to room
107 temperature, followed by addition of 8 mL aqua regia. After the residual char was fully solved, the
108 obtained transparent solution was removed to 50 mL volumetric flask and diluted to 50 mL constant
109 volume with ultrapure water. Inductively Coupled Plasma Atomic Emission Spectrometry
110 (ICP-AES) was carried out by an Optima 4300DV Instruments (Perkin Elmer Ltd., USA).

111

112 **2.3.5 MCC**

113 Microscale combustion calorimeter (MCC, Fire Testing Technology, UK) was used to investigate
114 the flammability of barium alginate film and sodium alginate film. 5 ± 0.05 mg sample was heated
115 to 700 °C (heating rate of 1 °C/s) at a stream of nitrogen flowing at 80 cm³/min. The volatile and
116 anaerobic thermal degradation products are mixed with a 20 cm³/min stream including 20% oxygen
117 and 80% nitrogen prior to entering a 900 °C combustion furnace. Each sample was run in three
118 replicates.

119

120 **2.3.6 TG-FTIR**

121 The TG-FTIR measurements were obtained by a TG analyzer (Perkin-Elmer STA 6000) coupled
122 with an Fourier transform infrared spectrometer (Perkin-Elmer Frontier FTIR) outfitted with a gas
123 cell. Gas products released from the TG analyzer were directly collected in the gas cell and
124 analyzed immediately using the FTIR spectrometer. About 10 mg of the samples were heated from
125 room temperature to 700 °C at a heating rate of 20 °C/min with a gas flow of 50 cm³/min under
126 nitrogen. FTIR spectra of the gaseous products were acquired continuously with the baseline
127 amended. The stainless steel pipe and the gas cell were preheated to 280 °C, to minimize secondary
128 reaction and tar condensation. The FTIR spectrometer was set to collect 16 interferograms and the
129 spectral range was set to be 4000-450 cm⁻¹.

130

131 **2.3.7 Py-GC-MS**

132 The fast pyrolysis analyzer (CDS5200) was coupled with GC-MS (Perkin Elmer Clarus
133 680GC-SQ8MS) systems to investigate the distribution of volatiles from barium alginate fast
134 pyrolysis against reaction temperature, and the carrier gas was He. About 300 µg of barium alginate
135 sample was loaded in the pyrolysis tube, and the pyrolysis temperature of furnace was set to be 700
136 °C with the flash heating rate of 20 °C/ms. The residence time for the sample was 15 s, to ensure
137 that most of the solid sample was pyrolyzed. The evolved volatiles were identified by GC-MS, with
138 the condition given as follows: the injector temperature was kept at 280 °C; the chromatographic
139 separation was performed with a HP-5 capillary column (0.25 mm); the temperature of the
140 chromatographic column was progressively increased from 40 °C (3 min) to 280 °C (5 min) with a

141 10 °C/min heating rate; the mass spectra were operated in electron ionization (EI) mode at 70 eV.
 142 The yield of the compounds can be determined by the characterized GC-MS spectrums, according
 143 to the database of NIST library and other previous reports.

144
 145 Scheme 1 Schematic illustration of preparation and characterization of barium alginate film

146

147 3. Results and discussion

148 3.1 Flammability of barium alginate film

149 3.1.1 LOI and UL94

150 Aiming to investigate the flame retardancy of barium alginate film, the LOI and UL-94 tests were
 151 employed and the relevant results were listed in Table 1. The LOI value of barium alginate film
 152 with the thickness of 2.0 mm was 52.0 %, and passed V-0 rating in UL-94 test, meaning that barium
 153 alginate film possessed high flame retardancy. In comparison, sodium alginate film had no
 154 classification in UL94 test and low LOI value (24.5 %). These results meant the introduction of
 155 barium ion into alginate significantly improved the flame retardancy.

156

157 3.1.2 MCC

Microscale combustion calorimetry (MCC) is a pyrolysis-combustion flow calorimetry, which has dynamic capability to measure HRR and other related parameters; MCC uses a few milligram sizes to avoid the samples preparation problems encountered for cone calorimetry (Yang, He, Lyon & Hu, 2010; Wang et al., 2011). Relevant data obtained from MCC test were shown in Table 1. From Table 1, both sodium alginate and barium alginate showed HRR curves with two peaks. The first peak heat release rate (PHRR) of sodium alginate was 105 W/g at 230 °C and the second one was 31 W/g at 453 °C, while those of barium alginate was 16 W/g at 270 °C, and 25 W/g at 450 °C, respectively. It was clear that barium alginate film showed much lower PHRR than that of sodium alginate due to the presence of barium ion. Usually, two possible reasons may induce such results. One was the addition of barium ion catalyzed alginate to form the char residues, reducing the release of flammable gases; the other was the addition of barium ion catalyzed alginate to form more inflammable gases, such as CO₂ and H₂O that would dilute the concentration of flammable products. Based upon the residual amounts shown in Table 1, it showed that barium alginate film had relatively lower residue compared with that of sodium alginate film (40.1 %, vs 47.4 %). This result indicated that the main reason to induce the high flame retardancy of barium alginate film was the latter. Detailed thermal degradation mechanisms were discussed in 3.4.

Table 1 Results of LOI, UL-94 and MCC tests

Sample	LOI (%)	UL-94	PHRR ₁ (W/g)	T _{PHRR1} (°C)	PHRR ₂ (W/g)	T _{PHRR2} (°C)	Residues (%)
Sodium alginate	24.5	NR	105	230	31	453	47.4
Barium alginate	52.0	V-0	16	270	25	450	40.1

Note: NR stands for no rating

3.2 Thermal degradation behaviors of barium alginate

Thermogravimetry was regard as a promising technique to study the thermal properties while the mass losses considered by this method depend on the volatility (or molar mass) of the fraction investigated (Aghamohammadi, Sulaiman & Aroua, 2011). This technique was used to compare the evaporation and cracking behavior of different polymeric materials. In order to understand the

182 effect of barium ion on the thermal oxidative stability and thermal stability of alginate, herein TGA
183 was used to investigate the thermal oxidative degradation and thermal degradation behaviors of
184 barium alginate and sodium alginate in air and N₂ atmosphere, respectively.

185

186 3.2.1 Thermal degradation behavior in N₂

187 The TG curves of barium alginate and sodium alginate in N₂ were presented in Fig. 1 a, and the
188 relevant data were shown in Table 2. Compared with sodium alginate, at the beginning of thermal
189 degradation of alginate, barium alginate had an obvious delay of thermal degradation. At the
190 beginning of thermal degradation of alginate, the mass loss was caused by the moisture evaporation
191 and the release of coordinated water. Barium ion formed outer-sphere complex with alginate, in
192 which barium ion or alginate or both generally retain their coordinated water when barium alginate
193 was formed. The obvious delay of thermal degradation in barium alginate was due to the thermally
194 more stability of coordinated water in barium alginate than that in sodium alginate. From Fig. 1 a,
195 barium alginate had three stages of weight loss, while sodium alginate only had two stages of
196 weight loss. Initial weight loss, from ambient temperature to 150 °C, was due to the moisture
197 evaporation and the release of coordinated water. The second step of rapid degradation for barium
198 alginate was situated at 185-340 °C, resulting in alginate thermal degradation. Compared with the
199 TG and DTG curves of sodium alginate in this temperature zone, barium alginate showed two sharp
200 peaks, while there was only one sharp weight loss peak for sodium alginate. Moreover, the
201 degradation temperature zone of sodium alginate was narrower than that of barium alginate. It
202 might be due to the catalysis effect of barium ion on the thermal degradation of alginate. For
203 sodium alginate, this stage might be associated with the fracture of glycosidic bonds, dehydration,
204 decarboxylation and decarbonylation of alginate. However, for barium alginate, the first rapid
205 degradation step in this temperature zone might be attributed to decarboxylation reaction under the
206 catalysis effect of barium ion and release CO₂; the second rapid degradation step might be due to
207 the fracture of glycosidic bonds, dehydration, and decarbonylation of alginate and release CO₂, H₂O
208 and other small molecular compounds; the third step appeared around 470-560 °C, which was
209 attributed to the thermal degradation of fragments formed in the second degradation steps.

210 The onset decomposition temperature (T_{onset}) of barium alginate was 144 °C. It was higher than
 211 that of sodium alginate, 106 °C. Herein, T_{onset} was defined as the temperature at which 5 % mass
 212 loss occurred. From Fig. 1 a it was noted that the maximum-rate decomposition temperature (T_{max})
 213 of barium alginate (207 °C) was lower than that of sodium alginate (242 °C); however, the
 214 maximum weight loss rate of T_{max} for barium alginate (4.3 %/min) was much lower than that of
 215 sodium alginate (15.1 %/min). The amount of the residues for barium alginate is higher than that of
 216 sodium alginate before 204 °C and after 232 °C. This was an interesting result which was different
 217 from the thermal results of zinc alginante, calcium alginate, aluminum alginate and iron alginate
 218 (Liu, Zhao, Zhang, Ji & Zhu, 2014; Liu, Wang, Zhao, Zhang, Ran & Zhu, 2014). In our previous
 219 studies (Liu, Zhao, Zhang, Ji & Zhu, 2014; Liu, Wang, Zhao, Zhang, Ran & Zhu, 2014), we found
 220 that the amounts of the residues for zinc alginante, calcium alginate, aluminum alginate and iron
 221 alginate were less than that of sodium alginate at higher temperatures, especially above 500 °C.
 222 However, the amount of the residues for barium alginate was much higher than that of sodium
 223 alginate from 232 to 700 °C. Furthermore, we studied the content of barium ion in barium alginate
 224 film by ICP, showing that the content of barium ion was 11.01 wt%, which was higher than sodium
 225 ion content in sodium alginate, 6.75 wt%.

226 Supposed there was no any interaction between metal ion and alginate during the thermal
 227 degradation, theoretically, both of barium alginate and sodium alginate would provide the same
 228 weight loss behaviors after subtracting the contents of barium and sodium, respectively. Based on
 229 this idea, we obtained the revised TGA curves (shown in Fig. 1 b) for both barium alginate and
 230 sodium alginate by subtracting the contents of metal ion and following the basic formula shown as
 231 below.

$$232 \quad M = (A - B) * 100 / (100 - B) \quad (1)$$

233 M was the revised mass percentage of alginate by subtracting the contents of metal ion; A was
 234 the experimental mass percentage of barium alginate or sodium alginate obtained from TGA test; B
 235 was the content of metal ion (barium or sodium). As mentioned above, if there was no any
 236 interaction between metal ion and alginate, M_{barium} should be the same with M_{sodium} . However, the
 237 result in Fig. 1 b showed significant difference between M_{barium} and M_{sodium} . In fact, M_{barium} was

238 much higher than M_{sodium} in the range between 235 °C to 545 °C, indicating that there existed strong
 239 interaction between barium and alginate on char forming compared with the interaction between
 240 sodium and alginate. Barium ion might catalyze the thermal degradation reaction of alginate to form
 241 more residues, reducing the release of combustible gases.

242 Fig. 1. TGA (a) curves of barium alginate and sodium alginate in N₂, TGA (b) curves of barium
 243 alginate and sodium alginate by subtracting the contents of metal ion in N₂ and TGA (c) curves of
 244 barium alginate and sodium alginate in air
 245

3.2.2 Thermal oxidative degradation behaviors in air

The TG curves of barium alginate in air were presented in Fig. 1 c, which were similar to those tested in N₂ atmosphere. Three stages were also found in thermal oxidative degradation process. The first stage (about 5.0 % weight loss) was attributed to the moisture evaporation from ambient temperature to 150 °C. The second stage (about 31.1 % weight loss) was the main weight loss between 186 and 315 °C on barium alginate, which might be associated with the fracture of glycosidic bonds, dehydration, decarboxylation and decarbonylation of alginate, whereas the first and second maximum-rate decomposition temperatures occur at 205 and 264 °C, respectively. The first maximum-rate decomposition temperature of barium alginate was lower than that of sodium alginate from 186 to 315 °C; however, the second maximum-rate decomposition temperature was higher than that of sodium alginate in this temperature zone. This also might be the catalysis effect of barium ion on the thermal degradation of alginate, which was similar to the behaviors in N₂. The last stage (463-508 °C) with the peak at 499 °C in thermal oxidative degradation was due to oxidization of carbonaceous residues within inorganic solid particles. Finally, barium alginate remained a solid residue (carbonaceous residues within inorganic solid particles) at 37.3 % of its original mass. Indeed, it was difficult to establish a distinct boundary among these thermal degradation stages because of the overlapping of the region of volatiles release and thermal oxidation of char (Gao, Li, Quan, Du & Duan, 2013).

Table 2 Thermogravimetric data of barium alginate and sodium alginate in air and N₂, respectively

Atmosphere	Samples	T _{onset} (°C)	T _{max1} (°C)	Rate of T _{max1} (%/min)	T _{max2} (°C)	Rate of T _{max2} (%/min)	Residue (%)		
							500 °C	600 °C	700 °C
In air	Sodium alginate	110	245	16.0	569	6.2	40.7	24.9	24.6
	Barium alginate	150	205	5.5	500	6.7	44.5	37.9	37.3
In N ₂	Sodium alginate	106	242	15.1	-	-	41.7	40.4	38.1
	Barium alginate	144	207	4.3	275	4.4	54.4	44.2	43.7

267 In order to understand the effect of oxygen on the degradation for barium alginate at high
268 temperature, the thermal degradation behaviors of barium alginate in air and N₂, respectively, had
269 been compared. The TG curve of barium alginate in air was accorded to that in N₂ below 234 °C,
270 indicated that the oxygen in air did not take part in the thermal degradation process of barium
271 alginate until the temperature reached 234 °C. By comparing the results from Figs. 2 and 4, it noted
272 that barium alginate degraded much more in air than its behavior in N₂ atmosphere at higher
273 temperatures, leading to the amount of the residues for barium alginate in air was less than that in
274 N₂. Also, all of the residues were relatively stable once the residues formed in both air and N₂. The
275 proposed thermal degradation mechanism would be discussed in detail in 3.4.

276

277 3.3 TG-FTIR analysis

278 TG-FTIR technique was utilized for characterization of gaseous compounds, which was allowed to
279 link to the weight loss signals and gaseous emission. In this context, FTIR provided the important
280 data for the identification of the functional groups of the polymeric materials (Yang, He, Lyon &
281 Hu, 2010). The Gram-Schmidt curves of barium alginate and sodium alginate were presented in Fig.
282 2 Absorbance information at different time obtained from Gram-Schmidt curves of barium alginate
283 and sodium alginate. From Fig. 2, it was noted that maximum evolution rates of absorbance
284 intensities for barium alginate and sodium alginate took place around 718 and 678 s, respectively;
285 there were shoulder peaks of absorbance intensities for barium alginate and sodium alginate at 607
286 and 728 s, respectively. Thus, the FTIR spectra at 678 and 728 s for sodium alginate and at 607 and
287 718 s for barium alginate were shown in Fig. 2. The broad bands at 3950-3500 and 1872-1300 cm⁻¹
288 were related to O-H stretching vibration of O-H groups and gaseous H₂O (Wu, Shen, Xiao & Zhang,
289 2013); the peaks at about 2358 and 667 cm⁻¹ were attributed to CO₂ (Zhao et al., 2014), and the
290 peak around 1750 cm⁻¹, which was overlapped with the absorbance peaks of gaseous H₂O, was
291 assigned to the C=O stretching vibration of carbonyl groups (Wang et al., 2013). From Fig. 2 d and
292 e, it was noted that the absorbance intensities of peaks for barium alginate at 3950-3500 and
293 1872-1300 cm⁻¹ in FTIR spectra of 607 s were stronger than those in FTIR spectra of 718 s. The
294 reason for this phenomenon was that the release amounts of gaseous water and compounds with

295 -CO- groups at 607 s were higher than those at 718 s, which can be obtained from Fig. 3. Based on
296 the results in Fig. 2, the evolved gases for both of sodium alginate and barium alginate are mainly
297 H₂O (3950-3500 cm⁻¹) and CO₂ (2358 and 667 cm⁻¹). However, the addition of barium ion
298 decreased obviously the absorbance intensities of other characteristic groups. The addition of
299 barium ion accelerated the thermal degradation of alginate, meaning that barium ion revised the
300 thermal degradation process of alginate, such as favoring decarboxylation of alginate as opposed to
301 the depolymerization of alginate at lower temperatures. In addition, several FTIR spectra of
302 different characteristic groups were selected for primary analysis at a function of time and the FTIR
303 spectra were presented in Fig. 3. It noted that the main gaseous products emitted of barium alginate
304 and sodium alginate were H₂O, CO₂, CO, =C-H characteristic groups, C-H characteristic groups
305 and C=O characteristic groups. The specific wavenumbers of the spectra peak for the main volatile
306 mentioned above were listed as follows: H₂O, 3736 cm⁻¹; CO₂, 2358 cm⁻¹; CO, 2180 cm⁻¹; =C-H,
307 3016 cm⁻¹; C-H, 2966 cm⁻¹; C=O, 1750 cm⁻¹. Obviously, the volatile emission of H₂O, CO₂, C=O
308 and CO characteristic groups mainly focus at lower temperature range. Compared with the
309 absorbance intensities of sodium alginate, the addition of barium ion decreased seriously the
310 absorbance intensities of H₂O, CO₂, C=O, CO, =C-H and -C-H at lower temperatures; however, it
311 increased the absorbance intensities of =C-H and -C-H at higher temperatures. The results above
312 indicated that the addition of barium ion decreased the release of combustible gases at lower
313 temperatures and reduced the flammability of alginate, which was accorded to the results of MCC.

Fig. 2. Gram-Schmidt curves (a), FTIR spectra of pyrolysis gaseous products emitted from barium alginate and sodium alginate at maximum evolution rate (b, c, d, e)

Fig. 3. FTIR spectra of different characteristic groups as a function of time for barium alginate and sodium alginate

3.4 Pyrolysis behaviors of barium alginate

To investigate the main components of gaseous products in the pyrolysis process of barium alginate, pyrolysis gas chromatography and mass spectrometry (Py-GC-MS) analysis were conducted. Compared with the mass spectra fragmentation pattern with the NIST library and published data, the highest likelihood of compounds identification were obtained. More than 50 peaks were displayed on the chromatograms, and a total of 9 main compounds were identified and

their structures were summarized in Table 3. The main compounds in Table 3 were as follows: carbon dioxide, 1-hydroxypropan-2-one, propan-2-one, methyl 2-oxopropanoate, toluene, 2,3-butanedione, butan-2-one, o-cresol, furfural and so on. These compounds mainly were divided into three groups: (1) carbon dioxide, (2) ketone (i.e. 1-hydroxypropan-2-one, propan-2-one, 2,3-butanedione and butan-2-one) and aldehyde (i.e. furfural), (3) unsaturated hydrocarbon (i.e. toluene). Compared with pyrolysis compounds of sodium alginate (Liu et al., 2015), there were much less compounds in barium alginate pyrolysis process, suggested that barium ion might have a catalysis effect on the thermal degradation process of alginate. Barium ion changed the thermal degradation process of alginate, such as favoring the decarboxylation of alginate as opposed to the depolymerization of sodium alginate.

337

Table 3 Analytical results of chemical constituents of 700 °C pyrolysis products of barium alginate

label	t _R (min)	Molecular formula	Name of compound	Molecular structure	M _w (g/mol)	Peak area (%)
1	1.50	CO ₂	carbon dioxide	O=C=O	44	28.7
2	1.75	C ₃ H ₆ O	propan-2-one		58	8.4
3	2.11	C ₄ H ₆ O ₂	2,3-butanedione		86	4.5
4	2.16	C ₄ H ₈ O	butan-2-one		72	4.4
5	2.73	C ₃ H ₆ O ₂	1-hydroxypropan-2-one		74	9.0
6	4.47	C ₇ H ₈	toluene		92	5.0
7	4.85	C ₄ H ₆ O ₃	methyl 2-oxopropanoate		102	5.4
8	5.74	C ₅ H ₄ O ₂	furfural		96	3.4
9	9.90 10.27	C ₇ H ₈ O	o-cresol		108	1.6 2.3

339 Considering the compounds distribution from barium alginate pyrolysis, carbon dioxide,
 340 1-hydroxypropan-2-one, propan-2-one, methyl 2-oxopropanoate, toluene, 2,3-butanedione,
 341 butan-2-one, o-cresol, furfural are the main products, the yields of which was 72.6% in total.
 342 According to the analysis of TG-FTIR and Py-GC-MS, a proposed thermal degradation mechanism
 343 of barium alginate was proposed: the addition of barium ion catalyzed alginate's decarboxylation
 344 and esterification in the pyrolysis process at the lower temperature zone by releasing the H₂O and
 345 CO₂, and decreasing the release of combustible gases. The fragments formed at lower temperatures
 346 continuously degraded at high temperature, releasing some low weight molecular products. Scheme
 347 2 presented a proposed thermal degradation mechanism of barium alginate.

Scheme 2 Proposed thermal degradation mechanism of barium alginate

351 4 Conclusion

352 Significant difference in the flame retardant properties, thermal degradation and pyrolysis
 353 behaviors were found from barium alginate film and sodium alginate film. Compared with that of
 354 sodium alginate film, barium alginate film owned much better flame retardant properties. The
 355 results of MCC indicated that the addition of barium ion mainly decreased the release of
 356 combustible gaseous products at lower temperatures and thus decreased the HRR values of barium
 357 alginate. The TGA results showed that barium alginate had higher thermal stability and char residue
 358 than those of sodium alginate. The TG-FTIR and Py-GC-MS results indicated during the thermal
 359 degradation barium alginate produced much less compounds than sodium alginate. This suggested

360 that the barium ion might catalyze the fragments formed in the pyrolysis process to form more
361 stable products. Also, the addition of barium ion mainly accelerated the decarboxylation and
362 esterification of alginate at the relatively low temperature and decreased greatly the release of
363 gaseous products, inducing that the flame [retardancy](#) of barium alginate was improved. These
364 important results achieved in the paper would provide powerful evidence to understand the flame
365 retardant mechanism of functionalized alginates and design new functional biobased materials with
366 excellent fire retardant properties.

367

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373 **References**

- 374 Aghamohammadi, N., Sulaiman, N. M. N. M., Aroua, K. (2011). [Combustion characteristics of](#)
375 [biomass in South East Asia. *Biomass and Bioenergy*, 35, 3884-3890.](#)
- 376 Atkins, E. D. T., Nieduszynski, I. A., Mackie, W., Parker, K. D., Smolko, E. E. (1973). [Structural](#)
377 [components of alginic acid. II. The crystalline structure of poly- \$\alpha\$ -L-guluronic acid. Results of](#)
378 [X-ray diffraction and polarized infrared studies. *Biopolymers*, 12, 1879-1887.](#)
- 379 Chen, H. B., Wang, Y. Z., Sánchezsoto, M., Schiraldi, D. A. (2012). [Low flammability, foam-like](#)
380 [materials based on ammonium alginate and sodium montmorillonite clay. *Polymer*, 53,](#)
381 [5825-5831.](#)
- 382 Gao, N. B., Li, A. M., Quan, C., Du, L., Duan, Y. (2013). [TG-FTIR and Py-GC/MS analysis on](#)
383 [pyrolysis and combustion of pine sawdust. *Journal of Analytical and Applied Pyrolysis*, 100,](#)
384 [26-32.](#)
- 385 Kong, Q. S., Wang, B. B., Ji, Q., Xia, Y. Z., Guo, Z. X., Yu, J. (2009). [Thermal degradation and](#)
386 [flame retardancy of calcium alginate fibers. *Chinese Journal of Polymer Science*, 27, 807-812.](#)
- 387 Li, D. M., Chen, L. M., Zhang, X. W., Ye, N. H., Xing, F. G. (2011). [Pyrolytic characteristics and](#)
388 [kinetic studies of three kinds of red algae. *Biomass and Bioenergy*, 35, 1765-1772.](#)

389 Liu, Y., Zhao, X. R., Peng, Y. L., Peng, H., Zhu, P., Wang, D. Y. (2015). Effect of reactive time on
390 the properties and the pyrolysis mechanism of zinc alginate films by TG-FTIR and Py-GC-MS.
391 *Materials and Design*, submitted.

392 Liu, Y., Zhao, J. C., Zhang, C. J., Ji, H., Zhu, P. (2014). The Flame Retardancy, Thermal Properties,
393 and Degradation Mechanism of Zinc Alginate Films. *Journal of Macromolecular Science, Part*
394 *B: Physics*, 53,1074-1089.

395 Liu, Y., Wang, J. S., Zhao, J. C., Zhang, C. J., Ran, J. H., Zhu, P. (2014). The flame retardancy and
396 thermal degradation behaviors of trivalent metal-alginate films. *Nanomaterials and Energy*, 3,
397 3-10.

398 Papageorgiou, S. K., Kouvelos, E. P., Favvas, E. P., Sapalidis, A. A., Romanos, G. E., Katsaros, F.
399 K. (2010). Metal-carboxylate interaction in metal-alginate complexes studied with FTIR
400 spectroscopy. *Carbohydrate Research*, 345, 469-473.

401 Pathak, T. S., Yun, J. H., Lee, S. J., Baek, D. J., Paeng, K. J. (2009). Effect of cross-linker and
402 cross-linker concentration on porosity, surface morphology and thermal behavior of metal
403 alginates prepared from algae (*Undaria pinnatifida*). *Carbohydrate Polymers*, 78, 717-724.

404 Qin, Y. M. (2008). Alginate fibres: an overview of the production processes and application in
405 wound management. *Polymer International*, 57, 171-180.

406 Ross, A. B., Anastasakis, K., Kubachi, M., Jones, J. M. (2009). Investigation of the pyrolysis
407 behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA. *Journal of*
408 *Analytical and Applied Pyrolysis*, 85, 3-10.

409 Ross, A. B., Hall, C., Anastasakis, K., Westwood, A., Jones, J. M., Crewe, R. J. (2011). Influence
410 of cation on the pyrolysis and oxidation of alginates. *Journal of Analytical and Applied*
411 *Pyrolysis*, 91, 344-351.

412 Shen, W., Hsieh Y. L. (2014). Biocompatible sodium alginate fibers by aqueous processing and
413 physical crosslinking. *Carbohydrate Polymers*, 102, 893-900.

414 Tod, C. W. (1946). Production of alginate solution. *US patent*, 2,405,861.

415 Wang, D. Y., Leuteritz, A., Kutlu, B., Landwehr, M. A., Jehnichen, D., Wagenknecht, U., Heinrich,
416 Gert. (2011). Preparation and investigation of the combustion behavior of

polypropylene/organomodified MgAl-LDH micro-nanocomposite. *Journal of Alloys and compounds*, 509, 3497-3501.

Wang, S. Q., Tang, Y. G., Schobert, H. H., Guo Y. N., Gao, W. C., Lu, X. K. (2013). FTIR and simultaneous TG/MS/FTIR study of Late Permian coals from Southern China. *Journal of Analytical and Applied Pyrolysis*, 100, 75-80.

Wu, S. L., Shen, D. K., Xiao, R., Zhang, H. Y. (2013). TG-FTIR and Py-GC-MS analysis of a model compound of cellulose-glyceraldehyde. *Journal of Analytical and Applied Pyrolysis*. 101, 79-85.

Yang, C. Q., He, Q. L., Lyon, R. E., Hu, Y. (2010). Investigation of the flammability of different textile fabrics using micro-scale combustion calorimetry. *Polymer Degradation and Stability*, 95, 108-115.

Zhang, C. J., Zhang, N. N., Wang, Z., Zhu, P. (2011). Flame retardant properties of calcium alginate fibers. *Dye Finish*, (8), 1-5.

Zhang, J. J., Ji, Q., Shen, X. H., Xia, Y. Z., Tan, L. W., Kong, Q. S. (2011). Pyrolysis products and thermal degradation mechanism of intrinsically flame-retardant calcium alginate fibre. *Polymer Degradation and Stability*, 96, 936-942.

Zhang, J. J., Ji, Q., Wang, F. J., Tan, L. W., Xia, Y. Z. (2012). Effects of divalent metal ion on the flame retardancy and pyrolysis products of alginate fibres. *Polymer Degradation and Stability*, 97, 1034-1040.

Zhao, J., Wang, X. W., Hu, J., Liu, Q., Shen, D. K., Xiao, R. (2014). Thermal degradation of softwood lignin and hardwood lignin by TG-FTIR and Py-GC/MS. *Polymer Degradation and Stability*, 108, 133-138.

440 **Figure Captions**

441 Fig. 1. TGA (a) curves of barium alginate and sodium alginate in N₂, TGA (b) curves of barium
442 alginate and sodium alginate by subtracting the contents of metal ion in N₂ and TGA (c) curves of
443 barium alginate and sodium alginate in air

444 Fig. 2. Gram-Schmidt curves (a), FTIR spectra of pyrolysis gaseous products emitted from barium
445 alginate and sodium alginate at maximum evolution rate (b, c, d, e)

446 Fig. 3. FTIR spectra of different characteristic groups as a function of time for barium alginate and
447 sodium alginate

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

449 Scheme 2 Proposed thermal degradation mechanism of barium alginate

450

451 **Table Captions**

452 Table 1 Results of LOI, UL-94 and MCC tests

453 Table 2 Thermogravimetric data of barium alginate and sodium alginate in air and N₂, respectively

454 Table 3 Analytical results of chemical constituents of 700 °C pyrolysis products of barium alginate