Thermal degradation properties of bio-based iron alginate film

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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 (TG-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. TG-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 H₂O, CO₂ 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.

Keywords: Iron Alginate; MCC; Py-GC-MS; TG-FTIR-MS; Thermal degradation mechanism

1. Introduction

In the last few decades, polysaccharides, a kind of [bio-based](#) 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 copolymer, 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 retardants ^[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. Zaafarani^[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](#). The results revealed the formation of metal hydroxide, oxalate and carbonate for Al^{3+} , Cr^{3+} and Fe^{3+} -alginate [complexes](#). And they were followed by degradation of these intermediate fragments to the corresponding metal oxides as the final products; however, Zaafarani did not investigate the effects of trivalent cations on the pyrolysis process of alginate.

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), thermogravimetric analyzer which was coupled with Fourier transform infrared spectroscopy and mass spectrometry ([TG-FTIR-MS](#)), and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). And the effect of iron ions on the pyrolysis process and pyrolysis mechanism of iron alginate [was](#) 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

Microscale combustion calorimeter (MCC) measurement was carried out by a 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.

TG 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) (Perkin Elmer Clarus680GC-SQ8MS) to study the formation of volatiles from iron alginate fast pyrolysis process against chemical reaction temperature. The

carrier gas was He, and about 300 μg of iron alginate was placed into the pyrolysis tube. The pyrolysis temperature of the furnace was 700 $^{\circ}\text{C}$, and the flash heating rate was 20 $^{\circ}\text{C}/\text{ms}$. 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 $^{\circ}\text{C}$ (3 min) to 280 $^{\circ}\text{C}$ (5 min) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$; the injector temperature was maintained at 280 $^{\circ}\text{C}$; 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), 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 curves of iron alginate and sodium alginate as a function of temperature is shown in Figure 1, and the data obtained from MCC test are listed in Table 1. From Figure 1, it is noted that iron alginate and sodium alginate show HRR curves with two peaks. The first peak heat release rate (PHRR) of iron alginate and sodium alginate take place with PHRR values of 15.5 and 105 W/g at 135 and 230 $^{\circ}\text{C}$, respectively; The second one appears with PHRR values of 29.6 and 31.4 W/g at 219 and 453 $^{\circ}\text{C}$. Compared to HRR curve of sodium alginate, it is observed that the results show two distinct characteristics because of the addition of iron ions. Firstly, there is a significant decrease in HRR values of iron alginate. Secondly, the first PHRR value takes place at lower temperature. This suggests that the addition of iron ions can promote the thermal degradation of alginate and catalyze alginate to form more amounts of inflammable gases, such as CO_2 and H_2O . And this results in reducing the release of flammable gases at lower temperature. However, the HRR values of iron alginate are similar with those values of sodium alginate at higher temperature, suggesting that iron ions do not have the flame retardant effect on alginate at higher temperature. From Figure 1 and Table 1, it can be obtained that the residual amount of iron alginate, 28.2 %, is much lower than that of sodium alginate, 47.4 %; while the HRR values of iron alginate are much lower than those of sodium alginate. This indicates that the addition of iron ions can catalyze alginate to produce more inflammable gases, such as CO_2 and H_2O , showing better flame retardant properties of iron alginate.

Figure 1 HRR curves of iron alginate and sodium alginate as a function of temperature

Table 1 Data obtained from the MCC parameters of iron alginate and sodium 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

3.2 TG-FTIR-MS analysis

TG analysis coupled with mass spectrometry (MS) and fourier transform infrared spectrometry (FTIR) allows to conform the proposed general thermal degradation mechanism of bio-based materials [25].

3.2.1 Temperature-programmed thermal degradation

The thermogravimetric analysis (TG) and their differential thermogravimetric analysis (DTG) curves of iron alginate at a heating rate of 10 °C/min in N₂ with a flowing rate of 100 mL/min are shown in Figure 2. The main loss stage of iron alginate take place in a wide temperature zoon (from 170 to 400 °C), and then iron alginate begins to degrade slowly with quite lower thermal degradation rates. The onset thermal degradation temperature (5 wt% mass loss) of iron alginate is 181 °C (T_{onset}). And then, the faster thermal degradation of iron alginate takes place with further increasing of temperature. The peak of mass loss rate, 5.6 %/min, appears around 198 °C (T_{max}). From room temperature to 600 °C, about 68.6% of the total weight is rapidly decomposed. The weight loss is ascribed to the intensive evolution of small gaseous molecules and the thermal degradation of alginate with the fracture of glycosidic bonds, releasing incombustible such as CO₂ and H₂O. Then, the formed intermediate compounds further decompose to produce the more

stable intermediate compounds at a slower rate of decomposition with increasing the temperature. The amount of char residue at 800 °C is about 28.3%.

Figure 2 TG and DTG curves of iron alginate

3.2.2 Evolved gas analysis during thermal degradation process of iron alginate

Generally speaking, chemical reactions taking place during alginate thermal degradation involved dehydroxylation, decarboxylation, decarbonylation, rearrangement, scission and condensation reactions. The reactions produce gases and char residues; some of the released gaseous compounds can be investigated by FTIR and MS techniques.

Figure 3 3D infrared spectra of evolved gases during iron alginate pyrolysis

FTIR is often utilized to differentiate a variety of organic and inorganic gas compounds for thermal degradation of polymeric materials ^[26]. 3D FTIR spectra of the evolution gases from iron alginate thermal degradation process including information of infrared absorbance, wavenumber and time are presented in Figure 3. According to the infrared spectra, the change in spectral intensity with time direction is as the same as TG results. Absorbance information at different

wavenumber and time can be observed from 3D FTIR spectra of iron alginate. It can be obtained from Figure 3 that most of the gases are evolved between 1000 and 3000 s and the evolved gases are mainly composed of H₂O (3750-3500 cm⁻¹) and CO₂ (2363 and 667 cm⁻¹). When further increasing the temperature, the absorbances of carbon monoxide, C=O and C=C appear at 2186-2109 and 1800-1600 cm⁻¹, respectively, resulting from the further thermal degradation of fragments formed. Some typical FTIR spectra of the thermal degradation gaseous compounds were chosen for primary analysis at different temperature. According to the TG data in Figure 2, the spectra obtained at 150, 181, 198, 210, 250, 300, 400, 450 and 500 °C are shown in Figure 4a and 4b.

From Figure 4a and 4b, it can be observed that the evolved gases of iron alginate thermal degradation are distinguished by the characteristic absorbance. In the beginning thermal degradation stage at 150 °C, H₂O and CO₂, the absorbance intensities of which are very weak, are shown in wavenumbers 3968-3496, 1515 and 2383-2317 cm⁻¹, which may be resulted from the releases of CO₂ and H₂O adsorbed by furnace. With temperature increased to 181 °C, T_{onset}, stronger CO₂ stretching absorbance waves take place at about 2357 and 667 cm⁻¹, which indicates the start of thermal degradation of iron alginate. The similar infrared absorbance of iron alginate thermal degradation is obtained at 181 and 198 °C (T_{max}), while the absorbance intensities at 198 °C are stronger than those at 181 °C. With the temperature increases, intensities of the absorbance waves are enhanced to some extent, and then reduced, which are accordant with TG results. On the basis of the Lambert-Beer law, the absorption spectra at a specific wavenumber linearly rely on the gas concentration [27]. Thus, the change of absorbance intensity in the entire thermal degradation process reflects the concentration change of the gaseous compounds. It can be seen from Figure 4a and 4b that the new absorbance waves at 2179 and 2113 cm⁻¹, which are attached to the stretching of carbon monoxide, appear when the temperature increases above 250 °C. The C=O and C=C stretching absorbance peaks in 1879-1600 cm⁻¹ represent the release of gaseous compounds containing aldehyde or ketone or organic acid or alkene groups. And the bands in 3968-3496 and 1515 cm⁻¹ are attributed to O-H stretching of water and -OH of organic acid or alcohols. The peak at 2937 cm⁻¹ is attributed to the stretching of saturated hydrocarbon bonds. The intensity of absorption wave in 3014 cm⁻¹, which attached to the stretching of unsaturated hydrocarbon bonds, increases with the increase of the temperature. And this indicates that unsaturated hydrocarbon compounds form at higher temperature because of the thermal degradation of fragments.

In order to analyze exhaustively the tendencies of absorption intensity for some functional groups with the increase of temperature, kinds of FTIR spectra for different functional groups are chosen for primary analysis at a function of temperature. According to Figure 4a and 4b, the main gaseous products emitted from thermal degradation process of iron alginate are H₂O, CO₂, CO, =C-H groups, C-H groups and C=O groups. The unambiguous wavenumbers of the spectrum peak for the volatile mentioned above are presented as follows : H₂O, 3733 cm⁻¹; CO₂, 2357 cm⁻¹; CO, 2179 cm⁻¹; =C-H, 3014 cm⁻¹; C-H, 2937 cm⁻¹; C=O, 1740 cm⁻¹. And the FTIR spectra of different groups mentioned above are depicted in Figure 5. It is noted from Figure 5 that the absorbance intensities of H₂O, C=O groups, C-H groups first increase quickly, decrease, and then increase slowly with increasing the temperature. The absorbance intensities of CO experience two lowering elevated process with the temperature increasing. The absorbance intensities of CO₂ and =CH- groups first increase and then decrease. It can be observed that H₂O, CO₂, gaseous products containing -CO- groups and compounds containing -CH- groups are firstly produced at the initial thermal degradation process of iron alginate (at about 170 °C).

However, CO and compounds containing =CH- groups are generated from 223 to 750 °C and from 357 to 750 °C, respectively. As can be seen from Figures 2 and 5 that H₂O, CO₂, gaseous products containing -CO- groups and compounds containing -CH- groups are mainly yielded in the major loss stage of iron alginate (from 170 to 400 °C). While CO and products containing =CH- groups are mainly produced at higher temperature zone. This indicates that the fragments formed at lower temperature further degrade to release CO and compounds containing =CH- functional groups at higher temperature zone. And according to the results of MCC and FTIR, the higher HRR values are not generated from the combustion of CO and compounds containing =CH- functional groups.

According to the results mentioned above, the chemical reactions of dehydroxylation, decarboxylation and the fracture of glycosidic bonds appear at the initial thermal degradation process of iron alginate to form the [fragments](#). And this results in the release of H₂O, CO₂, gaseous products containing -CO- groups and products containing -CH- groups. With temperature increases, the fragments formed further degrade to produce more stable residues, releasing H₂O, CO₂, CO, products containing -CO- groups, products containing -CH- groups and products containing =CO- groups. And the thermal degradation mechanism of iron alginate will be discussed in detail in 3.4.

Figure 4a FTIR spectra for the evolved gaseous products in gas phase of iron alginate

Figure 4b FTIR spectra for the evolved gaseous products in gas phase of iron alginate

Figure 5 FTIR spectra of typical groups as a function of temperature for iron alginate

Figure 6 presents the evolution of main gas products with temperature increases during iron alginate thermal degradation according to the ion intensities from MS. The main mass spectra (MS) in the TG process of iron alginate thermal degradation by TG coupled with MS analysis are as follows: in the plot of the ion intensity corresponds with the first TG step, fragments at m/z 17

(HO^+), 18 (H_2O) and 44 (CO_2) prove the release of H_2O [28] and CO_2 [29]. This indicates the chemical reactions of dehydroxylation and decarboxylation take place in the degradation process of iron alginate. H_2O and CO_2 evolutions are mainly concentrated from 158 to 400 °C, and the releases of them are in agreement with weight loss thermogravimetric data. It can be observed from Figure 6 that different trends of H_2O and CO_2 are observed that the intensities of CO_2 increase first and then decrease with increasing the temperature and reach the strongest peak at 200 °C; however, intensities of H_2O decrease first at lower temperature, and then increase, then decrease again at higher temperature, with increasing the temperature and reach the strongest peak at 204 °C. The reason is that iron alginate contains crystallization H_2O which can be released in the lower temperature. H_2O might produce from the evolution of bound water, crystallization water and the break of -OH groups in iron alginate. CO_2 mainly formed from break of $-\text{COO}^-$ groups in the chain of alginate and the degradation process of iron alginate. The thermal degradation mechanism of iron alginate will be discussed in 3.4.

Figure 6 Evolution curves of M/Z= 17, 18 and 44 during pyrolysis of iron alginate

3.3 Fast pyrolysis of iron alginate versus Py-GC-MS

The other way to investigate pyrolysis evolved components of bio-based materials is to utilize Py-GC-MS, which involves the characteristics of gaseous pyrolysis compounds [28]. In order to study the composition of gaseous compounds in iron alginate pyrolysis process, pyrolysis gas chromatography and mass spectrometry (Py-GC-MS) analysis on iron alginate had been explored. On the basis of the NIST library, the highest possibility of products identification was acquired. The total ion intensity of gases evolving from iron alginate pyrolysis is shown in Figure 7. Peaks of the major products were marked with numbers. Over 20 peaks are depicted on the chromatograms, and about 20 major compounds are identified, whose structures are characterized in Table 2 (the peak numbers in Figure 7 are in accordance with the labels in Table 2). From Figure 7 and Table 2, it is noted that the major compounds are as follows: CO_2 , furfural, 3-penten-1-ol, 2-cetobutyric acid methyl ester, 2, 3-butanedione, and the yield of them is 78.2%. Among the compounds, CO_2 and furfural are the typical products of iron alginate pyrolysis, the yield of which is 64.5%. And the possible thermal degradation mechanism of iron alginate will be investigated in 3.4.

Figure 7 Py-GC-MS detection of gaseous compounds obtained from pyrolysis of iron alginate

Table 2 Results of chemical formation pyrolysis products for iron alginate at 700 °C

label	t _R (min)	Molecular formula	Name of compound	Molecular structure	M _w (g/mol)	Peak area (%)
1	1.51	CO ₂	carbon dioxide	O=C=O	44	41.1
2	1.76	C ₅ H ₁₀ O	3-penten-1-ol		86	6.2
3	2.12	C ₄ H ₆ O ₂	2,3-butanedione		86	3.1
4	2.74	C ₆ H ₆	benzene		78	1.1
5	3.44	C ₅ H ₈ O ₂	2-methyl methacrylate		100	0.5
6	4.48	C ₇ H ₈	Toluene		92	0.7
7	4.70	C ₄ H ₆ O ₂	1,4-butanedial		86	1.2
8	5.05 7.26	C ₄ H ₄ O ₂	2(5H)-furanone		84	2.5
9	5.78	C ₅ H ₄ O ₂	furfural		96	23.4

10	6.76	C ₅ H ₄ O ₂	5-methylenefuran-2(5H)-one		96	0.7
11	6.97	C ₅ H ₈ O ₃	2-cetobutyric acid, methyl ester		116	4.4
12	7.55	C ₅ H ₆ O ₂	1,2-cyclopentanedione		98	1.2
13	9.22	C ₅ H ₄ O ₃	2H-pyran-3,4-dione		112	2.0
14	11.61	C ₆ H ₁₂ O ₃	1,2-O-isopropylidene Glycerol		132	1.1
15	11.86	C ₉ H ₁₈ O ₄	tetrahydropyran-2-yl diethylene glycol		190	0.9
16	12.31	C ₆ H ₁₀ O ₂	2-oxacycloheptanone		114	1.5
17	13.11	C ₈ H ₁₂ O ₂	5,5-dimethylcyclohexane-1,3-dione		140	0.8
18	14.49	C ₆ H ₁₄ O ₃	trimethylolpropane		134	1.5
19	19.98	C ₁₇ H ₃₄ O ₂	propan-2-yl tetradecanoate		270	2.7
20	21.35	C ₁₆ H ₃₂ O ₂	hexadecanoic acid		256	2.6

Compared to the pyrolysis products of sodium alginate^[30], there are less pyrolysis products in iron alginate pyrolysis process, which suggest iron ions could have the catalyzed effect on some chemical reaction happened during the pyrolysis process of alginate, resulting in the less gaseous compounds releasing. And this indicates that Iron ions had changed the pyrolysis process of alginate, favoring the dehydration, decarbonylation and decarboxylation of alginate except the depolymerization of alginate to further product combustible gaseous compounds. Under conditions of fast pyrolysis of alginate, disproportionation, dehydration, decarbonylation and decarboxylation reactions of various volatile products are all possible^[31]. Due to the catalysis effect of iron compounds, these chemical reactions mentioned above could be more efficient and selective^[32]. And most of the fragments formed might be changed to water, CO₂ and furfural on the catalysis effect of compounds containing iron. And the possible pyrolysis mechanism of iron alginate will be investigated in 3.4.

3.4 The possible pyrolysis mechanism of iron alginate

On the basis of the product distribution from iron alginate pyrolysis, carbon dioxide, furfural, 3-penten-1-ol, 2, 3-butanedione and 2-cetobutyric acid methyl ester are the major compounds, the yields of which are 78.2% in total. While the yield of CO₂, 41.1%, is much higher than that of furfural, 23.4%. On the basis of the analysis of TG-FTIR-MS and Py-GC-MS, the proposed pyrolysis mechanism of iron alginate is proposed to partial fragmentation of iron alginate by means of two major processes (a lower temperature thermal degradation process and a higher temperature thermal degradation process). The speculative pyrolysis mechanism of iron alginate is presented in Figure 8. TG-FTIR-MS indicated that the evolutions of CO₂, H₂O, compounds containing -CO- groups and compounds containing -CH- groups began at 170 °C and reached the maximum at 256 °C for CO₂ and at 223 °C for other chemicals mentioned above. According to this results of TG-FTIR-MS, it could be speculated that decarboxylation, esterification and fracture of glycosidic bonds with the evolution of H₂O and CO₂, which could be catalyzed by iron ions, are estimated to be favorable at lower temperature. However, the chemical reactions of decarboxylation and fracture of glycosidic bonds are more advanced than that of esterification and fracture of glycosidic bonds on the basis of the different yields of CO₂ and furfural. The pyrolysis of alginate with the fracture of glycosidic bonds to produce intermediate compounds takes place; and the reason is that the thermal stability of C-O bonds is less than that of C-C bonds in the hexatomic ring structure of alginate^[33]. And on the catalysis effect of compounds containing iron produced, some of the intermediate compounds underwent kinds of dehydration, rearrangement, decarboxylation, scission, condensation, and decarbonylation reactions to form a kinds of lower molecular weight compounds, such as H₂O, CO₂, furfural, CO and 2, 3-butanedione. With the temperature increases, the other gaseous products and residues can form residual chars, CO, H₂O, 2(5H)-furanone and 2-cetobutyric acid methyl ester and so on at higher temperature. There are also kinds of linear gaseous compounds, like 3-penten-1-ol, propan-2-yl tetradecanoate and hexadecanoic acid, which were produced through the hexatomic ring scission, following by dehydration and decarbonylation reactions at higher temperature^[34].

As discussed above, the compounds containing iron had the catalysis effect on the iron alginate pyrolysis process, producing more amount of CO₂, H₂O and other compounds with lower heat of combustion values. The residual char formed in the pyrolysis process of iron alginate protected the matrix from the mass and heat transfer. Both of these improve the flame retardant properties of iron alginate. As mentioned above, the flame retardant mechanism of iron alginate is the combination of gas-phased flame retardant mechanism and condense-phased flame retardant mechanism.

Figure 8 Speculative pyrolysis mechanism of iron alginate

4. Conclusions

Large differences in the flame retardancy and pyrolysis behavior were observed from the iron alginate and sodium alginate investigated by MCC and Py-GC-MS. The PHRR value of iron alginate was much lower than that of sodium alginate. The pyrolysis of iron alginate was found to yield much less products than sodium alginate. The iron ions appeared to exhibit a significant effect on the pyrolysis behavior of alginate. **TG-FTIR-MS** and Py-GC-MS results showed that iron ions might catalyze some chemical reaction on the pyrolysis process of alginate and change the pyrolysis process of alginate, releasing H₂O, CO₂ and other gaseous compounds with lower heat of combustion values. The results obtained from this study supplied some beneficial message for comprehending the flame retardant mechanism of alginate and designing biomaterials with better flame retardant properties.

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Captions

Figure 1 HRR curve of iron alginate and sodium as a function of temperature

Figure 2 TG and DTG curves of iron alginate

Figure 3 3D infrared spectra of evolved gases during iron alginate pyrolysis

Figure 4a FTIR spectra for the evolved gaseous products in gas phase of iron alginate

Figure 4b FTIR spectra for the evolved gaseous products in gas phase of iron alginate

Figure 5 FTIR spectra of typical groups as a function of temperature for iron alginate

Figure 6 Evolution curves of M/Z= 17, 18 and 44 during pyrolysis of iron alginate

Figure 7 Py-GC-MS detection of gaseous compounds obtained from pyrolysis of iron alginate

Figure 8 Speculative pyrolysis mechanism of iron alginate

Table 1 Data obtained from the MCC parameters of iron alginate

Table 2 Results of chemical formation pyrolysis products for iron alginate at 700 °C