

Effect of Cupric Ion on Thermal Degradation of Chitosan

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Received 10 December 2006; accepted 2 December 2007

DOI 10.1002/app.28001

Published online 11 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The thermal degradation of chitosan and chitosan–cupric ion compounds in nitrogen was studied by thermogravimetry analysis and differential thermal analysis (DTA) in the temperature range 30–600°C. The effect of cupric ion on the thermal degradation behaviors of chitosan was discussed. Fourier transform-infrared (FTIR) and X-ray diffractogram (XRD) analysis were utilized to determine the micro-structure of chitosan–cupric ion compounds. The results show that FTIR absorbance bands of $-N-H$, $-C-N-$, $-C-O-C-$ etc. groups of chitosan are shifted, and XRD peaks of chitosan located at 11.3, 17.8, and 22.8° are gradually absent with increasing weight fraction of cupric ion mixed in chitosan, which show that there are coordinating bonds between chitosan and cupric ion. The results of thermal analysis indicate that the thermal degradation of chitosan and chitosan–cupric ion compounds in nitrogen is a two-stage reaction.

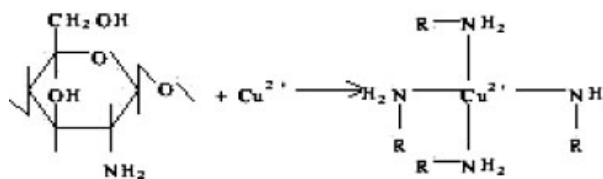
The first stage is the deacetylation of the main chain and the cleavage of glycosidic linkages of chitosan, and the second stage is the thermal destruction of pyranose ring of chitosan and the decomposition of residual carbon, in which both are exothermic. The effect of cupric ion on the thermal degradation of chitosan is significant. In the thermal degradation of chitosan–cupric ion compounds, the temperature of initial weight loss (T_{st}), the temperature of maximal weight loss rate (T_{max}), that is, the peak temperature on the DTG curve, and the peak temperature (T_p) on the DTA curve decrease, and the reaction activation energy (E_a) varies with increasing weight fraction of cupric ion. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 957–962, 2008

Key words: chitosan; cupric ion; thermal degradation; thermogravimetry analysis; differential thermal analysis

INTRODUCTION

Chitin is abundant in the shells of animals such as shrimp, crab, insects, as well as in the cell walls of plants such as fungus and algae,¹ and its output is just second only to the cellulose in nature. Chitosan, prepared by alkali deacetylation of chitin, is a nontoxic, positive charged and biodegradable polysaccharide.² Chitosan has reactive amine and hydroxy side groups, which offer possibilities of forming the cage form of net structure through hydrogen bonds or salt bonds, so that chitosan and its derivatives have stable coordination to metal ions,³ particularly to cupric ion.⁴ The chelation of the chitosan with metal ions is the one of the most important applications of chitosan. For example, the chitosan–metal ion complexes have found many applications in the wastewater treatment, the sorption of heavy metal ion from wastewater, the enrichment and examination of metal ion.^{5,6} The complexes of chitosan with many rare earth metal ions

and heavy metal ions express good catalitical activity to many chemical reactions.^{7,8} The chitosan–transition metal ions complexes have anticancer and antibacterial activity in addition to catalitical activity.⁹ In recent years, the researches on the chitosan–metal ion complex mainly have concentrated on the chitosan–Cu(II) complex. Ji et al. studied the chelating mechanism of chitosan with cupric ion, and the results indicated that the chelating was realized via four saccharide groups and one cupreous atom forming one chitosan–Cu(II) complex,^{10,11} followed as:



Su et al. computed the saturated adsorbing quantity of cupric ion was 39.6 mg g⁻¹ to spheroid allied chitosan resin through experiments, namely about 4% (w/w).¹² Wan and Petrisor studied peculiarities of cupric ion adsorbed through chitosan immobilized on sand and demonstrated the feasibility for *in situ* soil decontamination.¹³ Liu et al. used the chitosan–Cu(II) complex as the radical initiator, and demonstrated that the

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Contract grant sponsor: Guangdong Province of China; contract grant number: 2003A2030504.

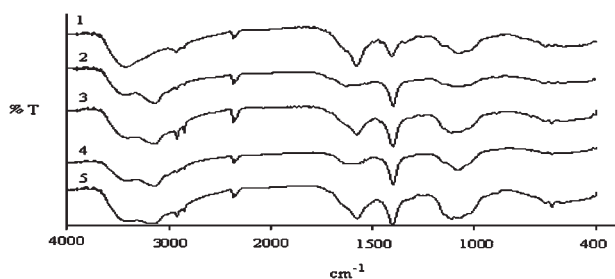


Figure 1 FTIR spectra of chitosan and chitosan-cupric ion compounds.

complex could initiate the graft copolymerization of methyl methacrylate.¹⁴ Kramareva et al. studied the structure and physicochemical properties of chitosan–Cu(II) complex prepared by different methods and determined its catalytic activity in the reactions of oxidation of *o*- and *p*-dihydroxybenzenes.¹⁵ The research of Yin et al. demonstrated that the existence of cupric ion could accelerate the degradation of chitosan by H₂O₂, but the effect of the amount of cuprate was no significant.¹⁶ The researchers still discovered that chitosan–Cu(II) complex had stronger adsorbable activity than active carbon under the same conditions.¹⁷ The results of XRD and thermal analysis of chitosan–metal ion complex show there are coordinating bonds and some structures, which are easy to break existed in the complex.^{18,19} But there are, unfortunately, few reports about the effect of cupric ion on the thermal stability of chitosan. In this article, Fourier transform-infrared (FTIR) and X-ray diffractogram (XRD) analysis are utilized to determine the micro-structure of chitosan and chitosan–cupric ion compounds. The thermal degradation of chitosan in the existence of cupric ion is systematically studied by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), and the thermal degradation mechanism of chitosan is discussed.

EXPERIMENTAL

Materials

Chitosan was obtained by Shanghai Greenbird Science and Technology Development Co. (Shanghai, China), its viscosity average molecular weight was 1.8×10^5 , and the degree of deacetylation of chitosan was more than 90%.

Preparation of chitosan–cupric ion compounds

The chitosan–cupric ion compound samples were obtained by mixing water solution of cupric sulfate with chitosan solution in 1% acetic acid, casting and drying. The samples were transparent homogeneous film containing 0–4% weight fraction of cupric ion, for Sample 1, pure chitosan (CTS), Sample 2, Cu²⁺/CTS =

1%, Sample 3, Cu²⁺/CTS = 2%, Sample 4, Cu²⁺/CTS = 3%, and Sample 5, Cu²⁺/CTS = 4%, respectively.

FTIR analysis

A Perkin–Elmer Spectrum-GX-1 infrared spectrometer was used to obtain FTIR data. FTIR spectra were recorded in the wave number range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹.

X-ray diffraction

X-ray diffraction patterns of samples were measured by a D/max IIIA diffractometer (Rigaku, Japan) and used a Cu K α target at 35 kV and 25 mA.

Thermal analysis

Thermogravimetric analysis and DTA were performed on a TG/DTA320 system (Seiko Instruments, Japan Tokyo). The mass of each sample was 5–6 mg. The carrier gas was nitrogen at a flow rate of 50 mL min⁻¹. The samples were heated from 30 to 600°C with the heating rate (B) of 10°C min⁻¹ to record the TGA, differential thermogravimetric analysis (DTG) and DTA curves.

Data processing

The kinetic parameters of a thermal decomposition reaction can be evaluated by dynamic experiments. In this case, the sample is heated from room temperature until its complete decomposition at a linearly programmed rate.

In thermogravimetric measurements, the extent of decomposition can be calculated as follows:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \quad (1)$$

where α is extent of decomposition; W_t , W_0 , W_f are the actual, initial, and final mass of the sample, respectively. A typical model for a kinetic process can be expressed as:

$$-\frac{d(1 - \alpha)}{dt} = kf(\alpha) \quad (2)$$

where $-d(1 - \alpha)/dt$ is the decomposition rate; $f(\alpha)$, the function of α , depends on the particular decomposition mechanism, the simplest and the most frequently used model of that is :

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where n is the reaction order.

TABLE I
Characteristic FTIR Bands of Chitosan and Chitosan–Cupric Ion Compounds

| Sample | FTIR (KBr) (cm ⁻¹) |
|--------|--|
| 1 | 3425.4 (–OH, –NH ₂), 1406.9 (–C–N–), 1077.9 (–C–O–C–), 650.9 (–N–H) |
| 2 | 3429.0 (–OH), 3133.6 (–NH ₂), 1401.2 (–C–N–), 1085.6 (–C–O–C–), 654.6 (–N–H) |
| 3 | 3431.7 (–OH), 3135.8 (–NH ₂), 1401.8 (–C–N–), 1113.9 (–C–O–C–), 619.6 (–N–H) |
| 4 | 3431.7 (–OH), 3136.6 (–NH ₂), 1401.2 (–C–N–), 1084.0 (–C–O–C–), 619.5 (–N–H) |
| 5 | 3431.7 (–OH), 3179.7 (–NH ₂), 1402.5 (–C–N–), 1113.4 (–C–O–C–), 619.6 (–N–H) |

k is the decomposition rate constant, which is assumed to obey the Arrhenius relationship:

$$k = Ae^{-E_a/RT} \quad (4)$$

where A is the preexponential factor (s⁻¹), E_a is the activation energy (J mol⁻¹), R is the gas constant (8.314 J mol⁻¹) and T is the absolute temperature (K). Substituting the eqs. (4) and (3) into eq. (2), we obtain

$$-\frac{d(1-\alpha)}{dt} = Ae^{-E_a/RT}(1-\alpha)^n \quad (5)$$

When a dynamic experiment is performed, the temperature T , changes linearly from the initial temperature T_0 , according to the heating rate u , during the time t , then:

$$T = T_0 + ut \quad (6)$$

Equations (5) and (6) may be combined to give:

$$\frac{d(1-\alpha)}{(1-\alpha)^n} = \frac{A}{u} e^{-E_a/RT} dT \quad (7)$$

This, according to Broido,²⁰ can be expressed as:

$$\ln \left[\ln \left(\frac{1}{1-\alpha} \right) \right] = -\frac{E_a}{RT} + \ln \left[\left(\frac{R}{E_a} \right) \left(\frac{Z}{u} \right) T_m^2 \right] \quad (8)$$

where T_m is the temperature of the maximum reaction velocity and Z is a constant, the activation energy is determined from the slope of the straight line which results by plotting $\ln\{\ln[1/(1-\alpha)]\}$ versus $1/T$.

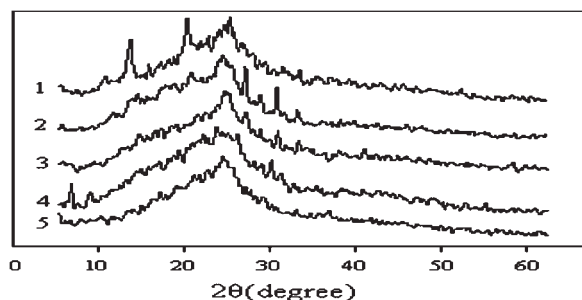


Figure 2 X-ray diffraction patterns of chitosan and chitosan–cupric ion compounds.

RESULTS AND DISCUSSION

FTIR analysis

Figure 1 shows the FTIR spectra of the chitosan and chitosan–cupric ion compounds. The characteristic FTIR bands of samples are listed in Table I. For chitosan (Sample 1), a strong and broad absorbent band centered at 3425.4 cm⁻¹ is attributed to –OH asymmetrical stretching vibration and –NH₂ stretching vibration. The absorption band at 1406.9 cm⁻¹ is caused by the coupling of –C–N– stretching vibration, and the absorption band at 1077.9 cm⁻¹ is –C–O–C– stretching vibration in glycosidic linkage.^{21,22} The absorption band at 650.9 cm⁻¹ results from –N–H stretching vibration.²³ For chitosan–cupric ion compounds (Samples 2–5), the strong and broad absorbent band is divided into two bands, the one corresponding to –OH asymmetrical stretching vibration, whose changes are no significant, the other corresponding to –NH₂ stretching vibration, which an increase of wave numbers is observed along with the increasing of weight fraction of cupric ion. The absorption wave numbers of –C–N– stretching vibration and –N–H stretching vibration of chitosan–cupric ion compounds are smaller than that of chitosan. These results indicate that it could be the interaction of –NH₂ in chitosan with cupric ion forming the chitosan–Cu(II) complex. It can be seen that the absorption wave numbers of –C–O–C– stretching vibration of chitosan–cupric ion compounds are more than that of chitosan, which is taken as an evidence of the decrease of the bond

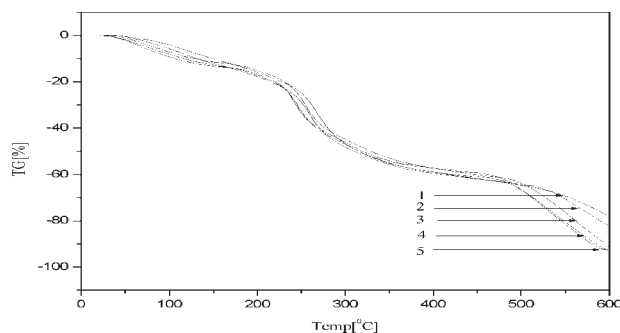


Figure 3 TG curves of thermal degradation of chitosan and chitosan–cupric ion compounds.

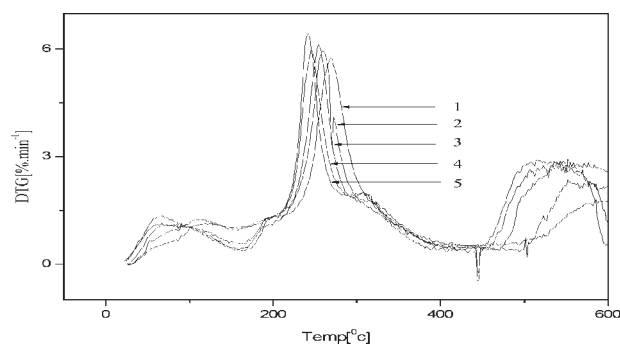


Figure 4 DTG curves of thermal degradation of chitosan and chitosan–cupric ion compounds.

energies of glycosidic linkage in chitosan, and chitosan–cupric ion compound is easier to degrade.^{16,21}

X-ray analysis

Figure 2 shows the X-ray diffraction patterns of chitosan and chitosan–cupric ion compounds. For chitosan (Sample 1), the XRD pattern exhibits its three characteristic peaks at 2θ 11.3, 17.8, and 22.8°. For chitosan–cupric ion compounds (Samples 2–5), it can be seen that the three characteristic peaks are gradually absent with the increasing of weight fraction of cupric ion mixed in chitosan, and the crystallinity of Samples 1–5 also gradually decreases, 23.4, 19.9, 12.5, 7.8, and 1.2%, respectively. The results indicate that the chitosan–Cu(II) complex formed is amorphous because of the interaction of $-\text{NH}_2$ in chitosan with cupric ion, which leads to the decrease of the crystallinity of chitosan²³ and its thermal instability.

Thermogravimetric analysis

The TG curves and the corresponding DTG curves of chitosan and chitosan–cupric ion compounds recorded in nitrogen from 30 to 600°C are shown in Figures 3 and 4 respectively. It can be seen that there are three peaks on the DTG curves. The first peak appears round 100°C, which Bihari-Varga explained as the evaporation of water.²⁴ So chitosan and chitosan–cupric ion compounds are degraded in two

TABLE II
Characteristic Temperatures for the Thermal Degradation of Chitosan and Chitosan–Cupric Ion Compounds

| Sample | The first stage (160–400°C) | | The second stage (400–600°C) | |
|--------|--------------------------------|-----------------------|---------------------------------|-----------------------|
| | T_{st} (°C) | T_{max} (°C) | T_{st} (°C) | T_{max} (°C) |
| 1 | 231.1 | 268.8 | – | 601.7 |
| 2 | 225.5 | 258.1 | – | 551.6 |
| 3 | 223.2 | 254.5 | – | 551.5 |
| 4 | 217.7 | 245.5 | – | 539.0 |
| 5 | 210.6 | 241.9 | – | 515.6 |

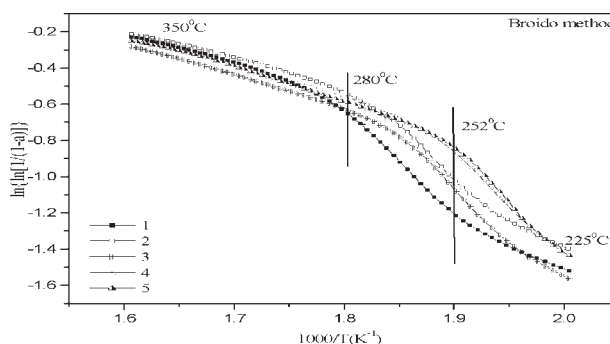


Figure 5 The relationships between $\ln\{\ln[1/(1-a)]\}$ and $1000/T$ in the first thermal degradation stage of chitosan and chitosan–cupric ion compounds.

stages corresponding to the second peak and the third peak respectively. The characteristic temperatures for the two stages of thermal degradation of chitosan and chitosan–cupric ion compounds are given in Table II. T_{st} is the temperature of initial weight loss and T_{max} is the temperature at maximum weight loss rate, that is the peak temperature on a differential thermogravimetry curve.

The first thermal degradation process occurs in the temperature range (160–400°C). For chitosan (Sample 1), it starts at 231.1°C, and reaches a maximum at 268.8°C. For chitosan–cupric ion compounds (Samples 2–5), the temperature of initial weight loss (T_{st}) and the temperature of maximal weight loss rate (T_{max}) decrease along with increasing weight fraction of cupric ion (C), which can be expressed in: $T_{\text{st}} = -5C + 231.2$ ($R^2 = 0.9735$) and $T_{\text{max}} = -6.645C + 267.0$ ($R^2 = 0.9698$), respectively.

The apparent activation energies (E_a) for the thermal degradation of chitosan and chitosan–cupric ion compounds in nitrogen are calculated from the TG curves using the method described by Broido. Broido method is based on eq. (8). Plots of $\ln\{\ln[1/(1-a)]\}$ versus $1/T$ for the temperature range 225–350°C, which is in the first thermal degradation stage, are shown in Figure 5. It can be seen that there are three distinct degradation periods. The E_a obtained for the three degradation periods are reported in Table III.

TABLE III
Activation Energies During the First Thermal Degradation Stage of Chitosan and Chitosan–Cupric Ion Compounds

| Sample | Period I (225–252°C), E_a (kJ mol ⁻¹) | Period II (252–280°C), E_a (kJ mol ⁻¹) | Period III (280–350°C), E_a (kJ mol ⁻¹) |
|--------|---|--|---|
| | 1 | 24.1 | 50.4 |
| 2 | 28.4 | 39.6 | 15.6 |
| 3 | 37.2 | 38.0 | 14.9 |
| 4 | 46.2 | 25.4 | 13.7 |
| 5 | 50.7 | 21.4 | 12.7 |

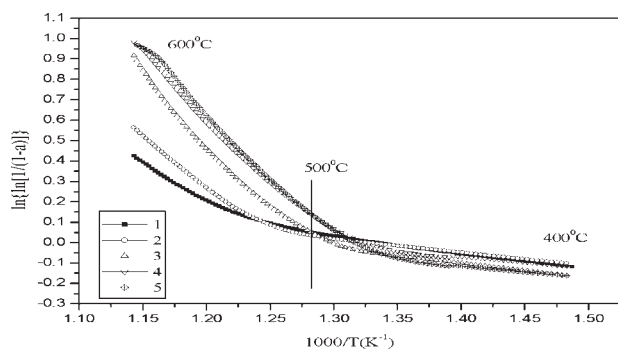


Figure 6 The relationships between $\ln\{\ln[1/(1-a)]\}$ and $1000/T$ in the second thermal degradation stage of chitosan and chitosan-cupric ion compounds.

In Period I (225–252°C), the deacetylation of chitosan,²⁵ E_a increases with increasing weight fraction of cupric ion. In Period II (252–280°C), the cleavage of glycosidic linkages of chitosan,² the decrease of E_a is observed with increasing amount of cupric ion. In Period III (280–350°C), the further cleavage of glycosidic linkages of chitosan, E_a slightly decreases with increasing weight fraction of cupric ion. The results indicate that, the conformation change of chitosan resulted from the mixing of cupric ion in chitosan has effect on the formation of new phases of the polymer, which partly decreases bond energies of glycosidic linkages in chitosan, consequently leads to its thermal instability. The conclusion is well correlated with that of Sreenivasan.²⁶

The second thermal degradation process occurs in the temperature range (400–600°C), where T_{\max} decreases along with increasing weight fraction of cupric ion (C) (Table II), which can be expressed in $T_{\max} = -18.48C + 588.9$ ($R^2 = 0.8617$). Plots of $\ln\{\ln[1/(1-a)]\}$ versus $1/T$ in the second thermal degradation stage are shown in Figure 6. It can be seen that there is two distinct degradation periods. The E_a obtained for the two degradation periods are reported in Table IV.

In Period I (400–500°C), the thermal destruction of pyranose ring where C_2 , C_3 , and C_6 predominate, forms formic acid, acetic acid, butyric acid, and a series of lower fatty acids^{27,28} and E_a decreases slightly

TABLE IV
Activation Energies During the Second Thermal Degradation Stage of Chitosan and Chitosan-Cupric Ion Compounds

| Sample | Period I (400–500°C), E_a (kJ mol ⁻¹) | Period II (500–600°C), E_a (kJ mol ⁻¹) |
|--------|--|---|
| 1 | 6.4 | 27.4 |
| 2 | 5.5 | 41.3 |
| 3 | 6.0 | 54.6 |
| 4 | 4.6 | 55.0 |
| 5 | 4.8 | 56.7 |

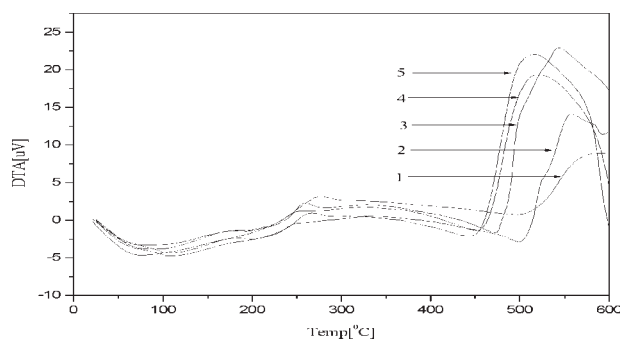


Figure 7 DTA curves of thermal degradation of chitosan and chitosan-cupric ion compounds.

along with increasing amount of cupric ion, which indicates that cupric ion may catalyze the thermal destruction of pyranose ring. In Period II (500–600°C), the further thermal destruction of pyranose ring and the decomposition of the residual carbon,²⁹ E_a increases with increasing amount of cupric ion.

Differential thermal analysis

DTA curves of chitosan and chitosan-cupric ion compounds recorded in nitrogen from 30 to 600°C are shown in Figure 7. Table V summarizes the heat effect data for the samples.

For chitosan (Sample 1), the exothermic peak at 277.8°C in the first stage (160–400°C) corresponds to the deacetylation of the main chain and the cleavage of glycosidic linkages of chitosan, and the exothermic peak at 592.8°C in the second stage (400–600°C) corresponds to the thermal destruction of pyranose ring and the decomposition of the residual carbon. For chitosan-cupric ion compounds (Samples 2–5), there are also two exothermic peaks, and all peak temperatures shift to lower temperature in two degradation stages with the increase of the amount of cupric ion, indicating that the chelating of chitosan with cupric ion leads to its thermal instability. These results are well correlated with the results of TGA.

TABLE V
Peak Temperatures and Heat Effect on the DTA Curves During the Thermal Degradation of Chitosan and Chitosan-Cupric Ion Compounds

| Sample | The first stage (160–400°C) | | The second stage (400–600°C) | |
|--------|--------------------------------|-------------|---------------------------------|-------------|
| | Peak temp. (°C) | Heat effect | Peak temp. (°C) | Heat effect |
| 1 | 277.8 | Exo | 592.8 | Exo |
| 2 | 266.7 | Exo | 556.8 | Exo |
| 3 | 261.6 | Exo | 544.4 | Exo |
| 4 | – | Exo | 522.8 | Exo |
| 5 | – | Exo | 517.4 | Exo |

CONCLUSIONS

The thermal degradation of chitosan and chitosan–cupric ion compounds in nitrogen is a two-stage reaction. The first stage is the deacetylation of the main chain and the cleavage of glycosidic linkages of chitosan, and the second stage is the thermal destruction of the pyranose ring and the decomposition of the residual carbon, which are both exothermic. The effect of cupric ion on the thermal degradation of chitosan is significant. In the thermal degradation of chitosan–cupric ion compounds, the temperature of initial weight loss (T_{st}), the temperature of maximal weight loss rate (T_{max}) and the peak temperature (T_p) on the DTA curve decrease along with increasing weight fraction of cupric ion. The reaction activation energy (E_a) varies with increasing weight fraction of cupric ion. The FTIR and XRD analysis results of chitosan–cupric ion compounds demonstrate that the coordinating bond resulted from the chelating of $-NH_2$ in chitosan with cupric ion decreases the bond energies of glycosidic linkages in chitosan and their crystallinity, which leads to their thermal instability.

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