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THE EFFECT OF METAL IONS ON THERMAL OXIDATIVE DEGRADATION OF COTTON CELLULOSE AMMONIUM PHOSPHATE

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Abstract

The thermal oxidative degradation of cellulose, and of cellulose ammonium phosphate and its metal complexes products were studied by thermal analysis, infrared spectroscopy and elemental analysis. The temperature of decomposition was lower for metal complexes of cellulose ammonium phosphate than those samples untreated by metal ions and the values of char yield were greater for treated cellulose than those untreated. This indicates the metal ions can catalyze the reaction of degradation and form more char.

Keywords: cellulose ammonium phosphate, fire proof, thermal analysis, thermal oxidative degradation

Introduction

Cotton cellulose is one of the most important natural materials that is intrinsically flammable, thus the emphasis on reducing combustibility has centered on the chemical modification of it by treating with flame-retardant. The primary role of a flame-retardant is to alter degradation process so that a lower percent of flammable volatiles is produced and a correspondingly larger amount of char is formed. It has long been known that the phosphorylation of cellulose is the simplest method to obtain durably flame-retarded cellulose [1]. In recent years, studies have been made on the effect of transition metal ions on the thermal degradation of cellulose ammonium phosphate [2–5].

However, to date complexes of cellulose ammonium phosphate with metals such as cerium(IV), lead, bismuth have not been reported. In order to understand the mechanism of the thermal oxidative degradation of cellulose ammonium phosphate and its metal complexes, coordinate complexes of ammonium phosphate with various metal ions were prepared and their thermal properties investigated by using infrared spectroscopy, thermal analysis and chemical analysis. This study shows that the combustibility of cotton cellulose has been reduced with the introduction of the metal ions.

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Experimental

Raw material

The following samples of cellulose, cellulose ammonium phosphate and its metal complexes were selected for the present work. Sample (*i*) was cotton cellulose (Hebei Province Dingzhou Sanitary Plant, China), dried in vacuo at 333 K for 1 h. Sample (*ii*), cellulose ammonium phosphate (CAP) was obtained by treating dried cellulose (4.86 g) and carbamide (7.20 g) with phosphorus oxychloride (6.89 g) in pyridine at 388 K for 24 h. The product was filtered, washed thoroughly with water and dried in vacuo. Samples (*iii-ix*) were prepared by treating the cellulose phosphate with 5% ferrous sulphate, copper sulphate, zinc sulphate, manganese sulphate, cerium(IV) sulphate, lead nitrate and bismuth nitrate, respectively. Each reaction mixture was stirred at ambient temperature for 72 h.

Thermal analysis

The differential thermal analysis (DTA) and thermogravimetry (TG) were carried out on a DT-40 thermal analyzer (Shimadzu, Japan) under the following conditions: sample mass: 4 mg, heating rate: 10 K min^{-1} in static air. Calcined alumina was taken as the reference material.

Infra spectrometry

For the IR study (FTS-40, USA), the residue of phosphorylated cellulose was analyzed by the KBr technique. The residual samples were prepared by heating them in a DTA cell. The heating temperatures were 473, 523, 573 and 633 K, respectively.

Elemental analysis

The mass fraction of P and Cl was obtained using a PE-2400 Elemental Analyzer (USA).

Results and discussion

The mass fraction of P, Cl and the residual char from decomposition of samples (*i-ix*) are given in Table 1. The data show that the char yields of samples (*ii-ix*) are more than that of the original cellulose, especially in the case of samples (*iii-ix*) those were treated with metallic cations. The results indicate that the combustibility is reduced for cellulose ammonium phosphate treated with metal ions, especially that treated with Mn^{2+}.

The existence of P and Cl in the sample (*ii*) make the char yield much higher than original cellulose. When heated strongly, the product yields phosphorus acid and polyphosphorus acid, which are effective in catalyzing dehydration and charring. This is the main reason why all phosphorus-containing samples are effective flame-retardants.

Table 1 Analytical data for cellulose, cellulose of ammonium phosphate and its metal complexes (mass fraction/%)

Sample No.	Compound	P/mass%	Cl/mass%	Char yield at 1123 K (air)/mass%
i	Cotton cellulose	---	---	4.1
ii	Cellulose ammonium phosphate	2.83	0.38	11.9
iii	Fe(II) complex of CAP	1.71	0.26	18.3
iv	Mn(II) complex of CAP	2.06	0.14	32.2
v	Zn(II) complex of CAP	2.54	0.32	17.4
vi	Cu(II) complex of CAP	1.91	0.34	16.5
vii	Ce(IV) complex of CAP	1.57	0.23	17.6
viii	Pb(II) complex of CAP	1.45	0.12	28.0
ix	Bi(III) complex of CAP	1.75	0.24	30.4

After treated with metallic cations the mass fraction of P and Cl of samples (*iii-ix*) is lower than that of the sample (*ii*), however the char yield has improved. This indicates that the metal ions can catalyst the forming of char.

From the DTA curves of samples (*i-ix*), the two exothermic peaks' temperatures were determined and are given in Table 2. Thermal analysis of original cellulose in air is shown in Fig. 1. Two exothermic peaks appear at 638 and 734 K. The first exotherm is due to the dehydration, decomposition and rearrangement of the products. The second exotherm is due to the cross-bridging and aromatic cyclization of charred residue. From Fig. 2, two exothermic peaks appear at 588 and 727 K for sample (*ii*). Obviously, the decomposition temperature has decreased. The first is due to the dehydration, dehydrohalogenation and dephosphorylation, while the second is due to the oxidation and aromatic cyclization of the charred residue, and the decomposition of the polyphosphorus acid [6, 7]. This is supported by the mass loss indicated by the TG curve. Figures 3–9 show the first exothermic peaks of the samples

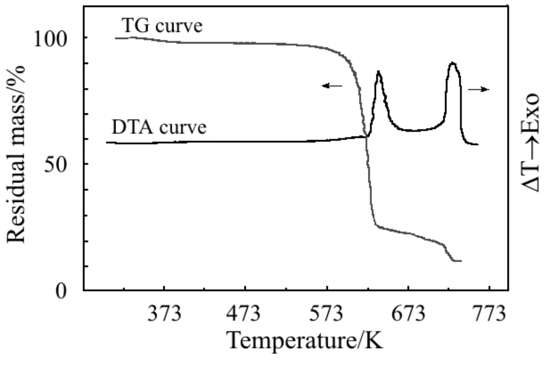

Fig. 1 Thermoanalytical curves of sample (*i*) in air

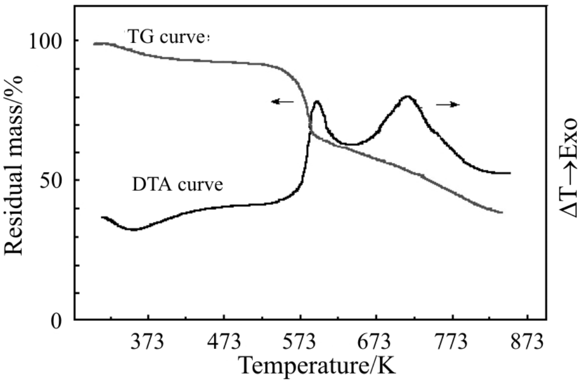

Fig. 2 Thermoanalytical curves of sample (*ii*) in air

(*iii-ix*) appear at 592, 607, 595, 577, 616, 593 and 599 K, and the second exothermic peaks at 711, 749, 764, 742, 769 and 776 K. Most of them are higher than that of sample (*ii*). Furthermore, the second peaks have become broader than that of sample (*ii*). All these indicate that the metal complexes changed the process of decomposition.

Table 2 Thermal characteristics of cellulose, cellulose of ammonium phosphate and its metal complexes

Sample No.	Compound	First stage	Second stage
		T_p/K	T_p/K
i	Cotton cellulose	638	734
ii	Cellulose ammonium phosphate	588	716
iii	Fe(II) complex of CAP	592	711
iv	Mn(II) complex of CAP	607	749
v	Zn(II) complex of CAP	595	764
vi	Cu(II) complex of CAP	577	742
vii	Ce(IV) complex of CAP	616	769
viii	Pb(II) complex of CAP	593	776
ix	Bi(III) complex of CAP	599	713

The TG curves of samples showed two significant areas of mass loss, which have been termed here the two stages of thermal oxidative degradation. The original cellulose shows a rapid rate of mass loss at 586–623 K. Similar mass loss curves for CAP and metal ions complexes were obtained. Samples (*ii-ix*) had a smaller mass loss at 623 K than sample of original cellulose. The figures show that introduction of metal ions in CAP has little influence on the thermal oxidative degradation. Degradation reactions of cellulose are accelerated and result in large amounts of residual products. The reason is that flame-retardants catalyze the decomposition reaction [4].

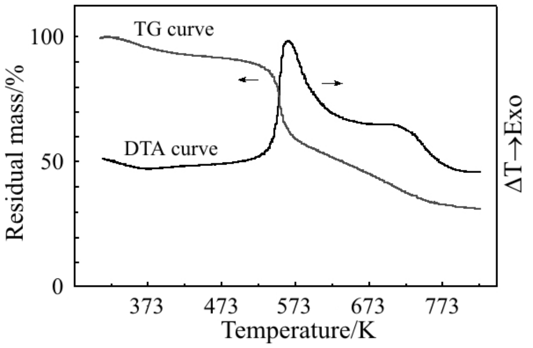

Fig. 3 Thermoanalytical curves of sample (*iii*) in air

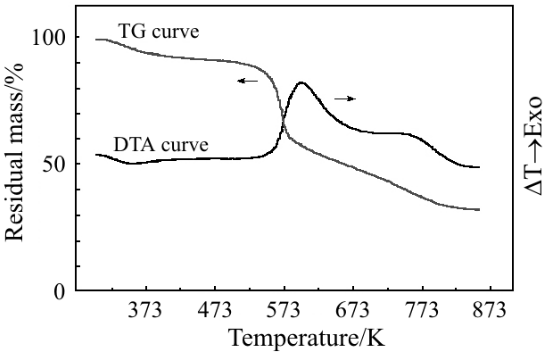

Fig. 4 Thermoanalytical curves of sample (*iv*) in air

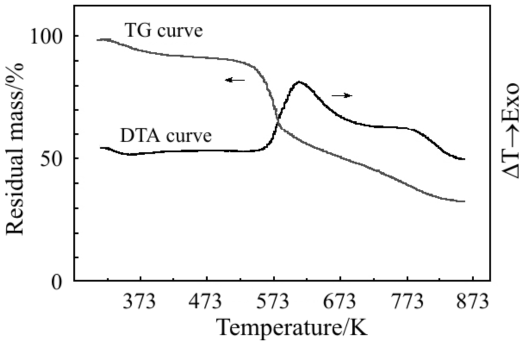

Fig. 5 Thermoanalytical curves of sample (*v*) in air

The IR spectra of cellulose ammonium phosphate are displayed in Fig. 10. At 523 K, band at 3400 cm^{-1} decreases and 2800 cm^{-1} disappears and new bands appear at 1720 (C=O), 1250 (P=O), 1100, 900 and 750 cm^{-1}. This indicates that skeletal rearrangement has occurred. The band at 1100 cm^{-1} is due to PO_4^{-3}, and those at 900 and

750 cm^{-1} are due to P–O–P and P–O stretching in polyphosphate. At this temperature, the absorption band at 1630 cm^{-1} is shifted to 1600 cm^{-1} (due to conjugated C=C).

Figure 11 shows the change of IR spectra of Mn(II) complex of CAP as example of metal complexes of CAP. At 473 K, the band at 2800 cm^{-1} has disappeared. At this temperature new bands appear at 1720, 1250, 1100, 900 and 750 cm^{-1}. The appearance of the

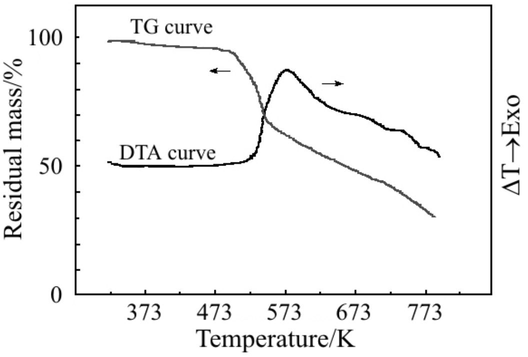

Fig. 6 Thermoanalytical curves of sample (*vi*) in air

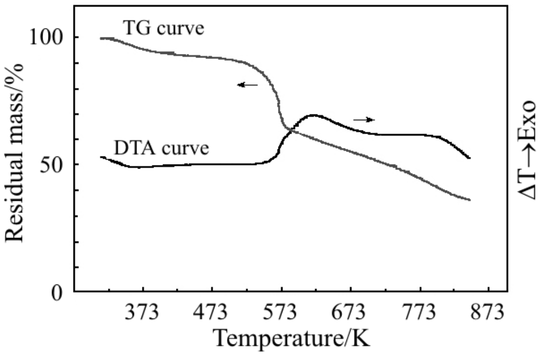

Fig. 7 Thermoanalytical curves of sample (*vii*) in air

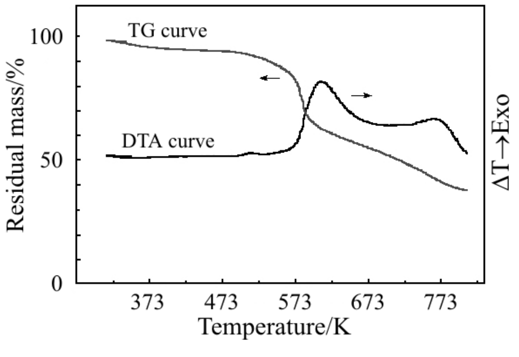

Fig. 8 Thermoanalytical curves of sample (*viii*) in air

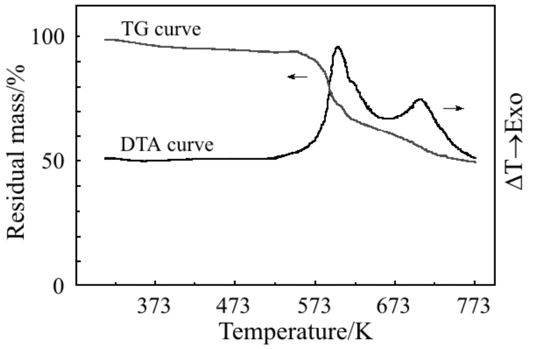

Fig. 9 Thermoanalytical curves of sample (*ix*) in air

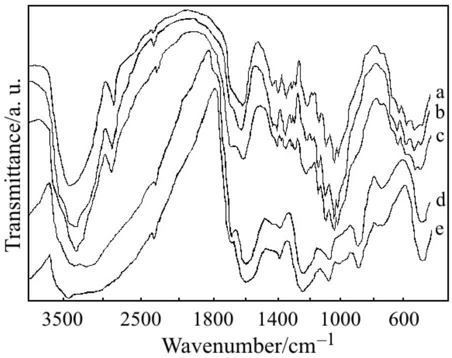

Fig. 10 IR spectra of cellulose ammonium phosphate: a – CAP; b–e – Char of CAP at 473, 523, 573 and 633 K, respectively

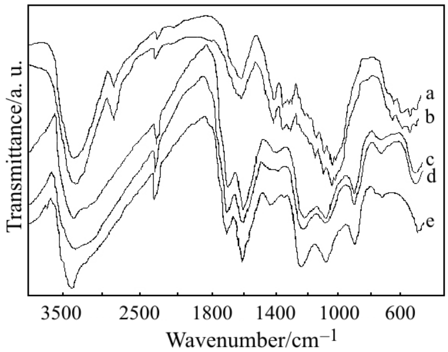

Fig. 11 IR spectra of Mn(II) complex of CAP: a – Mn(II) complex of CAP; b–e – Char of Mn(II) complex at 473, 523, 573 and 633 K, respectively

bands at 1720 and 1100 cm^{-1} indicates the formation of C=O and $M_x(PO_4)_y$ (M is the metal cation). These are similar to those observed with cellulose ammonium phosphate. The data indicate the formation of a similar type of compounds on decomposition of the metal complexes of cellulose phosphate to those of cellulose ammonium phosphate. Hence, the basic mechanism of degradation is the same in both instances.

DTA and TG data for CAP and its metal complexes show that for the introduction of metal ions result in (a) a decrease in the temperature of decomposition and (b) an increase in char yield compared with the untreated cellulose. The metal ions have effect on the decomposition of cellulose ammonium phosphate and reduce combustibility of products.

When heated, samples (*iii-ix*) decompose to give a metal phosphate of the form $M_x(PO_4)_y$ and phosphorus acid. Metal phosphates, being Lewis acid, enhance dehydration reaction. Both the decomposition products can polymerize to form poly-metal phosphate and polyphosphorus acid, which can further catalyze dehydration of cellulose.

The hydrogen chloride released in the decomposition process may react with metal phosphate to form metal chloride, which is similar to hydrogen chloride in promoting the dehydration, condensation and charring reaction [4].

References

1 A. R. Horrocks, Rev. Prog. Color., 16 (1986) 62.
2 B. Kaur, R. K. Jain and I. S. Gur, J. Anal. Appl. Pyrol., 9 (1986) 173.
3 B. Kaur, R. K. Jain and I. S. Gur, J. Anal. Appl. Pyrol., 11 (1987) 256.
4 C. M. Tian, Thermochim. Acta, 253 (1995) 243.
5 Sekiguchi Yuka and Sawatari Chie, Text. Res. J., 70 (2000) 71.
6 C. M. Tian and J. Z. Xu, J. Therm. Anal. Cal., 55 (1999) 93.
7 B. K. Kandola and A. R. Horrocks, Rev. Macromol. Chem. Phys., C36 (1996) 721.