J Therm Anal Calorim (2009) 98:245–251
DOI 10.1007/s10973-009-0122-4

Thermal degradation and smoke suspension of cotton cellulose modified with THPC and its lanthanide metal complexes

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Received: 29 October 2008 / Accepted: 4 March 2009 / Published online: 10 June 2009

Abstract Complexes of cell–THPC–urea–ADP with transition metal ion Co^{2+} and lanthanide metal ions such as La^{3+}, Ce^{4+}, Nd^{3+} and Sm^{3+} have been prepared. The thermal behavior and smoke suspension of the samples are determined by TG, DTA, DTG and cone calorimetry. The activation energies for the second stage of thermal degradation have been obtained by following Broido equation. Experimental data show that for the complexes of cell–THPC–urea–ADP with the metal ions, the activation energies and thermal decomposition temperatures are higher than those of cell–THPC–urea–ADP, which shows these metal ions can increase the thermal stability of cell–THPC–urea–ADP. Moreover, these lanthanide metal ions can more increase thermal stability of samples than do the transition metal ion Co^{2+}. The cone calorimetry data indicate that the lanthanide metal ions, similar to transition metal Co^{2+}, greatly decrease the smoke, CO and CO_2 generation of cell–THPC–urea–ADP, which can be used as smoke suppressants.

Keywords Cotton cellulose · Degradation · Flame retardant · Metal complexes · Smoke suspension

Introduction

Cotton cellulose is used extensively to make life pleasant, comfortable and colorful. Unfortunately, it is flammable and causes a fire hazard. According to fire statistics, about 50% of fires are caused by textiles in the world [1], and the cotton cellulose is one of important components in textiles. So the emphasis on reducing combustibility has centered on its chemical modification. There are also many studies on thermal degradation of cotton cellulose treated with flame retardants [2–5]. However, with environmental sustainability required, the effects of flame-retardants on both smoke generation and the toxicity of combustion products have become special important, as flame retardant cellulose has been reported to produce denser smoke than pure cellulose [6].

In previous papers [7–9], compounds of transition metals have been found to be effective smoke retarders. However, there is little information about the effects of lanthanide metal ions on smoke suspension and thermal degradation of cotton cellulose treated with flame retardants. So the main objective of the work reported here is to investigate the effects of lanthanide metal ions on the thermal degradation and smoke suspension of cotton cellulose modified with flame retardant.

In this paper, complexes of cell–THPC–urea–ADP with lanthanide metal ions such as La^{3+}, Ce^{4+}, Nd^{3+} and Sm^{3+} were prepared. To compare lanthanide with transition metal, transition metal ion Co^{2+} complex of cell–THPC–urea–ADP was also prepared. The thermal degradation of samples was studied from ambient temperature to 800 °C by TG, DTA, DTG. The smoke suspension of samples was determined by cone calorimetry.

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Experimental

Materials

Cotton cellulose of commercial grade (Hebei province, China) was selected for flame-retardant treatment. The cotton cellulose was immersed in 24% NaOH solution at room temperature for 24 h (mercerization process). The alkali was then filtered off and the sample was washed repeatedly with distilled water. The sample was dried in an oven at 60 °C and then stored in a desiccator.

Cotton cellulose treatment

The preparation of the samples is corresponded to references [7–9]. THPC (Shanghai, China) was neutralized with NaOH to give a pH value equal to 6.5 and its 45% solution was mixed with 22.5% urea solution. The pH value was adjusted to 6.5 and a small amount of ADP was added. The resulting mixture was used as the treating solution. The mercerized cotton cellulose was immersed in the treating solution for 30 min at room temperature. The treated cotton cellulose was dried at 60 °C in an oven for 60 min. Curing of these treated cellulose was carried out by heating at 160 °C for 5 min in the oven. After cooling, the sample was thoroughly washed with distilled water for an hour and dried in an oven at 60 °C.

Co^{2+}, La^{3+}, Ce^{4+}, Nd^{3+} and Sm^{3+} complexes of cell–THPC–urea–ADP were prepared by treating 6 g of cell–THPC–urea–ADP in each instance with 5% aqueous solutions of $CoSO_4 \cdot 7H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Ce(SO_4)_2 \cdot 4H_2O$, $Nd(NO_3)_3$ and $Sm(NO_3)_3$ at room temperature for 72 h under constant stirring. Each product was washed repeatedly with water until the filtrate was free from metal salt and dried overnight in an oven at 60 °C then stored in a desiccator.

Limiting-oxygen-index

The limiting-oxygen-index (LOI) value is the minimum amount of oxygen in oxygen–nitrogen mixture required to support combustion over 3 min or till specimen is consumed for more than 5 cm from the top. The higher the LOI value is, the more effective the flame-retardant treatment is. LOI values were determined in accordance with ASTM D2863-70 by means of a General Model HC-1 LOI apparatus. The results are given in Table 2.

Thermal analysis

Differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). DTA, TG and DTG were performed under a dynamic air (dried) atmosphere at a heating rate of 20 °C min^{-1}. α-Al_2O_3 was taken as the reference material.

Cone calorimetry

The test method using the cone calorimeter was ASTM M 1354, *Standard Test Method for Heat Release Rates for Materials and Products Using a Consumption Calorimeter* [10]. Approximately 13.1 MJ of heat were released per kilogram of oxygen consumed. The external heat fluxes usually chosen were 35 kW/m^2 because it corresponds to a common heat flux in mild fire scenario fire. Our samples were exposed to a Stanton Redcroft Cone Calorimeter under a heat flux of 35 kW/m^2. The cone data reported in this work were the average of three replicated experiments.

Elemental analysis

The elemental analysis was carried out using a PE-2400 Elemental Analyzer (USA). Phosphorus was estimated by the colorimetric method. Nitrogen was determined by the Kjeldahl method. The results are given in Table 2.

Results and discussion

The DTA, TG and DTG curves of (1) cotton cellulose, (2) cell–THPC–urea–ADP, (3) Co^{2+}, (4) La^{3+}, (5) Ce^{4+}, (6) Nd^{3+} and (7) Sm^{3+} complexes of cell–THPC–urea–ADP were obtained in a dynamic air atmosphere from ambient temperature to 800 °C and are shown in Figs. 1, 2, 3, 4, 5, 6, 7.

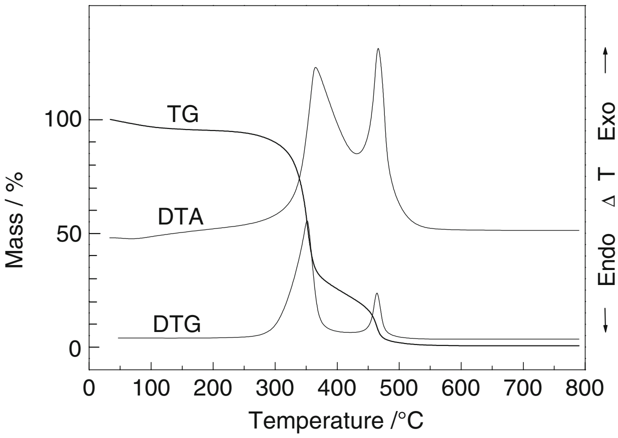

Fig. 1 Thermal analysis curves of cotton cellulose

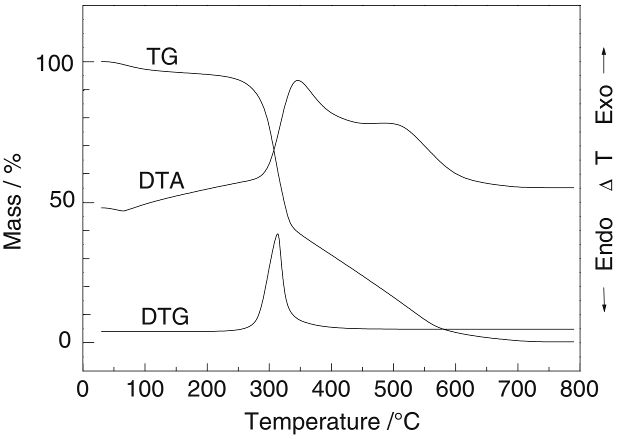

Fig. 2 Thermal analysis curves of cell–THPC–urea–ADP in air

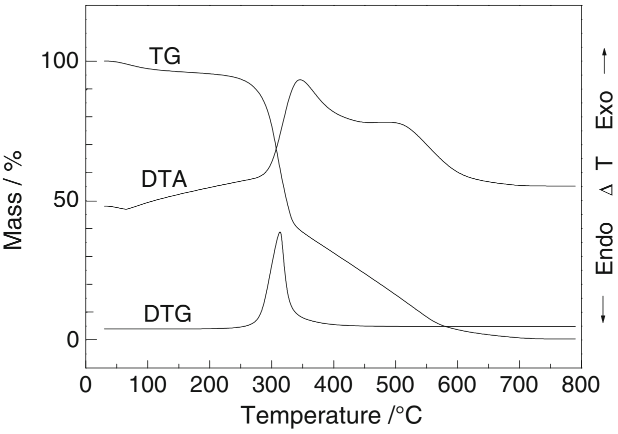

Fig. 3 Thermal analysis curves of Co^{2+} complex of cell–THPC–urea–ADP in air

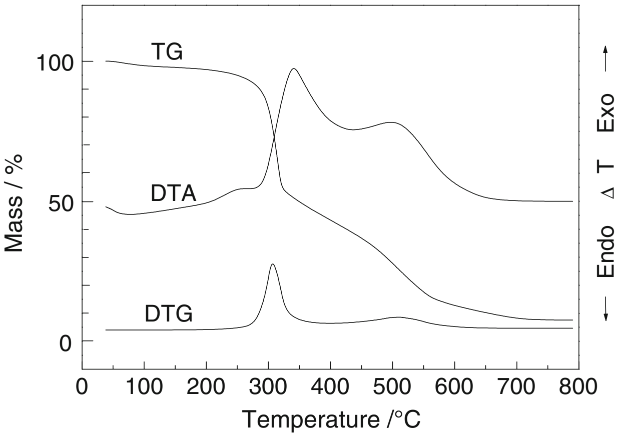

Fig. 4 Thermal analysis curves of La^{3+} complex of cell–THPC–urea–ADP in air

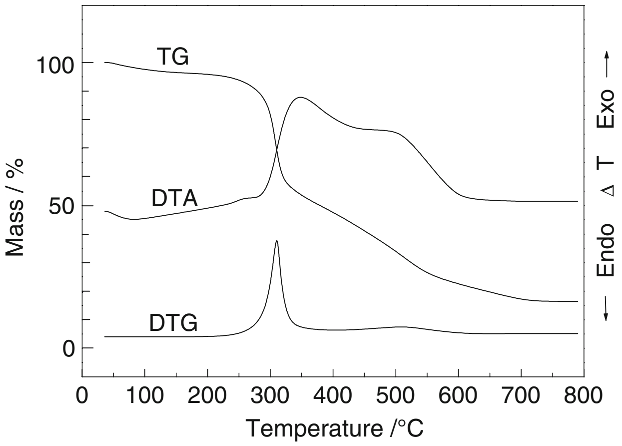

Fig. 5 Thermal analysis curves of Ce^{4+} complex of cell–THPC–urea–ADP in air

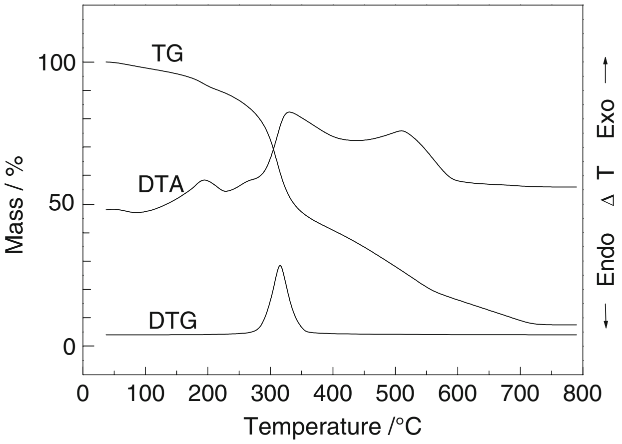

Fig. 6 Thermal analysis curves of Nd^{3+} complex of cell–THPC–urea–ADP in air

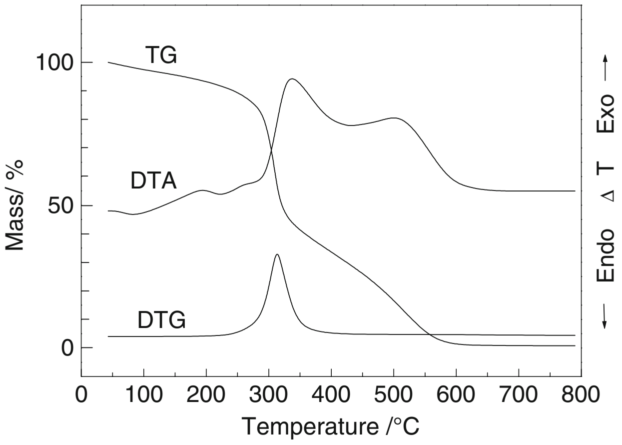

Fig. 7 Thermal analysis curves of Sm^{3+} complex of cell–THPC–urea–ADP in air

Differential thermal analysis

From the DTA curves of samples 1–7, the initiation temperatures (T_i), peak temperatures (T_p) and termination temperatures (T_t) of the various endotherms and exotherms were investigated and are given in Table 1. The DTA curve of cotton cellulose shows two large exotherms with their respective peak maxima at 366 and 468 °C. Before 350 °C, decomposition and dehydration occur to form some flammable volatile products, and the first exotherm peaking at 366 °C is due to the oxidation of these volatile products. Another exotherm, peaking at 468 °C, represents oxidation of the charred residues. The dehydration process dominates at low temperatures and ultimately leads to a carbonaceous residue. At higher temperatures, cleavage of glycosyl units by intra-molecular transglycosylation starts, forming ultimately a tarry mixture with levoglucosan as the major constituent [11]. Levoglucosan decomposes into volatile and flammable products and therefore plays a key role in the flammability of cellulose.

The DTA curve of cell–THPC–urea–ADP is quite distinct from that of pure cotton cellulose. The treated cotton cellulose seemed to decompose in two steps [12]. A breakdown or depolymerization of the THPC–urea–ADP finish, a catalyzed dehydration of the cellulose, and some bond formation occurred during the first step. Two large exotherms with peak maxima at 344 and 514 °C are shown in Fig. 3, respectively. The second step involved a breakdown of the cellulose chain, evolution of gases from both the cellulose and the finish polymer, and continuation of bond formation. The bond formation was probably due to a phosphorylation reaction at the C-6 hydroxyl group of the anhydroglucose unit as suggested [13]. Phosphorylation at this position would inhibit the formation of levoglucosan and prevent further breakdown to flammable gases. This would account for the increased amount of char formed over that for untreated cotton cellulose. The last large exotherm peaking at 514 °C is due to the combustion of the char [14].

In the DTA curves of the metal complexes of cell–THPC–urea–ADP (samples 4–7), the first peak, a new endotherm with peak maxima in the range 225–279 °C, represents depolymerization, a catalyzed dehydration of the cellulose and some bond formation. For the metal complexes (samples 3–7), there are also two large exotherms in each case. The decomposition stage, which is represented by the first exotherm, is very different in the decomposition temperature in all the complexes. The peak temperatures of La^{3+}, Ce^{4+}, Nd^{3+} and Sm^{3+} complexes are 346, 341, 348, 328 and 337 °C, respectively. The last exotherm, which is due to oxidative decomposition of the residual products, also shows considerable variation in the different complexes.

For cotton cellulose, the two exotherms are sharp and narrow, which shows a large rate of heat release. For the samples 2–7, the two exotherms become small and broad,

Table 1 Peak temperatures in DTA curves of samples 1–7

No.	Compound	DTA curve			Nature of peak
		T_i	T_p	T_t	
1	Cellulose	300	366	430	Exo (large)
		430	468	500	Exo (large)
2	Cell–THPC–urea–ADP	285	344	435	Exo (large)
		435	514	605	Exo (large)
3	Co^{2+} complex of cell–THPC–urea–ADP	283	346	439	Exo (large)
		439	515	608	Exo (large)
4	La^{3+} complex of cell–THPC–urea–ADP	250	278	290	Endo (small)
		290	341	431	Exo (large)
		431	510	620	Exo (large)
5	Ce^{4+} complex of cell–THPC–urea–ADP	254	279	290	Endo (small)
		290	348	442	Exo (large)
		442	500	603	Exo (large)
6	Nd^{3+} complex of cell–THPC–urea–ADP	196	229	278	Endo (small)
		278	328	439	Exo (large)
		439	512	595	Exo (large)
7	Sm^{3+} complex of cell–THPC–urea–ADP	193	225	280	Endo (small)
		280	337	434	Exo (large)
		434	507	601	Exo (large)

smallest for sample-6. Heat release is distributed between two broad peaks covering a wide area, resulting in a major reduction in rate of heat release and flammable products which fuel the flaming combustion reaction. In the other hand, the second exotherms become much smaller for the samples 2–7, which indicates that oxidation of the charred residues becomes more difficult due to the existence of flame retardants.

Thermogravimetry

From Figs. 1–7, it can be seen that the second stages in thermal decomposition of the samples, decompose mainly and quickly, play a key role attributed to the combustibility. So we mainly discuss this stage. Temperature Range (TR), Mass Loss (ML) at the second stage (quick mass loss rate) in TG, $T_{\max}$ in DTG are listed in Table 2. Generally, at lower temperatures, the thermal degradation of cellulose includes dehydration, depolymerization, oxidation, evolution of carbon monoxide, carbon dioxide, and formation of carbonyl and carboxyl groups and ultimately a carbonaceous residue; At higher temperatures, cellulose decomposes into a tarry mixture (mainly levoglucosan) which further decompose into volatile and flammable products [11, 15]. The main role of flame retardants containing phosphorus is to minimize the formation of levoglucosan by lowering the decomposition temperature of cellulose and enhancing char formation by catalyzing the dehydration and decomposition reaction [16, 17]. However, lowering the decomposition temperature of cellulose is to decrease its thermal stability, which is not favorable. So the two points must be considered simultaneously.

From Figs. 1–7 and Table 2, it can be seen that for the cotton cellulose (sample-1), initial decomposition temperature is 320 °C, the second stage is in a range 320–365 °C, the maximum in DTG is 352 °C, and the mass loss is 63.6%. For cell–THPC–urea–ADP, initial decomposition temperature is 255 °C, the second stage is in a range 255–315 °C, and the maximum in DTG is 300 °C, all these much decreased compared with those of cotton cellulose, which shows that the thermal stability of the cell–THPC–urea–ADP is much decreased because of the catalyzing dehydration and decomposition reaction. For samples 3–7, the decomposition temperature range is 280–340 °C, the maximum in DTG is in a range 306–314 °C, all higher than that of cell–THPC–urea–ADP, which shows that the thermal stability of samples is increased. There are no too much differences in these increases for samples 3–7. However, the mass losses for samples 4–7 (33.8–38.7%) are much less than that of sample-3 (50.5%), which shows that the thermal stability of decomposition intermediate for the lanthanide metal ions complexes is higher than that of transition metal ion Co^{2+} complex. Though the mass loss in the second stage for sample-6 is smallest, the mass loss in the fist stage is great which is not favorable.

Table 2 Thermal degradation and analytical data of samples 1–7

No.	TR (°C)	ML (%)	Ea (kJ/mol)	$T_{\max}$ (°C)	LOI (%)	P (%)	N (%)	M (%)
1	320–365	63.6	189.5	352	18.0	–	–	–
2	255–315	36.2	80.9	300	30.2	1.74	3.81	–
3	280–335	50.5	100.4	312	28.0	1.44	3.00	0.75
4	285–324	38.7	137.4	306	27.4	1.35	2.87	0.71
5	285–326	36.1	118.9	312	28.5	1.42	2.81	0.76
6	283–337	33.8	97.4	314	27.8	1.43	2.82	0.69
7	287–330	38.2	103.0	312	27.1	1.28	2.81	0.75

In order to understand the flame retardant properties of these samples, LOI of samples is measured, given in Table 2. From Table 2, we can see that samples 2–7 show high values of LOI. This suggests that the combustibility of cotton cellulose treated with flame retardants decreases. Moreover, the sample-2 containing highest content of phosphorus and nitrogen shows highest value of LOI. The second stage of decomposition for sample-2 occurs at lower temperatures (255–315 °C) and produces less flammable volatile products, resulting in higher flame retardancy.

The kinetic parameters for the second stage were determined using the following equation, given by Broido [15]:

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{\mathrm{Ea}}{R}\cdot\frac{1}{T} + \ln\left(\frac{R}{\mathrm{Ea}}\cdot\frac{Z}{\beta}\cdot T_{\mathrm{m}}^{2}\right)$$

where y is the fraction of the number of initial molecules not yet decomposed, T_{m} the temperature of the maximum reaction rate, β the rate of heating and Z the frequency factor.

Using the Broido method, from the slopes of the TG curves in Figs. 1–7, plots of $\ln(\ln(1/y))$ vs. 1/T for the second stage of thermal degradation were drawn and linear plots were obtained in each instance. The values of the energies of activation Ea determined from the slopes are given in Table 2.

For the second stage, the major degradation and mass loss stage, the energy of activation for sample-2 is 80.9 kJ/mol, is much decreased compared to cotton cellulose (189.5 kJ/mol). The reason is that the flame retardant catalyzes decomposition reaction. The lower decomposition temperatures (255–315 °C) also support this. The energy of activation for sample-3 is 100.4 kJ/mol, higher than that of sample-2, which shows the thermal stability of sample-3 is increased. The energies of activation are 137.4, 118.9, and 103.0 kJ/mol for samples 4, 5 and 7, respectively, higher than that of sample-3, which shows that these lanthanide

Table 3 SEA, CO and CO_2 yield values of samples 1–7

No.	SEA (m^2/kg) peak	average	CO yield (kg/kg) peak	average	CO_2 yield (kg/kg) peak	average
1	–	–	–	–	–	–
2	2900	186	1.76	0.0082	34.46	1.44
3	1697	140	0.38	0.0038	26.68	1.13
4	1932	153	0.58	0.0044	30.33	1.25
5	1879	147	0.71	0.0051	31.2	1.21
6	1892	151	0.67	0.0048	28.64	1.18
7	1432	161	0.61	0.0032	27.89	1.08

metal ions can more increase thermal stability of samples than transition metal ion Co^{2+}.

Cone calorimetry

Generally, the smoke production and toxic gas formation play a critical role in fire conditions. Carbon monoxide yield, carbon dioxide yield and specific extinction area of smoke (SEA) for the samples are measured by cone calorimeter, listed in Table 3. Cotton cellulose burns out in a few seconds, so there are no cone data for sample-1. The smoke production is measured by SEA. The higher the SEA value is, the more the smoke releases. From Table 3, we can see that for cell–THPC–urea–ADP, the peak and average values of SEA are 2900 and 186 m^2/kg while for the Co^{2+} complexes of cell–THPC–urea–ADP (sample-2) the peak and average values of SEA are 1697 and 140 m^2/kg, much decreased. It is well known that some compounds of transition metals are used as smoke suppressants [7–9]. For the complexes of cell–THPC–urea–ADP with lanthanide metal ions (samples 4–7), the values are 1932 and 153 m^2/kg, 1879 and 147 m^2/kg, 1892 and 151 m^2/kg, 1432 and 161 m^2/kg, respectively, also much decreased, which shows these lanthanide metal ions, similar to transition metal Co^{2+}, act as smoke suppressants. It is suggested that the metals act as flame inhibitors in the vapor phase under normal flame conditions, resulting in the formation of condensed char [11]. This means that the complexes of cell–THPC–urea–ADP with metal ions eliminated the negative effect of cell–THPC–urea–ADP on smoke formation in some degree, which is favorable.

Carbon monoxide yield is defined as the mass of CO formed from the unit mass of burned material. Generally, for the flame retardant modified cotton cellulose, the CO yield is higher than that of untreated one which is due to an incomplete combustion. For cell–THPC–urea–ADP, the peak and average values of CO yield are 1.76 and 0.0082 kg/kg. In the case of samples 3–7, the peak and average values of CO yield are 0.38 and 0.0038 kg/kg, 0.58 and 0.0044 kg/kg, 0.71 and 0.0051 kg/kg, 0.67 and 0.0048 kg/kg, 0.61 and 0.0032 kg/kg, respectively, all much decreased. Moreover, the values of CO_2 yield for the samples 3–7 are also much lower than those for sample-2. Thus, these metal ions decrease the associated CO, CO_2 generation and reduce the formation of volatiles, thereby enhancing char formation.

Conclusions

For complexes of cell–THPC–urea–ADP with metal ions, the activation energies and thermal decomposition temperatures are higher than those of cell–THPC–urea–ADP. The metal ions can increase the thermal stability of cell–THPC–urea–ADP. Moreover, lanthanide metal ions La^{3+}, Ce^{4+}, Nd^{3+} and Sm^{3+} can more increase thermal stability of samples than transition metal ion Co^{2+}. However, the two exotherms in DTA curves are very different in the decomposition temperature in all the complexes.

These lanthanide metal ions, similar to transition metal Co^{2+}, greatly decrease the smoke, CO and CO_2 generation of cell–THPC–urea–ADP, which can be used as smoke suppressants.

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