Thermal stability of cotton cellulose modified with gadolinium complexes

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Key words: cotton cellulose, gadolinium complexes, flame retardant, TG

Abstract: Complex of cell-THPC-thiourea-ADP with lanthanide metal ions Gd^{3+} has been prepared. The thermal stability and smoke suspension of the samples are determined by TG, DTA and cone calorimetry. Experimental data show that for the complexes of cell-THPC-thiourea-ADP with the metal ions, thermal decomposition temperatures are higher than those of cell-THPC-thiourea-ADP, which shows these metal ions can increase the thermal stability of cell-THPC-thiourea-ADP.

Key words: cotton cellulose, thermal stability, flame retardant, lanthanide metal complexes, smoke suspension

Introduction

Cotton is the most important textile fiber and there is a great demand all over the world for cotton fabrics that exhibit improved functional characteristics. Flame retardant cotton cellulose can be prepared by treatment with the compounds containing phosphorus and nitrogen in a suitable method. 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. Moreover, previous reports [1,2] have shown that modified cellulose containing phosphorus is very susceptible to dehydration and char formation.

In previous papers [3,4], compounds of transition metals have been found to be effective smoke retarders and simultaneously increase thermal stability of samples. 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. We have studied the effects of some lanthanide metal ions such as La^{3+}, Ce^{4+}, Nd^{3+} and Sm^{3+} on the thermal degradation of the flame retardant cellulose [5]. This time we choose some other lanthanide metal ions to investigate their effects on the thermal degradation and smoke suspension of cotton cellulose modified with flame retardant.

In this paper, complexes of cell-THPC-thiourea-ADP with Gd^{3+} were prepared as a supplement to lanthanide metal ions. The thermal degradation of samples was studied from ambient temperature to 800°C by TG and DTA.

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 [3]. 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% thiourea 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.

Gd^{3+}complexes of cell-THPC-thiourea-ADP were prepared by treating 6g of cell-THPC-thiourea-ADP in each instance with 5% aqueous solutions of $GdCl_3$ 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 (LOI)

The 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) and thermogravimetry (TG) were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). DTA and TG 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.

Results and Discussion

The DTA, TG curves of (1) cotton cellulose, (2) cell-THPC-thiourea-ADP, (3) Gd^{3+} complexes of cell-THPC-thiourea-ADP were obtained in a dynamic air atmosphere from ambient temperature to 800 °C and are shown in Figure 1.

Differential thermal analysis

Table 1 Peak temperatures in DTA curves of samples 1-3

No.	Compound	DTA curve			Nature of peak
		T_i	T_p	T_t	
1	Cellulose	230	363	403	Exo(large)
		403	459	539	Exo(large)
2	Cell-THPC-thiourea-ADP	255	326	414	Exo(large)
		414	485	614	Exo(large)
3	Gd^{3+} complex of cell-THPC-thiourea-ADP	143	178	208	Endo(small)
		208	328	416	Exo(large)
		416	485	606	Exo(large)

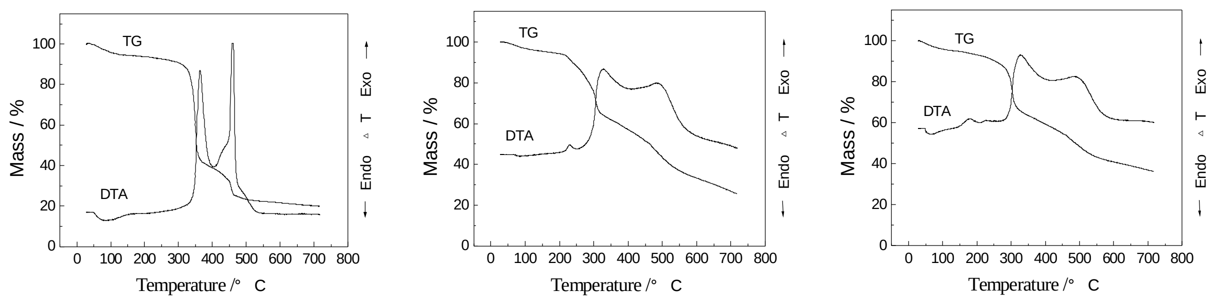
From the DTA curves of samples 1-3, the initiation temperatures (T_i), peak temperatures (T_p)

and termination temperatures (T_t) of the various endotherms and exotherms were investigated and are given in Table1. The DTA curve of cotton cellulose shows two large exotherms with their respective peak maxima at 363 and 459°C. Before 350°C, decomposition and dehydration occur to form some flammable volatile products, and the first exotherm peaking at 363°C is due to the oxidation of these volatile products. Another exotherm, peaking at 459°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. Levoglucosan decomposes into volatile and flammable products and therefore plays a key role in the flammability of cellulose.

The DTA curve of cell-THPC-thiourea-ADP is quite distinct from that of pure cotton cellulose. The treated cotton cellulose seemed to decompose in two steps. A breakdown or depolymerization of the THPC-thiourea-ADP finish, a catalyzed dehydration of the cellulose, and some bond formation occurred during the first step. Two large exotherms with peak maxima at 326 and 485°C are shown in Fig.1, 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 [6]. 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 485°C is due to the combustion of the char.

For cotton cellulose, the two exotherms are sharp and narrow, which shows a large rate of heat release. For the samples 2-3, the two exotherms become small and broad, smallest for samples 3. 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 exotherms become much smaller for the samples 2-3, which indicates that oxidation of the charred residues becomes more difficult due to the existence of flame retardants.

Thermogravimetry



Sample-1 Sample-2 Sample-3

Fig. 1 Thermal analysis curves of samples

From Figure 1, 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, and the char yield (CY) in 700°C in TG 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. 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 [7]. 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 Figures 11 and Table 2, it can be seen that for the cotton cellulose (sample-1), initial decomposition temperature is 326°C, the second stage is in a range 326-365°C, and the mass loss is 46%. For cell-THPC-thiourea-ADP, initial decomposition temperature is 214°C, the second stage is in a range 214-318°C, all these much decreased compared with those of cotton cellulose, which shows that the thermal stability of the cell-THPC-thiourea-ADP is much decreased because of the catalyzing dehydration and decomposition reaction. For sample 3, the decomposition temperature range is 260-320°C, all higher than that of cell-THPC-thiourea-ADP, which shows that the thermal stability of samples is increased.

Table 2 Thermal degradation and analytical data of samples 1-3

No.	Compound	TR (°C)	ML (%)	CY (%)	LOI (%)
1	Cellulose	326-365	46	20.2	18.0
2	Cell-THPC-thiourea-ADP	215-320	28	26.5	29.6
3	Gd^{3+} complex of cell-THPC-thiourea-ADP	260-320	22	36.8	27.8

Conclusions

For complexes of cell-THPC-thiourea-ADP with metal ions, the activation energies, thermal decomposition temperatures, and char yield in TG are higher than those of cell-THPC-thiourea-ADP. These complexes of cell-THPC-thiourea-ADP with metal ions can change the mechanism of thermal degradation in such a way as to reduce the decomposition temperatures of cotton, which can lead to less flammable volatile products and more char. The metal ions Gd^{3+}can increase the thermal stability of cell-THPC-thiourea-ADP. Moreover, the lanthanide metal ions Gd^{3+}can increase thermal stability of samples. However, the two exotherms in DTA curves are very different in the decomposition temperature in all the complexes.

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