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THERMAL DEGRADATION OF COTTON CELLULOSE

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Abstract

The thermal degradation of cotton cellulose treated with chemical mixtures containing P and N was studied by thermal analysis, infrared spectroscopy, Char yield and limiting-oxygen-index (LOI). Our experiments demonstrated the following facts. The temperatures and activation energies of pyrolysis were lower for cotton cellulose treated with flame retardants than those for untreated samples and the values of Char yield and LOI were greater for treated cotton than those for untreated one.

Keywords: degradation, DTA, flame retardant, IR, pyrolysis, TG

Introduction

With the development of society, the improvement of people's living standard and the increase of city population the consumption of textiles used in industry and civilian life increases swifty. Because fire disasters caused by textile always cause enormous losses, more and more people begin to think highly of studies on flame retarded textiles. Many papers have been published on the treatment of cotton cellulose with flame retardants [1, 2]. However, these investigations are mainly centred on looking for new flame retardants, systematic studies on flame retardant mechanisms are relatively rare. The main purpose of this paper is to study the thermal degradation of cotton cellulose treated with a series of flame retardants [that is, Tetrakis (hydroxymethyl) phosphonium chloride, ThPC+Dicyanamide, ThPC+urea and phosphoric acid+formaldehyde+Dicyanamide]. In order to solve this problem, thermal analysis, infrared spectroscopy, limiting-oxygen-index (LOI) and Char yield were used.

Experimental

Raw material

Cotton cellulose (Hebei Province Dingzhou Sanitary Plant, P. R. China) was immersed into water and heated for 30 min. After this procedure, the cotton cel-

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lulose was dried at 333 K, and then treated with a series of chemicals containing P and N as follows:

Preparation of flame retardant (I)

15.0 g of triethanolamine was slowly added into a solution containing 129.0 g of tetrakis (hydroxymethyl) phosphonium chloride (ThPC) (62% concentration) and 200 ml of water was then added and the mixture efficiently stirred. 50.0 g of urea and 47.0 g of hexamethylamine were added, and the mixture was filled up to 1000 ml with water. The temperature of this solution was controlled in the range from 343 to 353 K for 10 min. The reaction product contained the following components: 8% ThPC, 5% of urea and 1.5% triethanolamine.

Preparation of flame retardant (II)

129.0 g of ThPC (62%), 167.0 g of dicyanamide and 25.0 g of phosphoric acid (85% concentration) were stirred together in water at room temperature. The total volume was 1000 ml. The temperature of the mixture was controlled in the range from 333–343 K for 30 min to obtain the reaction product containing 8% of ThPC and 16.7% dicyanamide [2].

Preparation of flame retardant (III)

A solution of hydroxymethyl dicyanamidine phosphate was prepared with phosphoric acid, dicyanamide and methyl aldehyde. A solution of hydroxymethyl dicyanamide was prepared with phosphoric acid and formaldehyde. Before using the two solutions were mixed in the mole ratio 1:1.5. The method has been described in [3].

Thermal analysis

DTA and TG experiments were carried out on a DT- 40 thermal analyzer (Shimadzu, Japan), working under static air at a heating rate of 10 K min^{-1}. Calcined alumina was used as a reference material.

Infrared spectrometry

For the IR studies (Hitachi 260-50 IR spectrometer, Japan), the residue of cotton cellulose with and without flame retardant treatment 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, 623 and 673 K, respectively.

Limiting-oxygen-index (LOI)

The LOI value is the minimum amount of oxygen in an oxygen-nitrogen mixture required to support complete combustion of a vertically held sample that

burns downward from the top. The higher the LOI value, the more effective is the flame retardant treatment. LOI values were determined in accordance with ASTM D 2863-70 by means of a General Model HC-1 Limiting-oxygen-index apparatus.

Results and discussion

A comparison of LOI and Char yield for cotton cellulose without and with flame retardant treatment is given in Table 1. As can be seen, the values of Char yield and LOI for cotton cellulose without flame retardant treatment are the lowest. The values of Char yield for cellulose with flame retardant treatment are, with flame retardant I, II and III, 28.5, 34.5 and 29.8, respectively. The values of their LOI are 29.5, 42.0 and 32.0, respectively. The data indicate that the combustibility of the cotton treated with flame retardant is reduced.

Table 1 Thermal characteristics of modified cotton cellulose

Sample No.	First stage		LOI	Char yield/ wt%
	Exotherm/K	E/kJ mol^{-1}		
i*	638	219.5	18.0	0.49
ii	584	161.2	29.5	28.5
iii	592	159.0	42.0	34.5
iv	594	144.7	32.0	29.8

*i – cellulose; ii – iv cellulose modified with flame retardants (I) (II) (III), respectively

From the DTA–TG curve in Fig. 1 it can be seen that the thermal degradation of cellulose proceeds essentially through two types of reaction [4, 5]. At lower temperatures, between 520 and 640 K, there is a gradual degradation which involves depolymerization and dehydration, etc. At higher temperatures, a rapid volatilization occurs which is often accompanied by formation of levoglucosan (1,6-anhydro-β-D-glucopyranose). Under such conditions, levoglucosan breaks down to give smaller molecular species, i.e. furans, aldehydes, ketones, aromatic hydrocarbons, etc. Repolymerization of these volatiles leads to the formation of Char [4].

The first exothermic peak at 638, 584, 592 and 594 K respectively, for cotton cellulose without and with the different flame retardant treatments. The second exothermic peak is at 734, 609, 624 and 797 K, respectively. From the TG curve it can be seen that the value of the first mass loss is greater than that of the second. The first mass loss corresponds to the first, and the second to the second exothermic DTA peak.

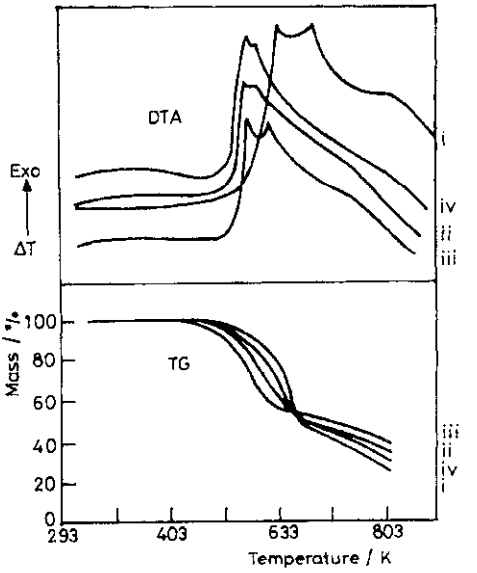

Fig. 1 DTA and TG curves of the thermal degradation of cellulose in air at a heating rate of 10 K min^{-1}. i pure cellulose; ii–iv cellulose modified with flame retardants (I), (II), (III), respectively

The kinetic parameters for the various stages of pyrolysis of cotton cellulose without and with flame retardant treatment were determined using the method described by Broido [7]. The equation for the Broido method can be written as

$$\ln(\ln 1/y) = -\frac{E}{RT} + \ln\left(\frac{RZ}{E\beta}T^2\right) \quad (1)$$

where y is the fraction of initial molecules not yet decomposed. T the temperature of maximum reaction velocity, β the rate of heating (K min^{-1}), Z the frequency factor and E the activation energy.

Using the Broido method, plots of $\ln(\ln 1/y)$ *vs.* $1/T$ for various stages of pyrolysis are given in Fig. 2. The values of the activation energy E are determined from the slope. The data in Table 1 indicate that the activation energies in the first stage are low for cotton cellulose with flame retardant treatment, compared with the untreated material. This is because these flame retardants can catalyze pyrolysis [8].

Figure 3 shows the changes in the IR spectrum for pure cellulose in air medium. When the temperature is raised, the band at 3200 cm^{-1} is decreased, the band at 2900 cm^{-1} (C–H) disappears and a new band appears at 1640 cm^{-1}.

The changes in the IR spectrum of cotton cellulose with flame retardant (II) treatment on heating are shown in Fig. 4. The intensities of the bands at 2900 cm^{-1}

(C–H), 2150 cm^{-1} (C≡N^+), 1550 cm^{-1} (N–H) and 1043 cm^{-1} (–CH_2OH) decrease with increasing temperature. When the temperature reaches 573 K, these band disappear. The band at 2300 cm^{-1} (C≡C) is less dependent on the temperature in our experimental range. Due to conjugation of C=C, the band at 1650 cm^{-1} (C=C) shifts to 1600 cm^{-1} as the temperature changes from 273 to 573 K.

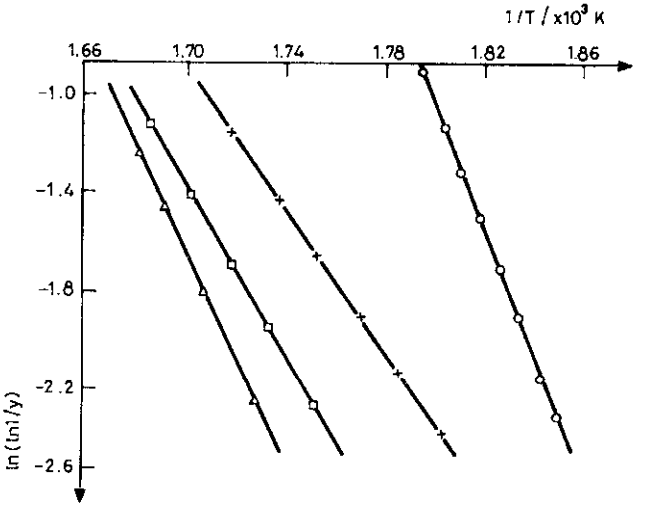

Fig. 2 Broido's plots for the first stage of pyrolysis: o – pure cellulose; x, Δ, □ – cellulose modified with flame retardants (I), (II), (III), respectively

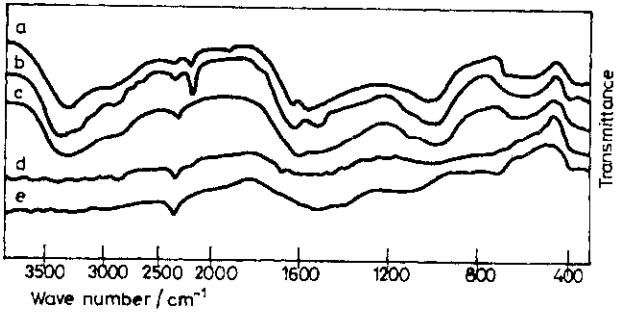

Fig. 3 IR spectra of cellulose (a) and its residue at 373 K (b), 423 K (c), 473 K (d) and 573 K (e)

Simultaneous use of chemicals containing P and chemicals containing N, such as urea and dicyanamide, can improve the properties of the flame retardant because of their simultaneous action. When heated, chemicals containing P can decompose to yield phosphoric acid, and then polyphosphoric acid which can cause a dehydration of cellulose. The main role of chemicals containing P catalysis of pyrolysis. Because of the above reasons, cotton cellulose with flame retar-

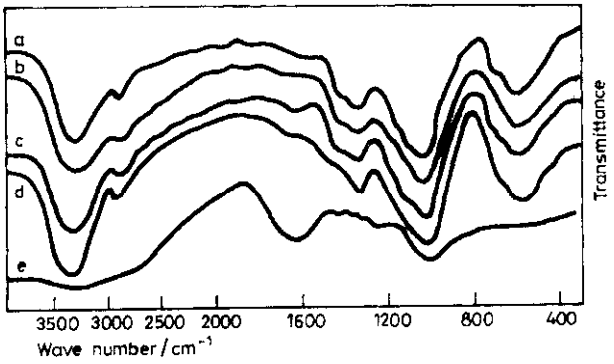

Fig. 4 IR spectra of modified cellulose (a) with flame retardant (II) (b), (c), (d), (e): its residue at 373 K (b), 423 K (c), 473 K (d) and 573 K (e), respectively

dant treatment can decompose and form carbon and water at relatively low temperatures. Because flame retardants can catalyze pyrolysis, activation energies and temperatures of pyrolysis for cotton cellulose with flame retardant treatment are low compared with pure cotton cellulose.

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