

# Fire-Retardant Properties of the Viscose Rayon Containing Alkoxy-cyclotriphosphazene

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**ABSTRACT:** The viscose rayon containing cyclotriphosphazene were prepared by the method of blending spinning. The combustibility and thermal stability of the fire-retardant viscose rayon were evaluated by 45 ° slope burning method, limit oxygen index (LOI), differential scanning calorimetry, thermogravimetry analysis. The results indicated that the LOI of the modified fiber could reach LOI  $\geq$  28, and the combustibility of the modified fiber could reach the fire-retardant standard of Japan industry standard JIS 10 91-77 (times of ignition  $\geq$  3 times). The analysis of the fiber's

thermal degradation suggested that the flame retardant plays a multirole of heat absorption, catalytic dehydration and carbonization, condensation-phase and gas-phase flame retardation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 698–702, 2006

**Key words:** fibers; flame retardance; thermal properties; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

## INTRODUCTION

Viscose rayon is widely applied to textile clothing and decorative fabric because of its excellent hygroscopic, ventilation, and good dyeing properties. With the rapid increase of the need for textile fire-retardant materials in market, the performance of textile flame retardance, such as multifunction, environmental protection, and durability, is becoming more and more important.<sup>1</sup> Flame-retardant materials based on cellulose and viscose rayon have been studied by many researchers long time.<sup>2–5</sup> One method for preparing these fire-retardant textiles is surface modification. However, the surface modification of textiles by fire-retardant agent has the disadvantage of the need for rigorous reaction treatment or conditions.<sup>6</sup> Another method for preparing fire-retardant textile is blending polymer materials with flame-retardant additives. The additives used must not leach or volatilize from the fire-retardant polymer materials during service.<sup>7</sup> The phosphazene derivatives show excellent fire-retardant and heat-resistant properties when they are used as fire-retardant function materials by themselves or fire-retardant additives.<sup>8–11</sup> However, there is seldom report about the fire-retardant properties of fire-retardant viscose rayon with the phosphazene derivatives as fire-retardant additives.

In this article, the hexa(alkoxy)cyclotriphosphazene was used as fire-retardant additive to prepare the blending modified fire-retardant viscose rayon. The fire-retardant viscose rayon not only has the advantages of no-halogen, high efficient, and durable fire-retardant properties, but also accords with the requirements for environmental protection compared with normal fire-retardant viscose rayon.<sup>12</sup> The combustibility and thermal stability of the fire-retardant viscose rayon containing hexa(alkoxy)cyclotriphosphazene were evaluated by the 45 ° slope burning method, limit oxygen index (LOI), differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA).

## EXPERIMENTAL

### Materials

Hexa(alkoxy)cyclotriphosphazene, was synthesized by referring to previous method reported by Quan Y and coworkers.<sup>13</sup> Viscose solution (cellulose content 9%), solidifying bath (H<sub>2</sub>SO<sub>4</sub> 130 g/L, Zn<sub>2</sub>SO<sub>4</sub> 10 g/L, Na<sub>2</sub>SO<sub>4</sub> 270 g/L) and RX-702 viscose rayon oiling agent were offered by Qingbai River chemical fiber factory of Chengdu. NaOH (analytically pure) was obtained from Chemical Reagent Factory of Chengdu. HCl (analytically pure) was obtained from Kelong Chemical Reagent Company of Chengdu.

### Preparation of the fire-retardant viscose rayon

Hexa(alkoxy)cyclotriphosphazene fire-retardant agent was blended with viscose solution, and then filtrated,

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TABLE I  
Combustibility of the Tested Viscose Rayon Samples

| Sample number | Contents of fire-retardant agent (%) | Titers (dtex) | Initial modulus (cN/dtex) | Breaking strength (cN/dtex) | LOI (%) | Times of ignition |
|---------------|--------------------------------------|---------------|---------------------------|-----------------------------|---------|-------------------|
| 1             | 0                                    | 2.32          | 29.1                      | 1.606                       | 19      | 1                 |
| 2             | 5.3                                  | 2.40          | 40.8                      | 1.833                       | 28      | 2                 |
| 3             | 8.2                                  | 2.51          | 38.3                      | 1.633                       | 29      | 4                 |
| 4             | 10.0                                 | 2.76          | 34.1                      | 1.449                       | 31      | 6                 |
| 5             | 18.2                                 | 3.06          | 24.5                      | 1.013                       | 33      | 7                 |

debubbled, and matured. The mixture was fed into viscose solution container and spun through a 0.08 mm  $\times$  200 hole spinneret. The fiber obtained was treated by normal treatment of desulphurizing, washing, oiling, etc.

### Physical-mechanical property testing

Titers of the fiber samples were tested with JN-B Precision Torsion Type Balance made by the Second Balance Instrument Company. The physical-mechanical properties were tested with YG-001A Fiber Electronic Tension Meter made by Taicang Textile Instrument Company. The regain percentages of fiber samples were tested in standard conditions with the DHS20-1 Multi-function Intra Moisture Content Tester made by Cany Precision Instruments Limited Company.

### Combustibility testing

Limit oxygen index (LOI) of the fiber samples was determined with the oxygen index instrument produced by ATLAS Company. The 45° slope burning method (Japan Industry Standard JIS 1091-77)<sup>14</sup> was adopted to evaluate the combustibility of the fiber samples.

### Thermal analysis

Thermal stability of the fire-retardant viscose rayon was measured in air atmosphere by differential scanning calorimeter (DSC) with CDR-4P Caloric Analysis Instrument made by Cany Precision Instruments Limited Company. The heating temperature range is 0 ~ 670°C, temperature rising rate is 10°C/min, differential thermal compensation unit measuring range is 0 ~ 120 mW, and sampling temperature range is 50 ~ 650°C.

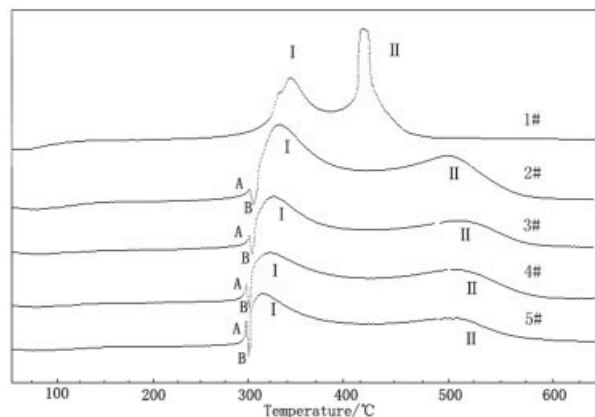
The weight loss of fire-retardant viscose rayon was measured in nitrogen atmosphere by thermogravimetry analysis (TGA) with STA449C Caloric Analysis Instrument made by Netzsch Company. Heating temperature range is 0 ~ 500°C, temperature rising rate is 20°C/min, and sampling temperature range is 50 ~ 500°C.

## RESULTS AND DISCUSSION

### Combustibility and physical-mechanical property of the fire-retardant viscose rayon

The data of the fiber samples' physical-mechanical properties in Table I show that with the increasing of content of the fire-retardant agent, the titer of fiber samples increased gradually while the initial modulus and breaking strength of fiber samples descended gradually. However, when the content of the fire-retardant agent was low, the fiber's modulus and strength were higher than those of the viscose rayon containing no fire-retardant agent. We thought that this phenomenon resulted from the hydrogen bonds between the oxygen atoms of the hexa(alkoxy)cyclo-triphosphazene molecules in the low orientation area of the fiber's amorphous region with the hydroxyl groups of different cellulose molecules. These hydrogen bonds made the interaction between different cellulose molecules stronger and made the molecules slip difficult when the fiber was stretched. Nevertheless, when the content of the fire-retardant agent was high, large amount of additives were filled in the middle and high orientation area of the fiber's amorphous region, which resulted in the diminishment of the fiber's degree of orientation and the increase of the fiber's interior defects. This was the main cause that the fiber's modulus and strength decreased gradually with the increasing of the fire-retardant agent contents.

The results of combustibility of the viscose rayon samples with different contents of fire-retardant agent in Table I exhibited that the LOI of the viscose rayon containing no fire-retardant agent was 19, while the additive amounts of the fire-retardant agent were 5.3%, 8.2%, 10.0%, and 18.2%, and the LOI of fire-retardant viscose rayon were 28, 29, 31, and 33, respectively. It was obvious that the LOI of the fiber increased gradually with the increasing of the fire-retardant agent contents, and all of them reached the requirement of fire-retardant standard (LOI  $\geq$  28). Times of ignition in Table I are the index of combustibility according to the 45° slope burning method of the Japan Industrial Standard JIS 1091-77. This index is used to indicate that how many times needed to



**Figure 1** DSC curves of fiber samples from no. 1 to no. 5 (contents of fire-retardant agent: 1#-0%, 2#-5.3%, 3#-8.2%, 4#-10.0%, 5#-18.2%).

ignite the fiber bundle in particular length before it is burned out. The data showed that the normal viscose rayon sample no.1 burned continuously after it was ignited. The fiber sample no. 2 containing 5.3% fire-retardant agent was an easy burning fiber too. The times of ignition were more than 3 times for the fiber samples from no. 3 to no. 5, which contained more than 8.2% fire-retardant agent, and suggested that the fiber began to show obvious fire-retardant results when the content of the fire-retardant agent exceeded 8.2%. The times of ignition of the fiber sample no. 5 containing 18.2% fire-retardant agent was 7 times. Among the 7 times of ignition test, there were 5 times that the sample extinguished immediately after the fire source was taken away, and 2 times extinguished after the fiber burned 5 s. It is obvious that when the content of the fire-retardant agent exceeded 18.2%, the fiber exhibited excellent fire-retardation.

#### Thermal stability of the fire-retardant viscose rayon

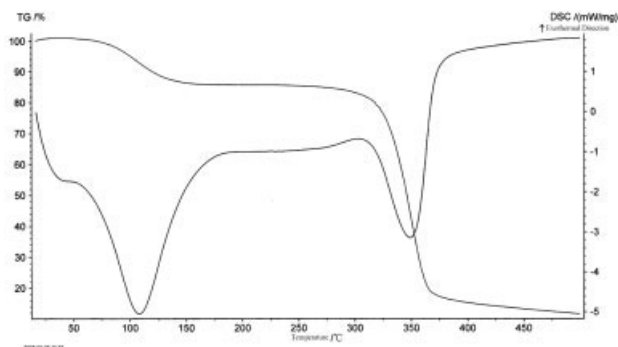
Figure 1 was the DSC curves of viscose rayon samples in air atmosphere. It could be found that there were an exothermic peak (Peak A) at 295°C and an endothermic peak (Peak B) at 305°C on the DSC curves of the fire-retardant fiber samples from no. 2 to no. 5, while there was no peak at corresponding position on the DSC curves of the normal viscose rayon sample no. 1. The other two exothermic peaks on the five DSC curves at the temperatures from 310 to 550 °C were named as Peak I and Peak II from low temperature to high temperature, respectively. The peak temperatures and enthalpies of Peak I and Peak II were listed in Table II.

Figure 1 showed that, the first peak (Peak I) of the normal viscose rayon sample no. 1 locating at the temperature near by 350°C was strong and wide, and

its enthalpy was 2237.98 J/g. At this stage, cellulose macromolecule decomposed into laevoglucose under the temperature, then the laevoglucose decomposed into coke and smaller molecules such as CO.<sup>15</sup> The second peak (Peak II) of the normal viscose rayon sample no. 1 located at the temperature around 410°C showed that the coke was oxidized further into CO<sub>2</sub> or secondary coke under the high temperature. On the DSC curves of the fire-retardant fiber samples from no. 2 to no. 5, the exothermic peak (Peak A) appeared at 295°C and the endothermic peak (Peak A) located at 305°C, respectively. Peak I of the fire-retardant fiber samples was located at the temperatures between 305°C and 390°C. Peak I were wider than that of the normal fiber and their initial temperatures and peak temperatures were ahead of 20–40°C than that of the normal viscose fiber sample, while their end temperatures delayed about 20°C. Peak temperatures of Peak II of the fire-retardant fiber samples were hysteretic about 90°C compared with that of the normal viscose rayon sample. All the results suggested that a exothermal pyrolysis reaction of the hexa(alkoxy)cyclo-triphosphazene fire-retardant agent began from the temperature 290 °C (Peak A), and a endothermic chemical reaction between the pyrolysis products of fire-retardant agent with celluloses occurred at the temperature between 295°C and 305°C(Peak B). These reaction led to the decomposition of cellulose into laevoglucose at a relatively low temperature than that of the normal viscose rayon. The change of the temperature of Peak I indicated that fire-retardant agent promoted the cellulose to begin to decompose under a low temperature, and the decomposition speed was slowed down. Because the decomposition temperature was relatively low, the decomposition speed of laevoglucose in air became lower than that of normal viscose rayon. The degradation products of fire-retardant agent were phosphoric acid, metaphosphoric acid, and polymetaphosphoric acid, which had strong function of dehydrating.<sup>6</sup> The dehydrating and charring function of fire-retardant agent made the decomposition products contain less CO. The charring products and the polymetaphosphoric acid played a role of isolating air, which was the condensation-phase flame

**TABLE II**  
Peak Temperatures and Enthalpies of Exothermic Peaks

| Sample number | Contents of fire-retardant agent (%) | Peak temperatures (°C) |         | Enthalpies (J/g) |         |
|---------------|--------------------------------------|------------------------|---------|------------------|---------|
|               |                                      | Peak I                 | Peak II | Peak I           | Peak I  |
| 1             | 0                                    | 353.6                  | 410.2   | 2237.98          | 1164.17 |
| 2             | 5.3                                  | 321.7                  | 489.2   | 1885.49          | 953.67  |
| 3             | 8.2                                  | 319.1                  | 496.9   | 1272.16          | 795.25  |
| 4             | 10.0                                 | 317.2                  | 498.6   | 1102.86          | 778.29  |
| 5             | 18.2                                 | 310.2                  | 501.2   | 940.08           | 417.16  |



**Figure 2** TGA-DSC graph of the fiber sample no. 1 (fire-retardant agent content 0%).

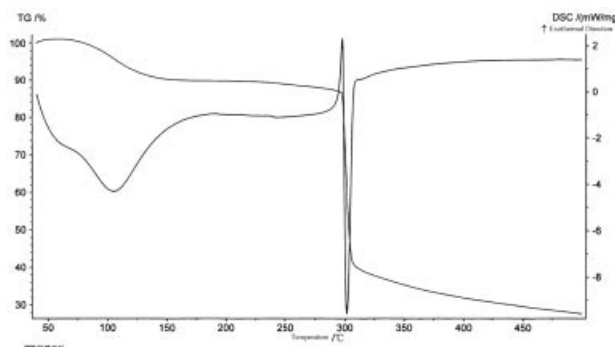
retarding effect. On the other hand, the  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{NO}_2$  that came from the burning of the nitrogen element in the fire-retardant agent played the roles of diluting  $\text{O}_2$  and catching free radical in the air, which were the gas-phase flame retarding effects.<sup>6</sup> The fire-retardant fiber decomposed slowly after 460°C, and their peak shapes as well as enthalpies was also smaller than that of normal viscose rayon sample. This phenomenon suggested that, with the continually increasing of temperature, charred materials could still react with oxygen of air, but the covering layer of polymetaphosphoric acid and the charcoal structure made the secondary oxidizing more difficult. The data in Table II showed that with the increasing of fire-retardant agent added, the peak temperatures of Peak I reduced gradually, while that of Peak II increased, and the enthalpies of the fiber samples from no. 2 to no. 5 decreased about 18–64% compared with that of normal fiber sample. It seems indicated that less heat was given off in the secondary oxidizing of the fire-retardant viscose rayon than that of the normal viscose rayon.

Figures 2 and 3 were the TGA-DSC curves of normal viscose rayon and viscose rayon containing 10.0% fire-retardant agent in nitrogen atmosphere. The exothermic peaks and endothermic peaks on the DSC curves were named as Peak I, Peak II, and Peak III (There was no Peak II on the DSC curve of the fiber sample no. 1.) from low temperature to high temperature, respectively. Two obvious weight loss stages on the TGA curves were named as Stage I and Stage II. Characteristic data of TGA-DSC graphs of the viscose rayon samples were listed in Table III.

The data of Figure 2, Figure 3, and Table III indicated that the adding of the fire-retardant agent made the shape and the numbers of peak on the DSC curves and the percentage of remained mass of the fiber take an obvious change. It was obvious that Peak I on the DSC curve in Figures 2 and 3 was the endothermic peak of fiber drying. The corresponding weight loss in this process resulted in the evaporation of the moisture in the fiber. Peak I of the fiber sample no. 4 on the

DSC curve appeared in the same position compared with the fiber sample no. 1, but the weight loss percentage of the fiber sample no. 4 was lower than that of the fiber sample no. 1, which suggested that the moisture regain of the fire-retardant viscose rayon was lower than that of the ordinary viscose rayon. This was verified by their regain percentages. Peak III on the DSC curve of fiber sample no. 1 began at the temperature of 300°C. This indicated that cellulose decomposed into laevoglucose at 300°C in nitrogen atmosphere and the laevoglucose decomposed into flammable gas such as CO or dehydrated into coke further. The coke could not be oxidized further in nitrogen. In the DSC curve of the fire-retardant viscose rayon in nitrogen atmosphere, some obvious changes occurred in the appearance of a newly Peak II and in the shape as well as in the endothermic temperature of the Peak III. Peak II as an exothermic peak appeared at the temperature of 295°C and the heat came from the pyrolysis reaction of fire-retardant agent at this temperature. The results of this reaction made the Peak III of the fire-retardant fiber sample no. 4 appear at a lower temperature than that of normal viscose rayon sample no. 1, then the cellulose began to decompose and char under a lower temperature. The quite narrow shape of Peak III indicated that cellulose was catalyzed to dehydrate and char rapidly by the fire-retardant agent.

From the TGA curves, it could be found that the weight loss percentages of the two samples on Stage I were about 10%, while the weight loss percentage of normal viscose rayon was higher than that of fire-retardant fiber. The adsorption water and combination water of viscose rayon was evaporated at this stage. Stage II was the main weight loss stage of the fiber samples, and its position corresponded to Peak III on the DSC curves at the same figure. Cellulose decomposed and charred at this stage. From the data in Table III, it could be found that the weight loss percentage of the fiber sample no. 1 at Stage II was 69.28%, while the weight loss percentage of the fire-retardant viscose



**Figure 3** TGA-DSC graph of the fiber sample no. 4 (fire-retardant agent content 10.0%).



**TABLE III**  
**Characteristic Data of TGA-DSC Graphs of the Viscose Rayon Samples**

| Sample number | Contents of fire-retardant agent (%) | Regain percentages (%) | DSC peak temperatures (°C) |        |        | TGA weight loss percentages (%) |         | Remained mass (%) |
|---------------|--------------------------------------|------------------------|----------------------------|--------|--------|---------------------------------|---------|-------------------|
|               |                                      |                        | Peak I                     | Peak I | Peak I | Stage I                         | Stage I |                   |
| 1             | 0                                    | 14.55                  | 108.26                     | None   | 348.91 | 14.86                           | 69.28   | 11.61             |
| 4             | 10.0                                 | 12.73                  | 104.90                     | 298.02 | 301.73 | 11.14                           | 57.29   | 27.65             |

rayon was 12% less than that of normal viscose rayon at the same stage. The remained mass of the fire-retardant viscose rayon was 16% more than that of normal viscose rayon. The results suggested that fire-retardant agent made cellulose fiber char at a relatively lower temperature, and the beginning decomposition temperature of the fire-retardant fiber sample was ahead of about 50°C than that of the normal viscose rayon. The fire-retardant viscose rayon produced more charcoal and less flammable material than that of the normal viscose rayon. The charcoal layer as a condensation-phase covering on the burned fiber played a role in insulating against heat and oxygen because the charcoal layer is difficult to burn.<sup>16</sup>

### CONCLUSIONS

Fire-retardant viscose rayon containing the hexa-(alkoxy)cyclotriphosphazene fire-retardant agent was prepared by blending method. The combustibility of the modified fire-retardant viscose rayon could reach the fire-retardant standard of Japan industry standard JIS 1091-77 (times of ignition  $\geq 3$  times), while its LOI was more than 28. The analysis of the DSC and TGA showed that the phosphazene fire-retardant agent took place chemical reaction at 295°C, and the reaction promoted cellulose decomposing and dehydrating in the fiber's burning or heating process. The decomposing and dehydrating temperatures of the fire-retardant viscose rayon were 30–40°C lower than those of the normal viscose rayon. The weight loss percentage

of fire-retardant viscose rayon was 12% less than that of the normal viscose rayon, while the remained mass of the fire-retardant viscose rayon was 16% more than that of the normal viscose rayon. All these experiment results suggested that the fire-retardant agent might play the multiroles of catalytic dehydration and carbonization, heat absorption, condensation-phase, and gas-phase flame retarding effects in the thermal degradation of the viscose rayon.

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