Study of a novel phosphorus-containing flame retardant for cotton fabric

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Abstract. In this paper, a high efficiency FR named HPA was applied to treat cotton fabric. The results of LOI values and vertical flammability test showed that HPA treated cotton fabric had the best flame retardancy (LOI value was 36.0%), when the FR concentration is 50 g/L, and cured at 180°C for 7 min. During the process of holding back the combustion, HPA behaves the excellent properties of FR for cotton fabric.

1. Introduction
Cotton fabric is one of the excellent natural materials and is one of the most widely used textile biopolymers in the world. However, cotton fabric is flammable easily [1]. Fires from cotton fibre textiles are causing many injuries, deaths and considerable financial losses [2]. So, flame retardant (FR) treatment of cotton fabric is extremely necessary in many applications for reducing their flammability [3]. FR exerts its flame retardancy by means of the heat absorbing, the covering effect, inhibition of chain reaction and gas dilution [4].

For cotton fabric, the most commonly used FRs are based on halogen and phosphorus compounds. The use of halogen FRs will generate poisonous substances such as dioxins when burnt at too low a temperature for normal commercial incinerators. Halogen FRs are bioaccumulation which is harmful to humans and the environment [5]. Therefore, the general trend is to substitute these FRs by non-halogenated alternatives. The mostly used phosphorus FRs are Proban and Pyrovatex CP [6]. They can react with the cotton fibre or form cross-linked structures on the fibre. These compounds can increase the formation of char, prevent the formation of levoglucosan and flammable volatiles, thus act as FRs for cellulose [7]. Proban and Pyrovatex CP, however, have the shortcoming of releasing formaldehyde which is known as a carcinogenic compound [8]. So, it is important to develop halogen-free and formaldehyde-free FRs for cotton fabrics.

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In this study, a phosphorus based FR named HPA was synthesized to treat cotton fabrics. It can behave excellent FR performance in the process of holding back the combustion.

2. Experimental

2.1. Materials
100% Cotton fabric, scoured and bleached, was obtained from the market (123.27 g/m²) was a FR agent.

2.2. Methods

2.2.1. Preparation of HPA solution. HPA was dissolved in distilled water. The concentration of HPA was ranging from 1% to 6%.

2.2.2. The treatment of cotton fabric with HPA solution. The cotton fabric was impregnated in HPA solution with the bath ratio of 1:20 under 50°C thermostatic water bath for 20 min.

2.2.3. Curing the FR finished cotton fabric. The HPA finished cotton fabrics were padded through two dips and two nips to reach an average wet pickup of 120%. After the treatment, the fabric was cured in an automatic shaping and drying machine (HL-3842, Nantong Sansi Electromechanical Science & Technology Co. Ltd., China) with different temperatures from 120°C to 190°C. The cured time is ranging from 5 to 15 min. Then the treated sample was washed thoroughly.

Figure 1. LOI values of HPA treated fabrics. (a) the fabrics cured 7 min at 180°C; (b) cured 7 min with 50 g/L FR; (c) cured at 180°C with 50 g/L FR; (d) The whiteness of HPA finished fabrics, cured 7 min at 180°C.

3. Results and discussion

3.1. The LOI values of HPA treated cotton fabrics
The LOI values of the fabric treated with HPA (6 specimens) are plotted against the concentration of the FR in figure 1(a). The cured time and temperature of every HPA treated sample are 7 min and 180°C, respectively. The LOI value of untreated cotton fabric is 16.0%. The LOI value of every FR treated samples is higher than that of untreated sample. When the concentration of HPA is 40 g/L, the LOI value is 27.0% which does not meet with the cotton fabric of FR standard LOI value of 28.0%. But the LOI values would reach 36.0% and 41.0%, respectively, when the concentration of HPA were 50 g/L and 60 g/L. Thus, the concentration of HPA should keep above 50 g/L. The curing temperature is also an important parameter to enhance the flame retardancy. From figure 1(b), the relationship between LOI value and curing temperature was exhibited. Besides, the cured time is 7 min, and 50 g/L
HPA is used for every specimen. When the curing temperature was 170°C, the LOI value was 29.0%. And LOI value would be up to 36.0%, if the curing temperature was 180°C. Therefore, the temperature must be at least 180°C.

The curing time is another important factor to increase the flame retardancy. The LOI values of HPA finished fabrics, cured at 180°C with 50 g/L FR were showed in figure 1(c). The LOI value increased a lot (from 25% to 37%) when the time expanded from 2 min to 9 min. If expanding the curing time continuously, the LOI value would not increase any more, kept 37%. So, the curing time of 7 min is the optimum. In addition, the whiteness of FR treated fabric cured 7 min at 180°C decreased with the increasing concentration of HPA in figure 1(d). The whiteness of control cotton fabric is 90.69%. When the concentration of HPA was 50 g/L, the whiteness of FR finished cotton fabric would decrease to 87.06%, this value is acceptable. The whiteness, however, would be 80.82%, if the concentration of FR was 60 g/L. It means that the concentration of 60 g/L is very high to damage the whiteness of the treated fabric.

From the results of LOI values and whiteness, there are three parameters, including FR concentration, curing temperature and time, affecting the flame retardancy of HPA treated cotton fabric. The optimum FR concentration is 50 g/L, the best curing temperature and time are 180°C and 7 min, respectively. HPA behaves excellent FR properties for cotton fabric. Because of the high temperature, the tensile strength, however, decreased to a certain degree (table 1).

| Samples                  | Tensile strength / (N) |
|--------------------------|------------------------|
|                          | Warp       | Weft       |
| Control cotton fabric    | 543.50     | 306.00     |
| 50g/L HPA treatment      | 460.00     | 263.50     |

3.2. The vertical flammability test of HPA treated cotton fabrics

The vertical flammability test test results were shown in table 2. The control fabric ignited and burned rapidly in the air, and the after flame time and afterglow time of control sample were 6 s and 11 s, respectively. After treated with 50 g/L HPA, there are lots of chars remained when removing the ignition source and the char length was 81 mm. And the treated sample has no after flame time and afterglow time, which means that after removing the ignition source, the flame extinguished immediately and no afterglow observed. Thus, the flame retardancy of cotton fabric treated with HPA improved greatly.

| Samples                  | After flame time (s) | After glow time (s) | Char length (mm) |
|--------------------------|----------------------|---------------------|------------------|
| Control sample           | 6                    | 11                  | 0                |
| 50 g/L HPA treated sample| 0                    | 0                   | 81               |

Figure 2. TG of the control and finished cotton fabrics.
3.3. The vertical flammability test of HPA treated cotton fabrics

Figure 2 showed the TG of the control and HPA finished samples. For the control sample, the weight decreased rapidly from 325 to 400°C with about 80% weight loss, and 5.3% ash was left until 580°C. The finished sample with FR, however, rapidly lost its weight ranged from 292.1 to 310.7°C with only about 46.73% weight loss and 38.64% residual was remained at 595°C. It was demonstrated that the decomposition temperature of the finished fabric was lower than that of the control fabric, and the amount of residue was much more than that of control sample at the end.

4. Results and discussion

During the process of holding back the combustion, HPA behaves the excellent properties of FR. From LOI values and vertical flammability tests, when the FR concentration is 50 g/L, and curied at 180°C for 7 min, the treated cotton fabric had the best flame retardancy and the LOI value was 36.0%. The treatment by HPA could protect cotton fabric from fire to a certain degree based on the TG results. HPA exerts its FR action on cotton fabric at a temperature well below that of the pyrolysis of these normal fabrics.

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