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Flame retardant finishing of cotton fabric based on synergistic compounds containing boron and nitrogen

Kongliang Xie*, Aiqin Gao, Yongsheng Zhang

College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

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ABSTRACT

Boric acid and compound containing nitrogen, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) were used to finish cotton fabric. The flame retardant properties of the finished cotton fabrics and the synergetic effects of boron and nitrogen elements were investigated and evaluated by limited oxygen index (LOI) method. The mechanism of cross-linking reaction among cotton fiber, Tri-HTAC, and boric acid was discussed by FTIR and element analysis. The thermal stability and surface morphology of the finished cotton fabrics were investigated by thermogravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. The finishing system of the mixture containing boron and nitrogen showed excellent synergistic flame retardancy for cotton fabric. The cotton fabric finished with mixture system had excellent flame retardancy. The LOI value of the treated cotton fabric increased over 27.5. Tri-HTAC could form covalent bonds with cellulose fiber and boric acid. The flame retardant cotton fabric showed a slight decrease in tensile strength and whiteness. The surface morphology of flame retardant cotton fiber was smooth.

1. Introduction

Cotton is one of the excellent natural materials that have wide application in the different productions (Hou & Sun, 2013; Hou, Zhang, & Wang, 2012; Wang & Lewis, 2002; Xie, Hu, & Zhang, 2012). However, cotton fiber is flammable. A large number of cellulose textiles and indoor decorations including carpets, curtains, wallpaper and so on, which are all easy to burn. The demands for flame retardant textile fabrics have a steady growth for the past decades, and have become an urgent exigency (Abou-Okeil, Ei-Sawy, & Abdel-Mohdy, 2013; Horrocks, Kandola, Davies, Zhang, & Padburg, 2005; Yang & He, 2011). The flame retardant finishing of cotton fabric is the most commonly used method to produce flame retardant textile fabric. The traditional flame retardants being used for cotton fabric are mainly flame retardant agent containing halogen and phosphorus. The use of halogen-based flame retardants to reduce the flammability of cotton is one of the most efficient ways of reducing the fire hazard. However, they have such noticeable disadvantages as the generation of toxic and corrosive gases during thermal degradation, such as HBr and HCl (Alongi, Mihaela, & Malucelli, 2011; Lu & Ian, 2002; Wu & Yang, 2007).

In recent years, various efforts have been made to develop halogen-free flame retardant (Lessan, Montazer, & Moghadam, 2011; Lu & Ian, 2002; Ye et al., 2013). Some compounds, containing phosphorus, silicon, boron, nitrogen, and other miscellaneous elements, have gained much attention as flame retardant in the polymer materials to replace halogen-containing flame retardants (Ho, Hwang, Shieh, & Chung, 2009; Wu & Yang, 2004). Boric acid and borate salts have been used as effective flame retardant additives, but they have been less studied than halogen, and phosphorus and other compounds (Armitage, Ebdon, Hunt, Jones, & Thorpe 1996; Dogan, Yılmaz, & Bayraml, 2010; Martin, Ronda, & Cadiz, 2006). In order to improve the flame retardant efficiency, the attempts taking advantage of the synergetic effects of two elements with flame retardant characteristics have been reported in the recent years (Jiang, Li, Hu, & Fan, 2010; Martin, Hunt, Ebdon, Ronda, & Cadiz, 2006; Song, Li, Liu, & Yang, 2012). However, the synergetic effects of boron and nitrogen elements with flame retardant characteristics have been scarcely reported.

The nitrogen atom with the characteristic of rich electronic structure and the boron atom with empty track can form coordination bond, and this maybe also produce crosslinking reaction with flame retardant agents containing boron. A 1,3,5-triazine derivative, containing multi-reactive and multi-cationic groups, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) has high nitrogen content. Moreover, Tri-HTAC is also able to form covalent bonds with cotton fiber and boric acid. In our recent research work, the modified cellulose with a 1,3,5-triazine derivative, containing the multi-reactive groups, has been investigated. The modified cotton

* Corresponding author. Tel.: +86 21 6779 2413; fax: +86 21 6237 8392.
E-mail address: klxie@dhu.edu.cn (K. Xie).

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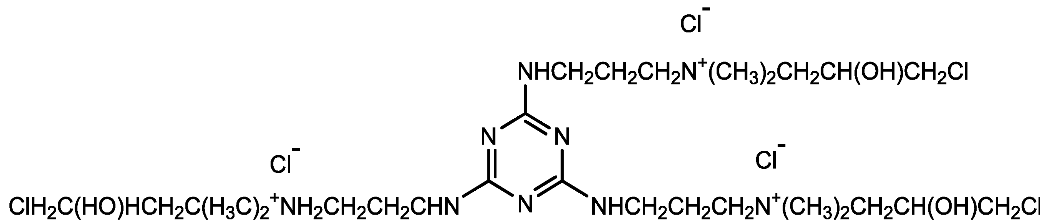


Scheme 1. Chemical structure of Tri-HTAC.

fabrics exhibit different behavior toward dyeing (Xie, Hou, & Sun, 2007; Xie, Hou, & Wang, 2008). The chemical structure of Tri-HTAC is shown in Scheme 1.

In this paper, boric acid and nitrogen-containing compound, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC), were cooperated and used to finish cotton fabric. The flame retardant properties of finished cotton fabrics and the synergetic effects of boron and nitrogen elements were discussed. The thermal stability of them was investigated by thermogravimetric analysis.

2. Experimental

2.1. Materials

Desized, scoured and bleached cotton fabric was obtained from Shaoxing Jinqiu Textile Company, Shaoxing, China. 1,3,5-Triazine derivative, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride, was obtained from Modern Textile Institute, Shanghai, China and other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Flame retardant finishing of cotton fabric

Tri-HTAC and boric acid were dissolved in distilled water to give certain concentration solutions by weight. Sodium hypophosphite monohydrate (SHMH) as a catalyst was added to the solution. pH of the mixture solution was adjusted to 6 by ammonia water. Cotton fabric was first impregnated in the solution, then padded through two dips and two nips to reach an average wet pickup of 100%, dried at 95 °C for 3 min, and cured in a curing oven (Roaches International Ltd., Staffordshire, England) at 160 °C for 3 min. In order to compare, the untreated sample was cured under the same condition.

2.3. Measurements

The LOI method was applied to evaluate the ignition and ease of extinction of a sample. LOI was measured according to an international standard ASTM D2863.

Fabric tensile strength was determined by using a H10KS Tensile Testing Machine (Hounsfield SDL Co., UK), according to ASTM Standard Test Method 5035-2006. Six specimens (three for warp and three for filling) were tested at a gauge length of 200 mm with a stain rate of 30 mm/min. The width of the specimen was 50 mm.

Fourier transform infrared (FTIR) spectroscopy was performed with a OMNI Sampler of the Nexus-670 FTIR-Raman Spectrometer (Nicolet Analytical Instruments, Madison, WI) with a resolution of 4 cm^{-1}, and measurements were carried out by using KBr pellets.

The nitrogen percentage was determined by Vario EL III (Elementar, Germany). The samples were dried under vacuum at the temperature of 50 °C before measuring. The boron percentage was determined by Inductively Coupled Plasma, Prodigy (Teledyne Leeman, Hudson, NH, USA).

Thermogravimetric analysis (TGA) was performed on TG 209 F1 (NETZSCH-Geraetebau GmbH, Selb, Germany) in the range from room temperature to 600 °C at a heating rate of 10 °C/min, under a constant flow of dry nitrogen.

For SEM analysis, the fabric materials were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

3. Results and discussion

3.1. Flame retardant finishing of cotton fabric

The flame retardant finishing of cotton fabric with the mixture compound, containing boron (boric acid) and nitrogen (Tri-HTAC), were evaluated by LOI. LOI, a testing method for evaluating the ignition and ease of extinction of a sample, is a quantitative and reproducible method with wide spread use in both industry and academic research. LOI shows good correlation to char formation (Yang & He, 2011). Fabric having LOI value of 21 or below ignites easily and burns rapidly in the air. Those with LOI values above 21 ignite and burn more slowly. Generally, when LOI values increase above approximately 26–28, fabric may be considered to be flame retardant (Abou-Okeil et al., 2013).

Borates are effective flame retardants because of impenetrable glass coating formed when they thermally degrade. The glass coating formed on the fiber surface can contribute to the intumescent effect, because they exclude oxygen and prevent further propagation of combustion. While Tri-HTAC 40 g/l, sodium hypophosphite monohydrate 30 g/l, curing temperature 160 °C, and time 3 min, the effect of the concentration of boric acid on the flame retardant property of cotton fabric was investigated. The results are shown in Fig. 1. As known, cotton fabric is easily burn. The LOI value of untreated cotton fabric (control sample) was measured and being 17.5. The cotton fabric was treated with the solution containing Tri-HTAC without boric acid, the LOI value of the treated cotton fabric increases to 22. This result confirms that the compound containing nitrogen, Tri-HTAC, possesses flame retardancy for cotton fabric. With increasing boric acid concentration, the LOI value of the

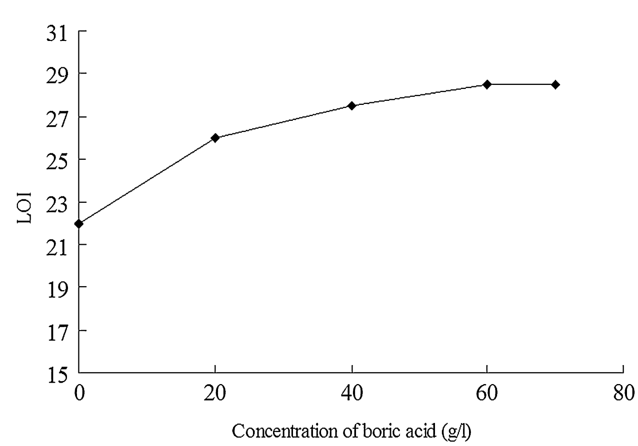


Fig. 1. Effect of boric acid concentration on the flame retardant property of finished cotton fabric.

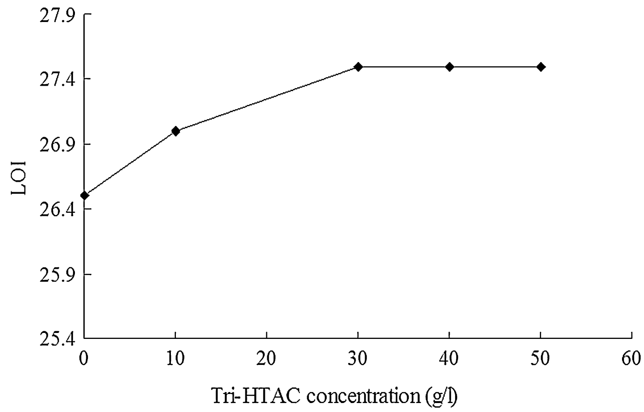


Fig. 2. Effect of Tri-HTAC on the flame retardant property of cotton fabric.

treated cotton fabric rapidly increases. When boric acid concentration is 40 g/l, the LOI value of the treated cotton fabric gets to 27.5. The results demonstrate that the mixture system, containing boron and nitrogen, shows an excellent synergistic flame retardancy for cotton fabric.

The effect of Tri-HTAC on the flame retardant property of cotton fabric was measured at boric acid 40 g/l, sodium hypophosphite monohydrate 30 g/l, curing temperature 160 °C, and time 3 min. Fig. 2 indicates that the effect of Tri-HTAC on the flame retardant property of cotton fabric is also obvious. With increasing Tri-HTAC concentration, the LOI values of the treated cotton fabrics noticeably increase.

The effect of sodium hypophosphite monohydrate (SHMH) on the flame retardant property of cotton fabric was also discussed. While boric acid 40 g/l, Tri-HTAC 40 g/l, curing temperature 160 °C, time 3 min, and the results are shown in Fig. 3. It can be seen that the effect of catalyst on the flame retardant property of cotton fabrics is also obvious. With increasing sodium hypophosphite monohydrate concentration, the LOI values of the finished cotton fabrics also increase. Sodium hypophosphite monohydrate as catalyst plays an important role in the flame retardant system.

The results show that the cotton fabrics finished with the mixture system containing boric acid 40 g/l, Tri-HTAC 40 g/l, and sodium hypophosphite monohydrate 30 g/l, have excellent flame retardant. The mixture system containing boron and nitrogen shows excellent synergistic flame retardant property for cotton fabric.

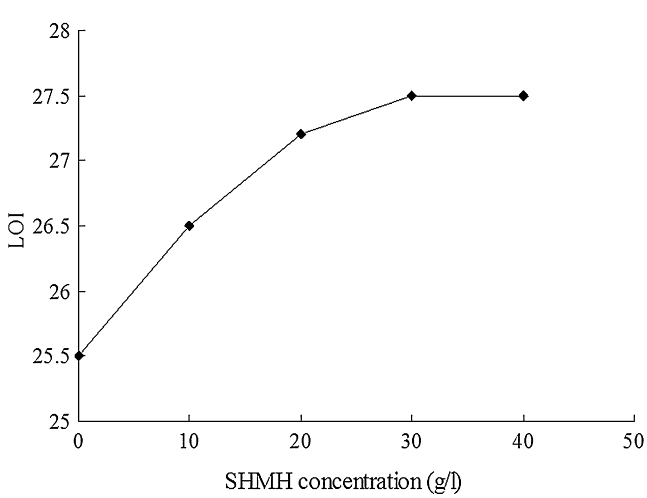


Fig. 3. Effect of SHMH concentration on the flame retardant property of cotton fabric.

Table 1
Tensile strength and whiteness of the finished cotton fabrics.

Samples	Whiteness	Tensile strength (N)	
		Warp	Weft
Control sample	79.83	377.10	762.30
Finishing sample	76.31	346.93	681.45

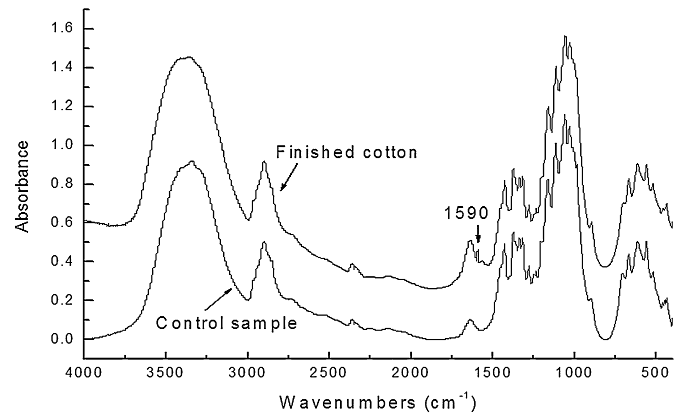


Fig. 4. FTIR spectra of the control and finished cotton fabrics.

3.2. Physical property and cross-linking reaction of the finished cotton fabric

Physical property of the flame retardant cotton fabric finished maybe change. The tensile strength and whiteness of the finished and control samples were measured. The finishing condition for cotton fabric was Tri-HTAC 40 g/l, boric acid 40 g/l, sodium hypophosphite monohydrate 30 g/l, pH 6, and curing temperature 160 °C, and curing time 3 min. The results are listed in Table 1. The tensile strength and whiteness of flame retardant cotton fabric had a slight decrease.

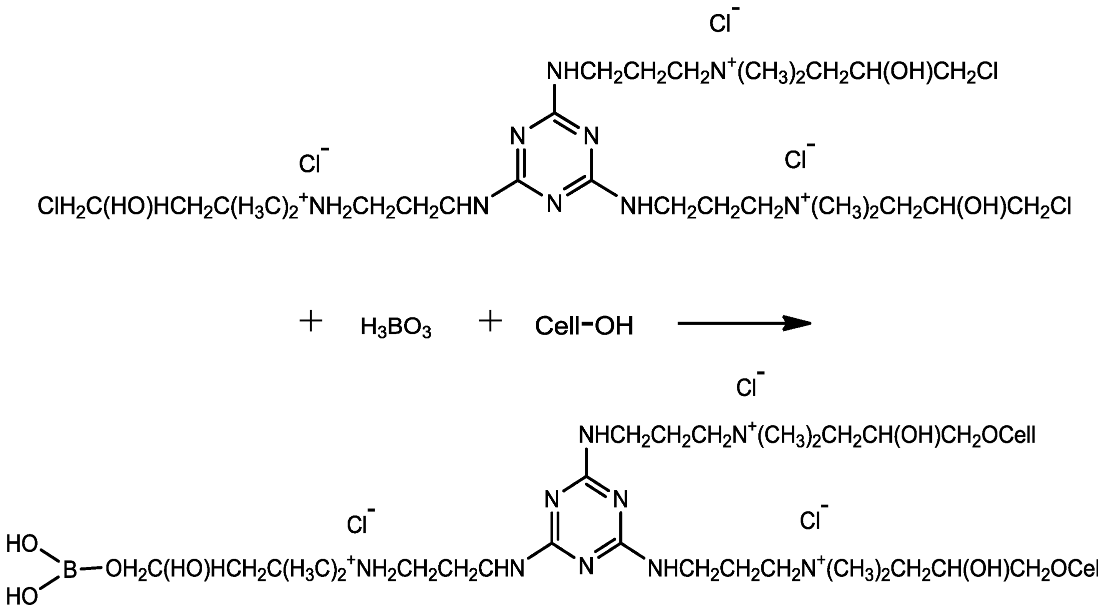
Tri-HTAC contains multi-reactive and multi-cationic groups. Tri-HTAC is an excellent and efficient grafting chemical for cellulose (Xie et al., 2007). The modified cotton cellulose exhibits different behavior toward dyeing compared with that of unmodified cellulose (Xie et al., 2008). Tri-HTAC is able to form covalent bonds with cellulose fiber and boric acid. The cross-linking reaction of cotton fabric with Tri-HTAC and boric acid are shown in Scheme 2.

The cotton fabric was finished with the mixture system, containing boric acid 40 g/l, Tri-HTAC 40 g/l, and sodium hypophosphite monohydrate 30 g/l. The finished sample was then washed in warm water 40 °C and air-dried at room temperature. FTIR spectra of the control and finished cotton fabrics were measured (shown in Fig. 4). FTIR spectrum of the finished cellulose assures the presence of —N=C at 1594 cm^{-1} (1,3,5-triazine cycle). However, the absorbance peaks of B—O— are not obviously observed in Fig. 4.

The nitrogen and boron percentages of the flame retardant cotton fabric were measured. The results are summarized in Table 2. The nitrogen and boron contents of the control cotton are less than 0.005%. The nitrogen and boron contents of the flame retardant cotton fabric are 0.222% and 0.733%, respectively. After washing, the nitrogen and boron contents of the flame retardant cotton

Table 2
Element analysis of the control and finished cotton fabrics.

	Control sample	Finished sample	Finished sample after washing
N %	0.005	0.222	0.193
B %	0.005	0.733	0.148



Scheme 2. Cross-linking reaction of cotton fabric with Tri-HTAC and boric acid.

fabric are 0.193% and 0.148%, respectively. The results demonstrate that Tri-HTAC forms covalent bonds with cellulose fiber. Although the quantity of the boric acid by cross-linking reaction with cotton and Tri-HTAC is low, the boron content in the fiber still maintains 0.148%. It indicates that a small amount of boric acid is cross-linked.

3.3. Thermal property of the finished cotton fabric

The cotton fabric was finished with the mixture system containing boric acid 40 g/l, Tri-HTAC 40 g/l, and sodium hypophosphite monohydrate 30 g/l. The thermal property of the flame retardant cotton fabric was investigated by TGA. Fig. 5 illustrates the TG decomposition curves of the control and flame retardant cotton fabrics. It can be obviously observed that first rapidly weight loss temperature of the finished cotton fabric is at 255–270 °C. For the control cotton, the rapidly weight loss temperature initiates at 309 °C. It can be attributed by the dehydration reaction of boric acid on the finished cotton fabric. The dehydration reaction mechanism of boric acid is shown in Scheme 3.

The water of hydration is lost by endothermic decomposition and therefore both dilutes and cools, by absorbing the thermal energy from the flame. Thus boron is found to exert its flame retardant action on polymeric materials at a temperature well below that of the normal pyrolysis of these materials. Fig. 5 also shows that the residual weight ratio of the finished cotton fabric is 40.45% at 600 °C. However, the residual weight ratio of the control cotton fabric only is 6.30% at 600 °C. It demonstrates that the flame

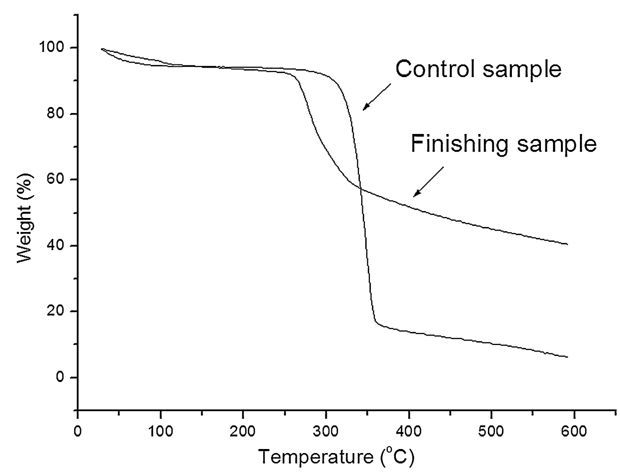


Fig. 5. Thermal stability of the control and finished cotton fabrics.

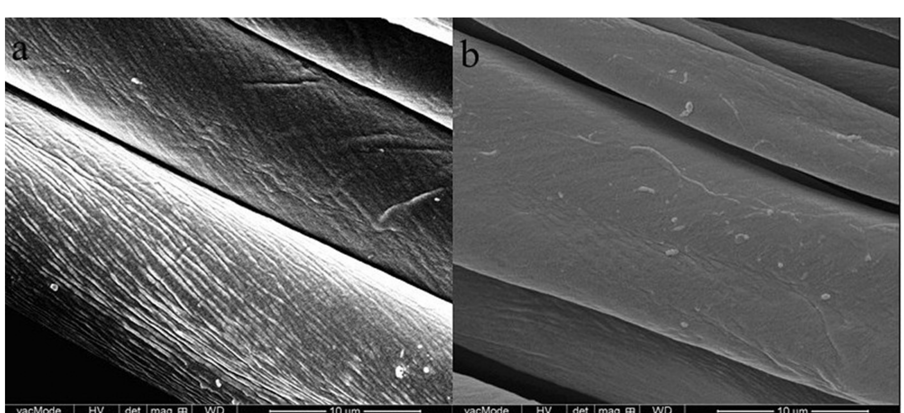


Fig. 6. SEM micrographs of cotton fibers: (a) control fiber and (b) flame retardant fiber.

$$2H_3BO_3 \xrightarrow[T_1]{-2H_2O} 2HBO_2 \xrightarrow[T_2]{-H_2O} B_2O_3$$

T_2 260-270 °C (Martin, Ronda, & Cadiz, 2006)

Scheme 3. Dehydration process of boric acid.

retardancy of the finished cotton fabric shows good correlation to char formation because of glass coating formed on the fiber surface. The flame retardant action of the boron-containing compounds on cotton fabric is chemical as well as physical. It is found that these inorganic boron compounds promote char formation in the burning process. The result is in agreement with that of LOI. Data of TG curves demonstrate that the mixture system, containing boron and nitrogen, shows excellent flame retardant property for cotton fabric.

3.4. Surface morphology of cotton fabric

SEM analysis was used to characterize any changes in the surface morphology of fiber. Representative SEM micrographs, taken at the magnification of 5000 of control and flame retardant cotton fibers, are shown in Fig. 6. There is slight pitting and cracking or crazing on the unmodified cotton surface. However, the surface morphology of flame retardant cotton fiber is smooth. The morphological changes are mainly because cotton fibers swell in the crosslinking reaction process. The flame retardant mixture, containing boric acid, Tri-HTAC, and sodium hypophosphite monohydrate, penetrates into cotton fiber and occurs cross-linking reaction.

4. Conclusions

Boric acid and nitrogen-containing compound, 2,4,6-tri[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC), were cooperated and used to finish cotton fabric. The cotton fabric finished with the mixture system, containing boric acid 40 g/l, Tri-HTAC 40 g/l, and sodium hypophosphite monohydrate 30 g/l, has excellent flame retardant. The LOI value of the finished cotton fabric increases to 27.5. The mixture system, containing boron and nitrogen, shows excellent synergistic flame retardant for cotton fabric. Tri-HTAC is able to form covalent bonds with cellulose fiber and boric acid. The tensile strength and whiteness of flame retardant cotton fabric shows a slight decrease. The surface morphology of flame retardant cotton fiber is smooth. The flame retardant mixture, containing boric acid, Tri-HTAC, and sodium hypophosphite monohydrate, penetrates into cotton fiber and occurs cross-linking reaction.

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