Carbohydrate Polymers 98 (2013) 706–710

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 25 April 2013
Received in revised form 27 May 2013
Accepted 15 June 2013
Available online 25 June 2013

Keywords:
Cotton
Flame retardant
Synergistic property
Compound containing boron
LOI

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

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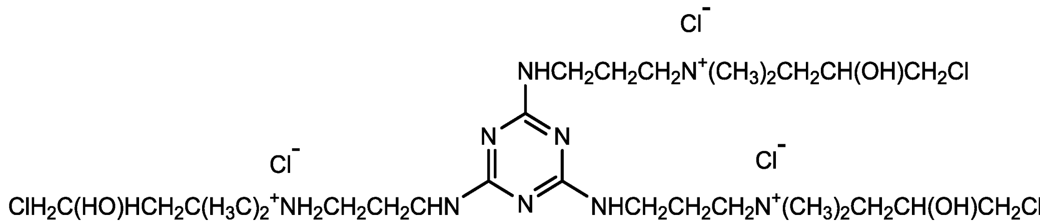
0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.06.014



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

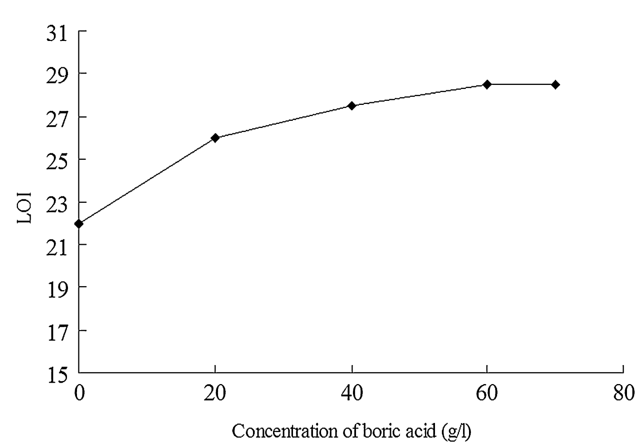


Fig. 1. Effect of boric acid concentration on the flame retardant property of finished cotton fabric.