

Thermal stability and flame retardancy of guanidinium and imidazolium borate finished cotton fabrics

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Abstract The aim of this study was to investigate the effect of guanidinium nonaborate (GB) and imidazolium borate (IB) on thermal stability and flammability properties of cotton fabrics. The flame retardant and thermal stability properties of treated cotton fabrics were investigated using limiting oxygen index (LOI) and thermogravimetric analysis. The residues remained after LOI test were characterized by conducting attenuated total reflectance-Fourier-transform infrared spectroscopy and scanning electron microscopy with a wavelength-dispersive X-ray spectrometer. The results showed that both boron compounds increased the LOI value of cotton fabric as the amount increased by several combined flame retardant effects. IB-treated cotton fabrics had higher LOI value than GB-treated ones due to the higher increment in char yield which was the predominant flame retardant action of both boron compounds.

Keywords Cotton · Flame retardant · Boron- and nitrogen-containing compounds · LOI

Introduction

Cotton is widely used natural textile fiber in many forms such as woven, knitted, and nonwoven. Cotton is easily flammable with leaving a char consisting mainly of carbon, and its inherent flammability restricts its use in many fields. Accordingly, it is necessary to make cotton fabric flame retardant for wider application. Non durable, semi durable,

or durable flame retardant finishing is applied depending upon where it is used [1, 2]. Phosphorus [3–10], silicon [11–14], and boron compounds [15–21] are widely used for imparting halogen-free flame retardant property to cellulose-based materials. Boron compounds including borax, boric acid, ammonium pentaborate, and their mixture are widely used for non durable flame retardant finishing of cotton fabrics [22].

Qu et al. studied the thermal degradation and flammability properties of wood impregnated with potassium carbonate, sodium metasilicate nonahydrate, and borax. They found that borax forming glassy protective layer was effective flame retardant for wood. Borax also enhanced the dehydration and inhibited the depolymerization of wood [19]. Xie et al. used boric acid and nitrogen-containing compounds together for their synergistic effect to improve the flammability properties of cotton fabric. The flame retardant treatment increased limiting oxygen index (LOI) value to 27.5 by favoring the char formation in the condensed phase [20]. Alongi et al. used various flame retardants including zinc borate (ZnB) and boron phosphate as smoke suppressants in combination with silica-based coatings synthesized through sol-gel process. There was no remarkable decrease observed in the concentration of CO and CO₂ with the addition of boron phosphate whereas first peak of CO and CO₂ reduces with the addition of ZnB [15]. Lazko et al. improved the fire resistance of insulating material based on flax fibers using aluminum trihydroxide, ZnB, melamine phosphate, and melamine borate. According to the flammability tests, melamine borate showed better performance than the other flame retardants used [18]. Karacan et al. studied the effect of combined boric acid and phosphoric acid finishing on thermal stability properties of viscose rayon fibers. They found that the finishing treatment improved thermal

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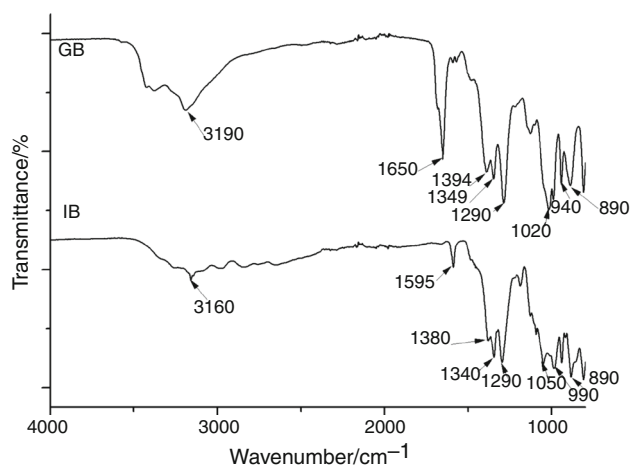


Fig. 1 The FTIR spectra of GB and IB

stability, favored char formation, and reduced the evolution of volatile by products [17].

As our best knowledge, this is the first study that investigates the effect of guanidinium nonaborate (GB) and imidazolium borate (IB) on thermal stability and flammability properties of cotton fabrics. Thermal stability and flammability properties of cotton fabrics were investigated by thermogravimetric analysis (TG) and LOI, respectively. The char residues remained after LOI test were investigated by conducting attenuated total reflectance-Fourier-transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy with a wavelength-dispersive X-ray spectrometer (SEM-WDX).

Experimental

Materials

Scoured knitted 100 % cotton fabric was obtained from KARSU TEKSTIL (Kayseri, Turkey). Analytical grade boric acid, guanidinium carbonate, and imidazole were purchased from Sigma Aldrich.

Synthesis of GB and IB

The GB was prepared by aqueous stoichiometric reaction of guanidinium carbonate with boric acid [23]. 6 mol boric acid was added to 2 M guanidinium carbonate solution (500 mL) at 318 K. The mixture was heated to 363 K and stirred for 1 h. After the reaction was complete with a yield of 83 %, the product was filtered and washed with distilled water. The synthesis of IB was made through the reaction of imidazole with boric acid in aqueous media [23]. Imidazole (70 g) was dissolved in distilled water (225 mL)

at 313 K, and boric acid (185.5 g) was added. The mixture was heated to 363 K and maintained with stirring for 1 h. After the reaction was completed, the mixture was cooled down to room temperature. The precipitated IB as white crystals was filtered and washed with distilled water. The GB and IB were characterized by ATR-FTIR. The FTIR spectra of GB and IB are shown in Fig. 1. Similar peaks in different regions are seen in ATR-FTIR spectra of GB and IB. The broad band in the range of 3,584–2,846 cm^{-1} corresponds to symmetric stretching vibrations of N–H and O–H groups. The characteristic peaks seen between 1,394 and 1,290 cm^{-1} arise from asymmetric stretching of B–O in trigonally coordinated boron (BO_3 group). The peaks seen between 1,050 and 890 cm^{-1} are the characteristics of asymmetric stretching modes of B–O in tetrahedral boron (BO_4). The bands seen at 1,650 and 1,595 cm^{-1} arise from the bending vibrations of N–H group for GB and IB, respectively [24–27].

Flame retardant treatment

2 and 5 mass% aqueous solution of GB and IB were prepared for flame retardant application. GB and IB were not soluble in water at room temperature. Thus, the solutions of GB and IB were prepared at 333 K. Before the flame retardant treatment, cotton fabrics were dried at 333 K for 24 h. Cotton fabrics were treated with the aqueous solution of boron compounds at 333 K for 30 min and padded through a laboratory padder (Termal, Turkey) to control wet pick up of 100 % on the fabrics. The treated fabrics were dried at 363 K for 8 min. The amount of charged material on cotton fabrics was calculated by mass difference before and after treatment. The calculation was made according to the following formula:

$$A = (W_f - W_i) / W_i * 100, \quad (1)$$

where A was the percentage mass increase; W_i was the mass of the fabric before treatment; W_f was the mass of fabric sample after treatment. The resulting fabrics contained 2 ± 0.1 and 5 ± 0.2 mass% boron compounds. For sample coding, the abbreviations C, GB, and IB are used for cotton fabric, guanidinium nonaborate, and imidazolium borate, respectively. The sample coded as C-2 GB refers to the flame retardant finished cotton fabric which contains 2 mass% GB.

Characterization

LOI values of the fabrics were measured using Fire Testing Technology Limiting Oxygen Index Analyzer instrument, according to the standard oxygen index test ASTM D2863. TG was carried out on Perkin Elmer Diamond TG/DTA at a heating rate of 10 $^\circ\text{C min}^{-1}$ up to 1,073 K under nitrogen

Table 1 TG data of fabric samples

Sample	T_5 %/K	T_{max} /K	Char yield/% at 1,073 K	
			Experimental	Calculated
C	573	635	8.6	–
C/2 GB	570	613	19.2	9.4
C/5 GB	566	609	29.3	10.6
C/2 IB	566	609	24.4	9.6
C/5 IB	551	607	33.5	11.2

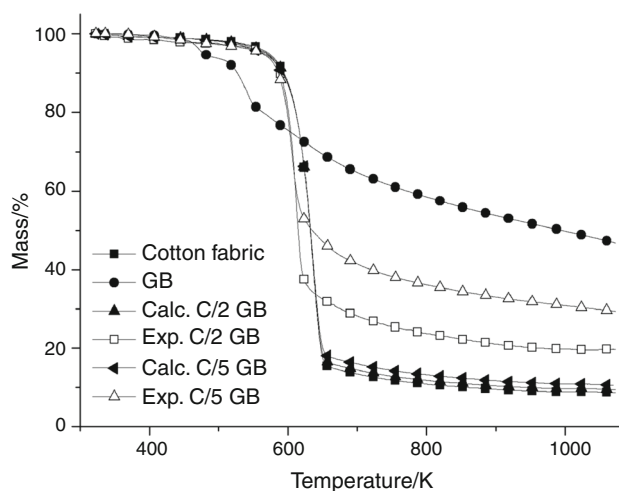
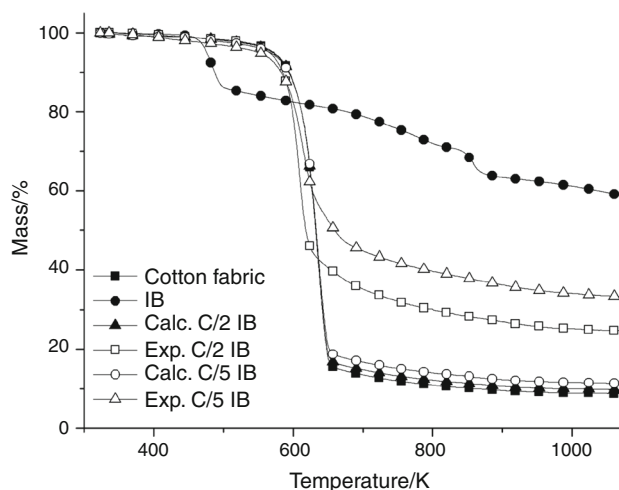
flow of 50 mL min⁻¹. Residue analyses remained after LOI test were performed using SEM-WDX (LEO 440 computer controlled digital, 20 kV) and ATR-FTIR (Bruker Optics IFS 66/S series FT-IR spectrometer) at an optical resolution of 4 cm⁻¹ with 32 scans. All specimens were sputter-coated with Au/Pd before SEM-WDX examination.

Results and discussion

Thermal stability

Thermal degradation properties of boron compounds, pristine, and flame retardant-treated cotton fabrics are investigated by TG under nitrogen atmosphere. TG data of all fabric samples are given in Table 1. The calculated (calc.) and experimental (exp.) TG curves of GB- and IB-treated fabric samples are shown in Figs. 2 and 3, respectively. The calculated TG curves are obtained on the basis of common additive rules. As already demonstrated in the literature [23, 24], the degradation of GB (Fig. 2) and IB (Fig. 3) occurs in two steps in nitrogen via dehydration (first step) and the degradation of amine moiety (second step). The detailed analysis carried out by Schubert et al. [23] and Wood et al. [24] showed that the gaseous products of water, CO₂, and NH₃ are formed during the degradation of both boron compounds. Also in our case, the same mechanism has been observed, and at the end of the test at 1,073 K, GB and IB retain 46 and 58 % of their mass, respectively.

The mass loss of cotton fabric takes place in a single step, with a maximum of mass loss rate at 635 K by leaving char residue (8.6 %) consisting mainly of carbon at 1,073 K. Cotton fabric mainly degrades by the decomposition of glycosyl units at low temperatures and the depolymerization of them at high temperatures under nitrogen atmosphere [2, 11, 15]. The inclusion of both boron compounds decreases the initial thermal stability (T_5 %) of cotton fabric as the amount increases due to the lower dehydration reaction temperatures of boron compounds. It is noted that the similar trends are observed when the dehydrated flame

**Fig. 2** TG curves of GB- and GB-treated fabric samples**Fig. 3** TG curves of IB- and IB-treated fabric samples

retardant additives are used in the previous studies [28, 29]. The mass loss of flame retardant-treated cotton fabrics takes place at lower temperatures in a single step regardless of boron compound type. The reduction in T_{max} value increases as the amount of boron compounds increase due to the formation of borate esters. As stated in the previous studies that boric acid, a decomposition product of GB and IB, reacts with hydroxyl groups of cellulose and cellulose borate ester which has lower decomposition temperature than cellulose formed [2, 22, 30].

The difference between the exp. and calc. char yields gives information about the thermal stabilization effect of flame retardant additives. According to Table 1, exp. char yields are much higher than calc. ones with the addition of both boron compounds. The exp. char yields are 104 and 154 % higher than the calc. char yields with the addition of

Fig. 4 SEM images of char residues remained after LOI test at low ($\times 100$) and high ($\times 2,500$) magnifications

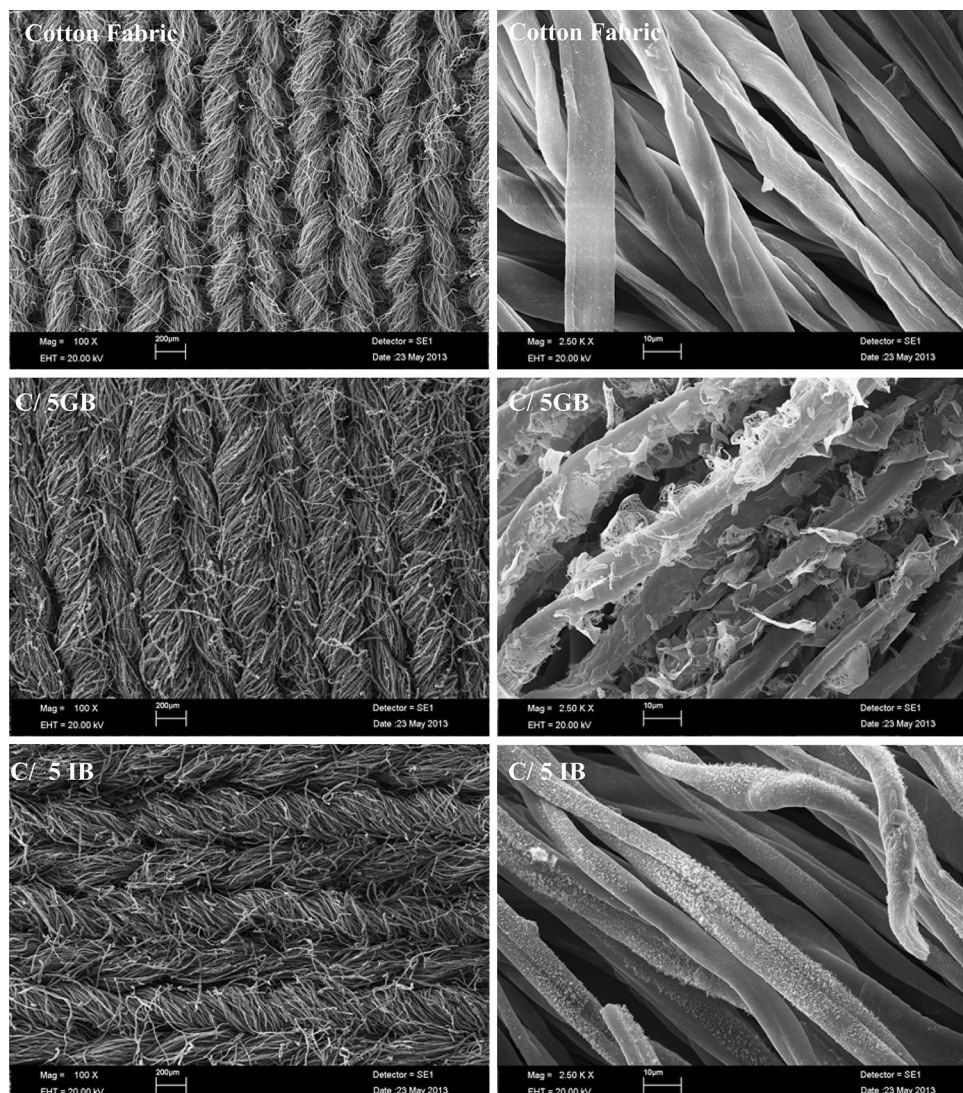


Table 2 LOI values and chemical composition of char residues remained after LOI test

Sample	LOI/%	Chemical composition/%			
		C	O	N	B
C	18.8	80.2	19.7	–	–
C/2 GB	21.4				
C/5 GB	24.6	77.4	16.8	1.6	4.1
C/2 IB	22.2				
C/5 IB	25.8	78.4	17.1	1.2	3.2

2 mass% GB and IB, respectively. As the amount of boron compound reach to 5 mass%, the difference between exp. and calc. char yields further increase. It is thought that the addition of boron compounds promotes the char formation through both physical and chemical ways. The formation of glassy protective layer as physical effect protects the

underlying substrate and promotes the char formation. It is proposed that the reactions of boric acid and nitrogen-containing intermediates with cellulose favor the char formation. The borate ester formation via reaction with boric acid and cellulose favors the char formation [2, 22, 30]. During the thermal degradation of GB and IB, nitrogen-containing intermediates which are basic in nature are formed [23, 24]. As stated in the previous studies that investigate the effect of nitrogen-containing flame retardants including guanidine compounds on thermal stability of cellulosic materials, the basic intermediates can react with cellulose to form more thermally stable char [31, 32]. Accordingly, it is thought that these intermediates can react with cellulose and form thermally more stable char.

The char residue characterizations support proposed mechanisms stated above. SEM images of char residues at low ($100\times$) and high ($2,500\times$) magnifications are presented in Fig. 4. According to Fig. 4, the surface

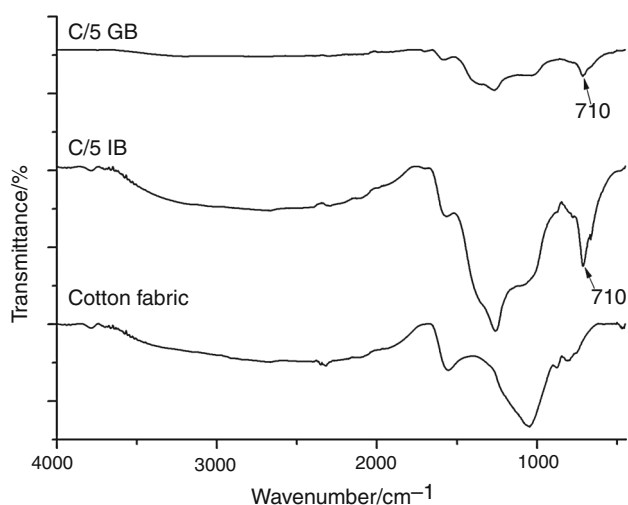


Fig. 5 ATR-FTIR spectra of char residues remained after LOI test

morphology of pure cotton fabric is different from boron compounds treated cotton fabrics. Both cotton fabric and 5 mass% GB- and IB-treated cotton fabrics retain the integrity of fiber structure after LOI test. Pure cotton fabric has smooth surface. Whereas, irregular surface coating which protects the underlying material is observed on the surface of flame retardant-treated fabric samples due to residual products of boron compounds after the combustion. According to the results of SEM-WDX analyses in Table 2, the presence of nitrogen in the char structure supports the proposed reaction of basic nitrogen-containing intermediates with cellulose. Figure 5 shows the ATR-FTIR spectra of char residues remained after LOI test. GB- and IB-treated cotton fabrics show additional peaks at 710 and 1,580 cm^{-1} due to the stretching vibrations of aromatic C–H and C=C groups, respectively [33]. It can be concluded that GB and IB favor the formation of aromatic char structure in the condensed phase. The findings in the previous study also support this conclusion. Karacan et al. showed that the boric acid treatment of viscose rayon fiber favored the formation of aromatic char structure [17].

Limiting oxygen index

The flame retardant properties of cotton fabrics treated with IB and GB are evaluated by LOI. The pristine cotton fabric has a LOI value of 18.8 %. The flame retardant finishing of cotton fabric increases the LOI values as the amount of boron compounds increases. It is thought that the increase in LOI value arises from several combined flame retardant effects exerting by IB and GB. Both boron compounds undergo endothermic decomposition (heat sink action), release non combustible gases (diluting effect in the gas phase), and promote char formation in the condensed phase.

IB-containing cotton fabrics have slightly higher LOI values than GB-containing ones due to the higher char yield. As stated in the previous studies that there is a relationship between LOI values of cellulosic materials and char yield. As the char yield increases, LOI value of cotton fabric increases [26, 32, 34]. Accordingly, the LOI values of IB-treated cotton fabric are higher than GB-containing ones.

Conclusions

In this study, we assessed the possibility of using two boron compounds, IB and GB, as flame retardant additive for cotton fabrics. According to TG data, both boron compounds reduce T_{max} and promote char formation as the amount increases. Physical and chemical effects govern the increase in char yield. The formation of protective layer on cotton fabric, the reactions of cellulose with degradation products of IB and GB, and the promotion of aromatic char structure cause increase in char yield. According to LOI test results, both boron compounds increase the LOI value of cotton fabric as the amount increases by exerting various flame retarding effect. IB-containing cotton fabrics have higher LOI value than GB-containing ones due to higher char yield. The increase in char yield is predominant flame retardant effect of both boron compounds, although they exert several combined flame retardant effects including promoting char formation, heat sink action, and diluting effect in the gas phase.

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