Facile Flame Retardant Finishing of Cotton Fabric with Hydrated Sodium Metaborate

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Abstract

Flame retardant (FR) cotton fabric was facilely prepared using hydrated sodium metaborate (SMB) crystalized in-situ in the interstices and on the surface of cotton fabric via one-pot impregnation approach, and the thermal, FR and mechanical properties were investigated. TGA results showed that SMB treatment improved the thermal stability of cotton fabric and enhanced the char yield. The treated cotton also had an LOI value of 28.5 % with an afterglow time of less than 1 s in the UL-94 test (V-0). Considerable reductions in peak heat release rate (PHRR ~ 91.8 %), total heat release (THR, ~ 47.2%), peak carbon monoxide and carbon dioxide produced (PCOP ~28.6, PCO$_2$P ~ 85.5 %) were obtained. The postburn residues examined by SEM and Raman spectroscopy revealed a preserved fabric structure with high graphite content. SMB treated cotton fabrics demonstrated negligible changes in the tensile strength and the elongation at break. The result demonstrates SMB as an effective flame-retardant for cotton fabrics.

Keywords: Cotton fabric; flame retardant; cone calorimeter; sodium metaborate; mechanical properties

1 Introduction

Cellulose is one of the most readily available natural resources with varieties from various sources (Bayer and Lamed 1992; Kaplan 1998; Thakur and Thakur 2014; Zhu et al. 2006). Meanwhile, cellulose from plants has over the years remained the primary resource of raw material for the textiles industry with wide applications as beddings and clothing due to its luster and comfort (Bashar and Khan 2013; Ravandi and Valizadeh 2011; Sabir 2017). However, the low thermal stability, easy ignitability, and rapid combustion of cellulosic remain a major setback for applications that require high-performance fire protection (Alongi et al. 2012; El-Shafei et al. 2015; Zhang et al. 2016). The urge to improve FR properties of cellulosic textiles materials for the reduction of fire hazards has been the major preoccupation for FR experts over the years (Aenishänslin et al. 1969; Chen et al. 2015; Li et al. 2010; Wu and Yang 2007). All the efforts in this regard are aimed primarily at developing economical, yet highly efficient and environmentally benign FR finishing for cotton fabrics to reduce its flame vulnerabilities (Abou-Okeil et al. 2013; Aenishänslin et al. 1969; Alongi et al. 2012; Wu and Yang 2007).

Surface modification and crosslinking chemistries remain the most popular approaches to achieving FR finishing for cotton fabric with the use of the traditional FRs (Aenishänslin et al. 1969; Chen et al. 2015; Yang et al. 2012b). The most effective FRs hitherto used for most polymers including cotton fabrics are the halogen-based but their applications, especially for household textiles products, have been limited due to the noticeable effects like the production of toxic fumes and harmful gases during combustion in addition to several mutagenic health effects associated with their continual exposure (El-Shafei et al. 2015; Wu and Yang 2007). Hence, the continual quest for environmentally friendly alternative FRs for cotton fabrics

Over the years, alternative halogen-free FRs comprising boron, silicon, nitrogen, phosphorus, and other substituents have been developed for various polymers including cotton (Horrocks et al. 2005; Lu and Hamerton 2002; Wang 2008; Yang et al. 2012a). In recent years, water-based techniques for conferring durability on fabric has been investigated extensively (Alongi et al. 2014; Chang et al. 2014; Paul 2014). These processes range from the use of silicon-based amino compounds through the sol-gel technique to the traditional layer by layer approach based on the alternating deposition of charged anionic and cationic polyelectrolytes (Chen et al. 2015; Huang et al. 2012; Sasaki et al. 2015). These techniques create nanometer thin multilayer coatings on the surface of material via electrostatic interactions (Alongi and Malucelli 2015; Huang et al. 2012). Lately, various boron-based salts have been used as FR additives for cellulose but have received less attention compared to the halogen, phosphorus, and other FR compounds (Gaan and Sun 2007; Hirschler 2015). This phenomenon is mainly due to its supposedly poor durability because of its water solubility (Zhang et al. 2016). As a result, synergetic effects of boron and other compounds have been explored (Martin et al. 2006a; Martin et al. 2006b). Typically, boron and nitrogen elements have been reported as alternative FR that produce crosslinking reaction to promote material charring and generation of non-flammable nitrogen oxides which tend to interfere with the usual mechanism of fires (Xie et al. 2013).

Despite the increasing use of boron-containing compounds as FRs for cellulosic materials, the application of hydrated sodium metaborate (SMB) as a sole FR for cotton fabric remains a grey area notwithstanding its ability to produce water molecules during combustion to mitigate the thermal degradation of cellulose and subsequent glassy charring due to the boron-oxygen groups in its structure (Nine et al. 2017b). SMB have high thermal stability, inexpensive, nontoxic, and above all ensure control release of water molecules during combustion (Nine et al. 2017b). SMB can also function as chemical heatsink similar to the metal hydrates during combustion when undergoing endothermic decomposition (Nine et al. 2017a; Nine et al. 2017b; Zhang et al. 2017). The boronic glassy chars can serve as a physical protective barrier to prevent the exchange of organic volatiles in the flame and reduce smoke and toxic fumes production (Feng et al. 2017; Tawiah et al. 2018). Based on this supposition, graphene oxide was intercalated with SMB and a significant improvement in FR performance for cellulosic materials (Nine et al. 2017b).

Herein for the first time, we report the application of hydrated sodium metaborate for FR finishing of cotton fabric in one-pot impregnation approach. SMB was crystalized in-situ in the interstices of cotton fabric, and its FR properties were evaluated. The FR mechanism of hydrated sodium metaborate is based on the hydrating properties of SMB in addition to the glassy charring effect of boron-hydroxyl compounds when exposed to flames.

2 Experimental

2.1 Materials

A mercerized plain-woven cotton fabric was supplied by Saintyear Holding Group Co., Ltd, China (weight 120 g/m^2, density: 84 x 163/inch). The fabric was used without further treatment. Sodium borohydride was purchased from Sigma Aldrich, Germany. Other analytical grade reagents were supplied by Hong Kong Labware Ltd. and used without further purification. The entire experiment was done with deionized water.

2.2 Treatment of cotton

Sodium borohydride (4 g) was dissolved in 20 mL DI water and stirred for 30 min at room temperature (RT). The cotton fabric was impregnated by padding at a pick-up rate of 80 %. The treated fabric was covered and allowed to age for 24 h to allow the development of sodium metaborate (SMB) crystals in-situ in the interstices of the fabric according to the following reaction (Lo et al. 2007).

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2$$

The aged cotton fabric was dried at RT for 12 h and in an oven at 80 °C for another 12 h to obtain SMB treated cotton fabric

The fabric was thoroughly rinsed with DI water to remove the unfixed crystals on the surface of the fabric. The sample was dried at 80 °C for 12 h. The treated fabric was conditioned (RH 65% at 20 °C) for 24 h before for further measurements. The mass add-on was calculated using equation 1.

$$Add\ on\ (\%) = \frac{W2-W1}{W1}\ x\ 100\ \% \qquad \text{(Eq. 1),}$$

where W1 indicate the weight of cotton fabric before padding, and W2 is the weight of the cotton fabric after padding, drying and rinsing.

Washing durability of the SMB on the cotton fabric was assessed using standard washing powder (AATCC 1993) in DI water at the boil for 30 minutes under gentle stirring. The SMB treated fabric was rinsed with DI water several times after washing and dried in an oven at 80 ^{o}C. The sample was conditioned for 24 h, and the weight loss was calculated using equation 2.

$$Weight\ loss\ (\%) = \frac{W_a-W_b}{W_a}\ x\ 100\ \% \qquad \text{(Eq. 2),}$$

where Wa is the weight of the cotton fabric before standard washing treatment, and Wb is the weight of the fabric after standard washing, drying, and conditioning.

2.3 Characterization

FTIR spectrometer with an attenuated total reflection (ATR) attachment was used. The spectra of the samples were scanned in the range 4000−650 cm^{-1} at 4 cm^{-1} after averaging 8 scans.

X-ray diffraction (XRD) of cotton fabrics were taken on a Rigaku Smartlab X-Ray diffractometer in reflectance parallel alignment mode with Cu K_α line focused radiation of 1760 W (40 kV, 44 mA) and a Ge crystal detector fitted with a 10.0 mm incident slit. Pieces of fabrics (treated and untreated) were mounted and analyzed successively using a 0.0200° θ/2θ step scan from 5.0 – 60.0° with a scan speed of 5°/min^{-1}.

TGA (Mettler Toledo, Switzerland) was used to evaluate the thermal stability of the treated and untreated cotton fabrics in the range of 40 -700 ^{o}C at 20 ^{o}C/min in air.

The morphology of the SMB treated, and the untreated cotton fabrics, as well as the residual char, were observed with a scanning electron microscope (JEOL JEM-2100F, Japan) fitted with an EDS.

Limiting oxygen index (LOI) was evaluated according to ASTM D2863-13 standard using ZR-1 Intelligent Oxygen Index Analyzer (China). Samples measuring 5 cm × 15 cm were tested for each specimen.

The vertical burning test (VBT) was done according to GB/T 5455-1997 standard. Sample size 30 cm × 8 cm were placed inside the sample holder with dimensions W329 × D329 × H767 mm with butane gas and flame height of 40 mm within 12 s.

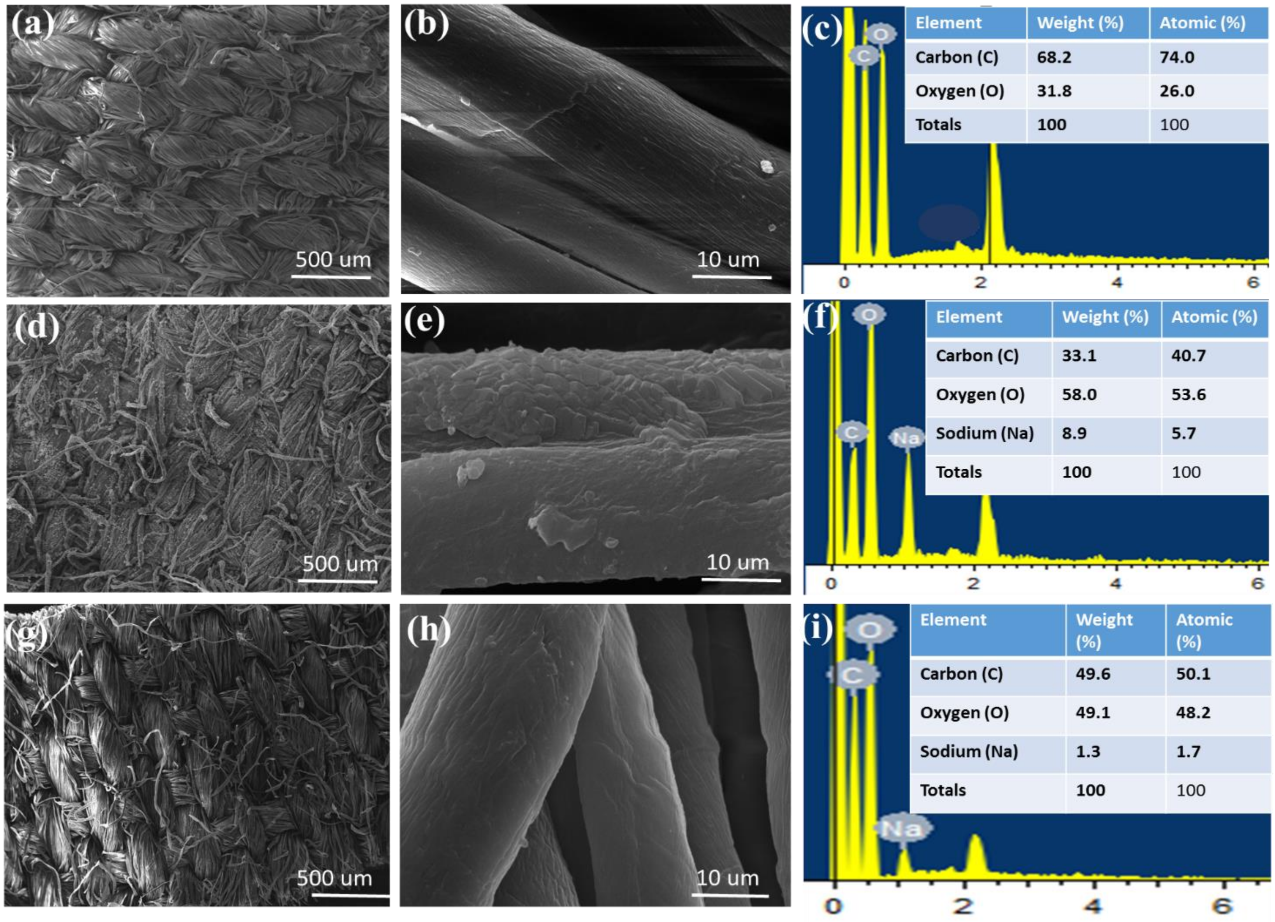
Cone Calorimeter (Fire Testing Technology Ltd., UK) was performed according to ISO 5660-1 standard. Two double pieces of each specimen with dimensions (100 × 100 × 0.02 mm^3) was tested at a heat flux of 35 kW/m^2.

The mechanical properties were evaluated according to ISO 13934-1 with Instron Tension Tester. Samples size 25 x 5 cm were tested at a drawing speed of 5 cm/min at a clamping distance of 20 cm.

3 Results and discussion

3.1 Morphology

The SEM images and EDS analysis for control (untreated fabric), SMB treated, and washed cotton fabrics are shown in Fig.1 The control fabric appears smoother compared to the treated sample (See Fig. 1 a-b). The sample presents densely rough surface morphology due to SMB deposition as shown by Fig. 1 (d-e). The EDS analysis shows high carbon (68.2%) and oxygen (31.8%) contents for the untreated cotton. After treatment with SMB, the weight of oxygen increased (58.0%), whereas the weight of carbon decreased (33.1%) due to increasing content of O and the introduction of Na on the surface of cotton due to SMB deposition. Na (8.9%) can be observed from the EDS analysis of the treated fabric but missing from the control sample. The surface of the washed cotton fabric appears relatively rough compared to the untreated fabric. As confirmed from the EDS elemental scan, the content of Na decreased but not removed completely. Meanwhile, the boron in all the three samples could not be detected because it is a light element which often goes undetected by most EDS devices. That notwithstanding, it is evident from the SEM and EDS analysis that the cotton fabric has been coated by SMB. The weight gained by the SMT treated cotton fabric was determined to be 18.6%; meanwhile, after laundry, the sample lost weight by 9.4%, indicating a reduction in SMB content.



(c)

Element	Weight (%)	Atomic (%)
Carbon (C)	68.2	74.0
Oxygen (O)	31.8	26.0
Totals	100	100

(f)

Element	Weight (%)	Atomic (%)
Carbon (C)	33.1	40.7
Oxygen (O)	58.0	53.6
Sodium (Na)	8.9	5.7
Totals	100	100

(i)

Element	Weight (%)	Atomic (%)
Carbon (C)	49.6	50.1
Oxygen (O)	49.1	48.2
Sodium (Na)	1.3	1.7
Totals	100	100

Figure 1. SEM images of: (a, b) untreated cotton fabric, (d, e) SMB T. cotton fabric, (g, h) laundered cotton fabric. EDS profiles of: (c) untreated cotton, (f) SMB T. cotton fabric, and (i) laundered cotton fabric.

3.2 Chemical properties

FTIR and XRD were used to study the functional groups and the crystal structure of SMB, treated and untreated cotton fabrics, and the spectra are shown in Figure 1a. Obvious peaks belonging to the control sample dominates the treated fabric, but the most important peaks of SMB can also be found on the treated fabric. Typically, the characteristic peaks of asymmetric and symmetric B-O stretching vibrations in SMB can be found at 1436 and 1422 cm^{-1} – consistent with the literature (Pişkin et al. 2013). Other noticeable peaks of SMB at 1657 and 900 cm^{-1} belonging to the H-O-

H asymmetric stretching vibrations can also be found in SMB and the treated fabric respectively. This clearly confirms the presence of SMB on cotton fabric beyond the weight gained (18.6%) after treatment. The XRD pattern in Fig 1 (b) further confirms the presence of SMB on the cotton fabric. Obvious peaks belonging to SMB can be found on the treated sample in addition to the established peaks of cotton fabric. However, a slight shift in XRD peaks to lower theta angle is observed. The shift could be attributed to several reasons including changes in the stoichiometric composition after SMB padding and rinsing; a shift emanating from the doppler effect during counts, and lastly, a decrease in crystallize sizes and lattice strain resulting from the differences in ionic radii between the main element in cotton and raw SMB. A similar phenomenon was observed in the washed sample, but the intensity of the pristine SMB peaks were lower compared to the SMB treated fabric without standard laundry.

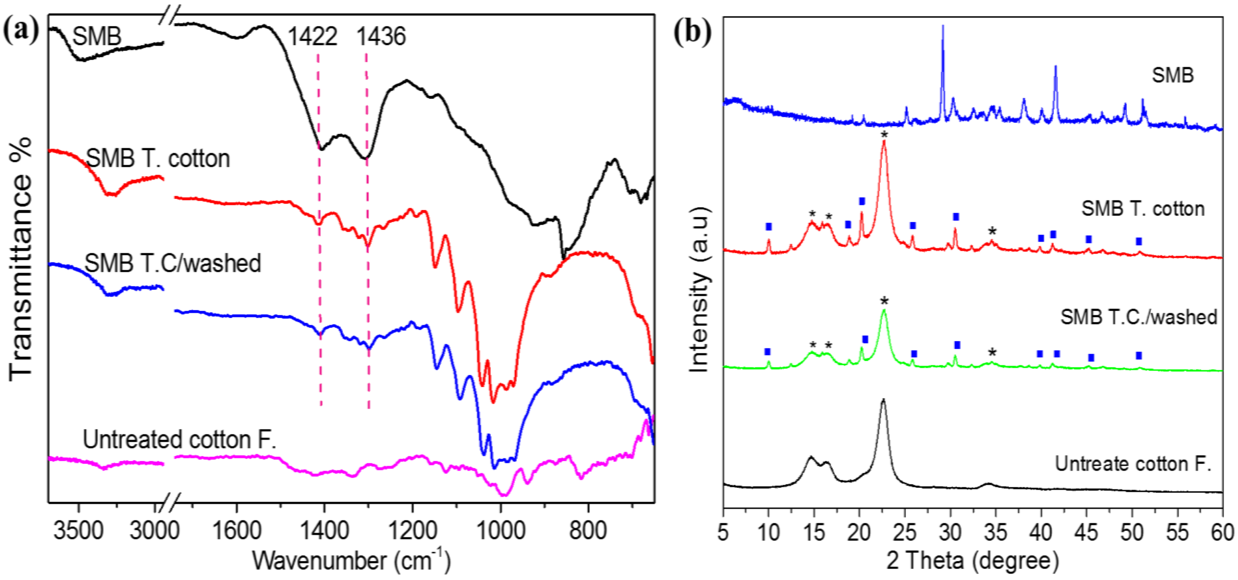


Figure 2. (a) FTIR spectra and (b) XRD of untreated cotton fabric, SMB, SMB treated cotton and SMB treated but washed cotton fabric.

3.3 Thermal properties

The thermal properties of SMB, control sample and SMB treated cotton fabric were evaluated, and the results are presented in Fig. 3 with the detailed data accessible from Table S1. The control sample lost approximately 11.1 % weight in the temperature range of 170 - 300 °C due to dehydration of anhydroglucopyranose chain segments (Alongi et al. 2012; Brillard et al. 2017). The second stage decomposition that occurred in the temperature range of 300 - 380 °C is due to degradation of the fibers in the amorphous region of the cotton (Brillard et al. 2017; Zhu et al. 2004). In this stage, the weight loss is swift, and the evolution of most of the pyrolysis products are produced. The main pyrolysis product is l-glucose together with all kinds of combustible gases leading to the generation of volatile flammable products (Zhu et al. 2004), and subsequent formation of char (2.4%). SMB showed high thermal stability with a minimal weight loss around 100 – 200 °C due to the loss of crystal water and dehydration. SMB remained thermally stable beyond T_{max} yielding higher char residue (91.6%). Upon treatment of cotton, the TG curve showed initial decomposition behavior similar to SMB with the initial weight loss lower than that of the control sample but higher than SMB (See Table S1). At T_{max}, the SMB treated cotton (18.6 % weight gain) showed a minimal mass loss rate (M.L.R) of - 0.4% compared to - 2.4% for the control sample and eventually yielded higher char residue (~ 41.5 %) than the control sample (2.4%). After laundered fabric had early onset decomposition similar to the untreated cotton fabric but had a higher char residue of ~ 18.4 %. During the pyrolysis process, the SMB catalyzes reactions of dewatering, decarboxylation, and charring which interrupts and slows down the reactions that result in l-glucose. This process ultimately minimizes the decomposition rate, which is the case of SMB treated cotton fabric observed in Figure 3 (b) and Table S1. This makes SMB suitable FR for cellulose due to the condensed phase FR activity in addition to the thermal cooling effect provided by the hydrated water molecules for self-extinguishing actions which leads to the formation of sealant boronic char (Chan et al. 2018). The char acts as a physical barrier that reduces physical contact between the flame and the unburnt cotton fabric, which eventually stops the rest of the fabric from burning.

3.4 Combustion behavior

Figure 3b shows the LOI values of the control, SMB treated cotton fabric before and after washing accordingly. The control sample had an LOI value of 17.2%, which makes it very flammable under normal conditions. The SMB treated, and the washed cotton fabrics had LOI values of 28.5 and 23.6 % representing 65.7 and 37.2% increase respectively in flame retardancy. It is evident that the FR efficiency reduced after washing but still much better compared to the control sample. The remarkable increase in LOI values may be due to the hydration effect of SMB and the improve char yields (see TGA and Table S1, and 2 respectively). The water molecules cool down the flame while the char acts as a thermal shield/barrier which hinders the transfer of heat and fuel to stop further combustion.

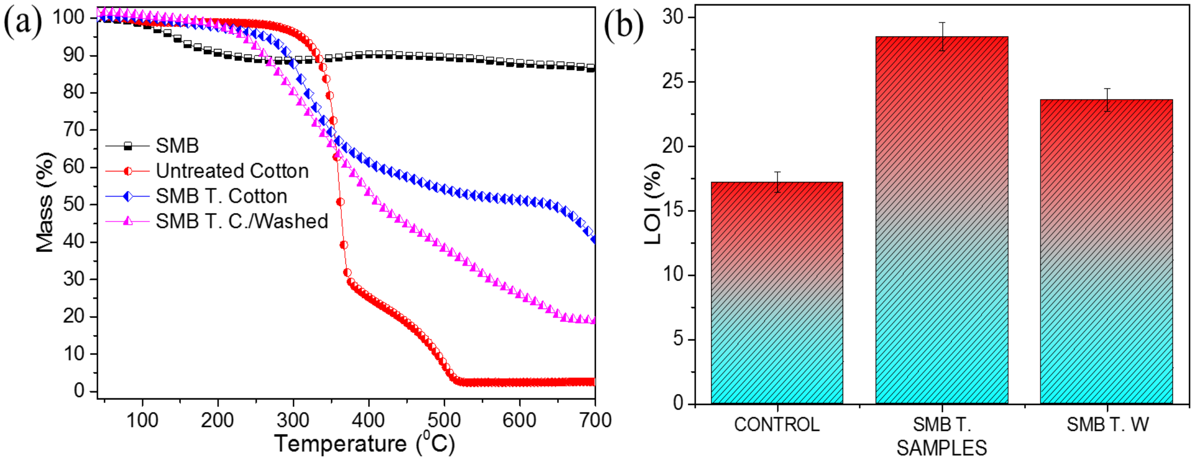


Figure 3. (a)TGA of control (untreated cotton), SMB, SMB treated cotton fabric, SMB treat but laundered cotton fabric. (b) LOI performance of control (untreated cotton), SMB treated cotton fabric, and SMB treated but laundered cotton fabric.

The UL-94 test provides a practical means of assessing the flammability of materials for specific end use. The samples were burned directly for 12 s at the bottom of the fabric samples the entire burning phenomenon is displayed in Fig. 4. The untreated fabric (control) (Fig. 4 (a)), burned actively and almost entirely, leaving a minimal amount of char as shown in Fig. 4 (16s). However, the SMB treated cotton fabric with weight add-on 18.6 % could not ignite and burn easily unlike the untreated sample. A prolonged time was therefore used to ascertain the burnability, but the little char residue generated could not allow the fire to burn the rest of the specimen. Also, the flame could not be sustained when the burner is removed probably due to the release of water molecules by SMB and the formation of glassy char due to the presence of the boron-hydrogen moieties (see Fig. 4b). The char provided great heat shielding effect and served as a barrier to volatiles flame enhancement gases which prevented the sample from continuous burning. When the burner was removed, the specimen self-extinguished quickly within 1 s with no after-flame effect and thus left ~ 2 cm char. The burning tests indicate that SMB is thermally stable with high flame retarding efficiency – consistent with the TGA results. Also, the washed specimen (weight loss 9.4%) (Fig. 4 c) burned but less vigorous compared to the control specimen and left more char. At the 12 s, the control specimen got burnt entirely whereas less than 1/3 of the washed specimen got burnt, indicating a possible delay in fire spread in real life applications. Unlike the control specimen which had no char residue after the entire burning process, the washed specimen had significantly higher char residue possibly due to the presence of SMB remaining in the interstices of the fibers. Although the flame retardant efficiency of the washed sample reduced, its FR performance was still better than the untreated sample.

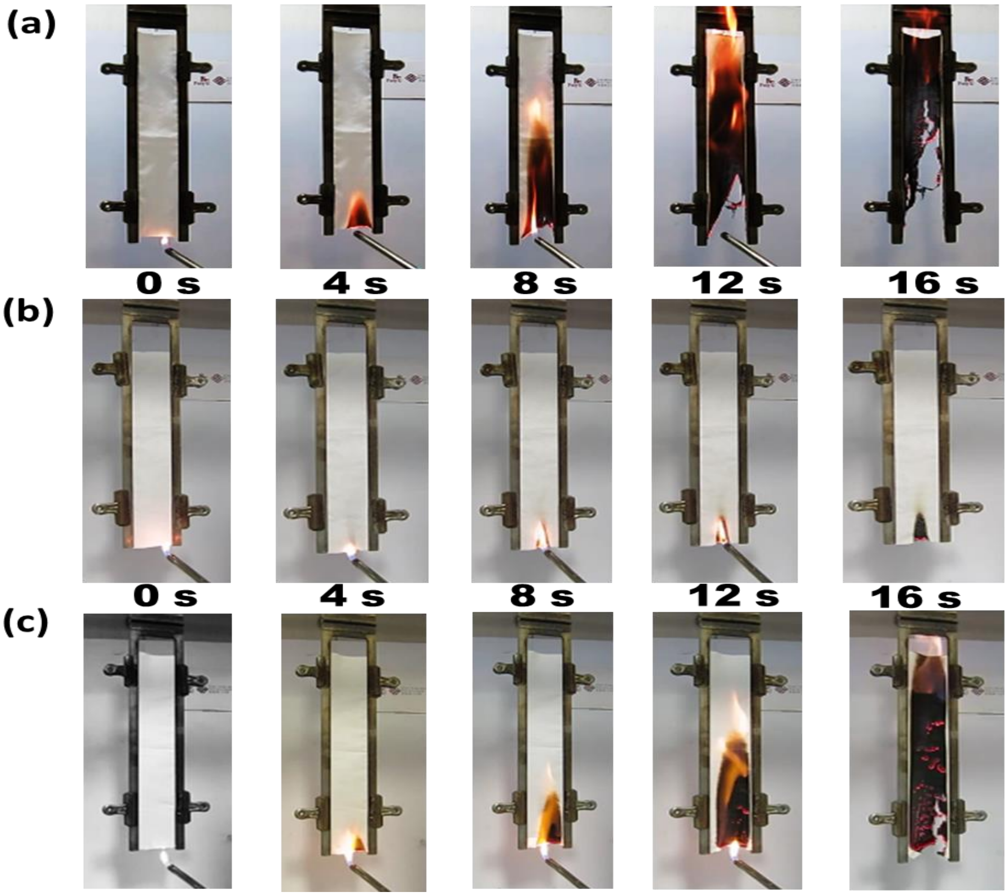


Figure 4. Digital images of UL-94 test: (a) untreated cotton fabric, (b) SMB treated cotton fabric, and (c) laundered cotton fabric.

Cone calorimeter (CC) was used to study the flammability of the SMB treated cotton fabric, washed sample and the control fabric due to its ability to simulate the behavior of materials in a real fire scenario. Heat release rate (HRR) and total heat release (THR) are the two vital parameters for assessing the flammability of polymers because they are reliable indicators of the size and fire growth rate (Babrauskas and Peacock 1992). Moreover, since fire deaths are caused more by toxic fumes than burns (Gann et al. 1994), smoke and toxic fumes analysis is very useful for predicting the fire toxicity of polymeric materials. Details of CC results are shown in Fig. 5 and Table S2. The washed sample basically had the same TTI as the untreated due to the reduction in SMB loading. The SMB treated, however, had relatively higher TT1(~ 5 s) similar to the phenomenon observed during the UL94 test. This indicates that SMB treated fabric could delay fire propagation.

Fig. 5 shows the HRR of the SMB treated fabric, control sample, and the washed specimen. The control sample and the washed sample showed strident peaks, and subsequent sharp drop whereas the SMB treated fabric displayed no definite peak but instead showed a broad prolonged line due to smoldering. No visible flame was seen during the test, unlike the control and the washed specimen. This phenomenon led to a substantial reduction in PHRR by ~ 91.8%. After standard washing, the PHRR reduced by ~ 38.6 %, indicating a reduction in FR efficiency compared to the Unwashed sample. Meanwhile, ~38.6 reduction is still a significant improvement in fire safety compared to the control sample. A similar reduction in THR was observed for all samples (Fig. S2, Table S2). The increases in PHRR and THR were due to the formation of protective glassy char layer by the boron component in addition to the thermal cooling effect by SMB due to the release of water molecules. This phenomenon can be confirmed by the percentage char residue shown in Table S2 and the digital images after CC displayed in Fig. 5(a-c) and supplementary Fig. S3 (a-c). The control sample burnt almost completely leaving a little char residue of 8.6 % whereas the SMB treated, and washed samples had ~ 43.1 and ~ 20.2 % char residues respectively (See Fig. S2, Table S2). From Fig.5c, the SMB treated sample had considerably more quantity of char with the fabric structure intact. It is evident that the improvement in char formation led to the reduction in flammable volatiles gases in addition to the release of water molecules. Consequently, less volatile pyrolysis gases and heat remained in the combustion zone, which reduced the intensity of the flame.

With regards to smoke production during CC (Fig. 5c), SMB treated sample demonstrated prolonged smoke release due to smoldering caused by SMB with only ~ 1.5% reduction in TSR. After standard standing washing, the smoke production time decreased along with ~ 35.3 % reduction in TSR. The PCOP of SMB treated cotton fabric decreased by ~ 28.6 %. However, after the standard washing, this figure reduced to ~14.3 % possibly due to the reduction in the barrier effect by boronate char (Fig. 5d), which allowed the escape of smoldering CO gases. The improved PCOP by the treated sample is due to the active physical barrier effect of the compact char despite the incomplete combustion. It is worth noting that, averagely, the SMB flame retarded cotton fabric produced more CO than the control and the washed sample, however, in terms of PCOP, the treated fabric performed better. Fig. 4 (d) shows the peak CO_2 produced for the control and the SMB treated samples. Generally, the ratio of CO_2/CO is an indication of combustion proficiency by showing the degree of alteration from the fractionalized oxidative product (CO) to full oxidization product (CO_2) (Gann et al. 1994). The SMB treated cotton showed ~ 85.5 % decrease in $CO_{2,}$ but after standard washing, it decreased to ~ 35.7 % compared to the control sample, suggesting a reduction in FR efficiency. Meanwhile, its FR performance is still better compared to some unwashed FR systems by other groups (Abou-Okeil et al. 2013). This makes SMB an efficient FR for cotton fabric.

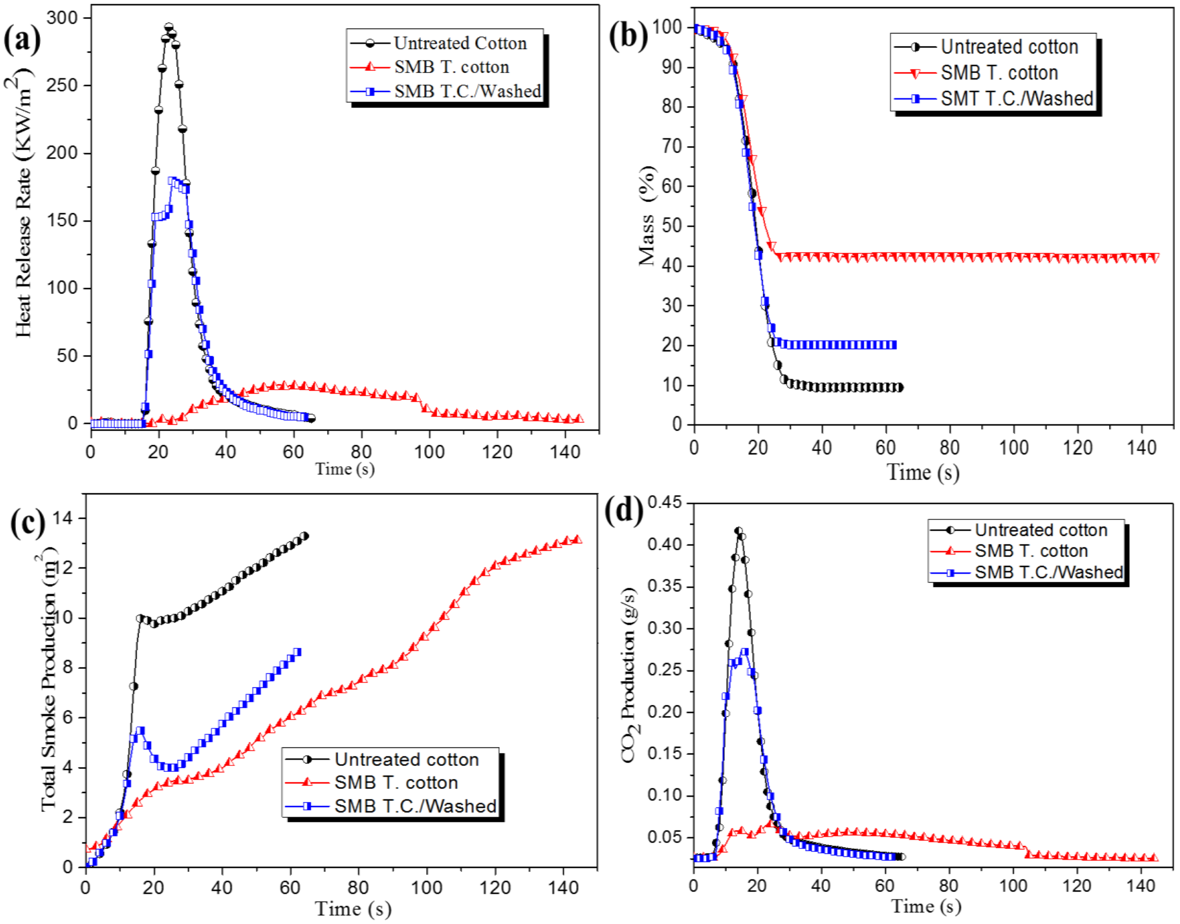


Figure 5. Cone calorimeter curves of untreated and SMB treated cotton fabrics: (a) peak heat release rate, (b) mass loss curve, (c) total smoke production, and (d) CO_2 production.

3.5 Residual char analysis

The digital and SEM images of the residual chars presented in Fig. 6 (a-c). The control sample and the treated but washed samples (Fig. 6 a, c) showed crumpled fragile char whilst the SMB treated sample showed preserved undulating fabric structure/morphology (Fig.6b). The SEM images displayed fragilely thin fibers swamped together into one big mass for the untreated fabric. (see Fig. Suppl. 3a). Similar appearance could be observed for the washed sample, but its weave structure is quite distinctive (Fig. 6c and suppl. Fig 3c). Nonetheless, the fabric structure appears more loosely bound and preserved. The SMB treated fabric (Fig. 6b, suppl. Fig. 3b) has its fabric structure intact, which is a characteristic feature of intumescent type FRs on cotton fabrics. The fiber shape of cotton was ribbon-like and undamaged. The intumescent material charring of SMB is based on the release of water molecules in the structure for self-extinguishing action with the boron content providing glassy sealant char to limit the inflow of oxygen and other volatile gases, which serves as heat-sink and thus provide strong intumescent char that restrains physical collapses and penetration of pyrolysis gases. The controlled release of water molecules by hydrating SMB during combustion cools down the flame and reduce the burning of cotton fabric.

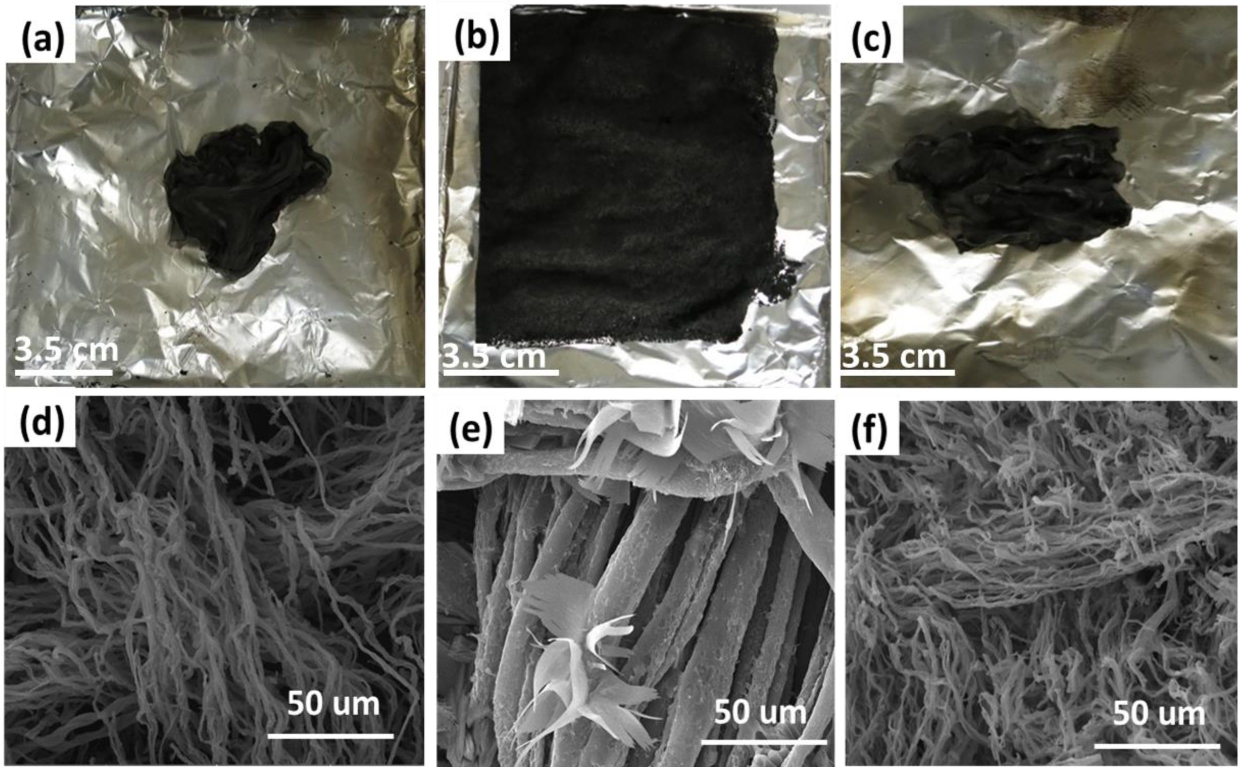


Figure 6. Digital images and SEM micrographs of char residue after CCT: (a, d) untreated cotton fabric, (b, e) SMB treated cotton fabric, and (c, f) SMB treated but laundered cotton fabric.

Fig. 7 shows the FTIR and the Raman spectra of the residual chars obtained after CCT. Obvious peaks belonging to B-O stretching vibrations can be found around 1422 cm^{-1} in the SMB treated and the washed sample in the FTIR spectra (Fig. 7a). However, the intensity of the washed sample was less compared to the unwashed. This suggests a reduction in the content of SMB in the cotton fabric after washing – consistent with the weight loss observed after standard washing (9.4%). More so, characteristically deep and broad absorption bands around 3380 cm$^{-1,}$ and the 1654 cm^{-1} found in the char residue of SMB treated and the washed samples can be attributed to adsorbed water. These peaks were obviously missing in the control sample.

Fig. 7(b) shows the Raman spectra of the samples. Obvious D and G bands at 1354 and 1586 cm^{-1} corresponding to amorphous/glassy and graphitic char content in the residues are observed. The integrated intensity (determined as the area under D and G bands) of D and G (ID/IG) is directly proportional to the ratio of amorphous and graphitic char contents present in the residues, with lower ID/IG values suggesting higher graphitic char yield and vice versa. It is evident from the Raman spectra that the untreated cotton had high ID/IG value of 0.92 compared to 0.60 of the SMB treated fabric. The low ID/IG value of SMB treated fabric indicates the presence of more stable graphitic char. The higher graphitic char content possibly led to the distinct preservation of the fabric structure as shown in Fig. 6 (b). Meanwhile, the small peak in the middle of D and G can be ascribed to the presence of BO_3 groups from the pyrolysis of SMB(Angeli et al. 2012). The content of graphitic char for the washed sample reduced resulting in lower ID/IG value of 0.85. Therefore, similar to the SMB treated sample, the fabric structure remained relatively intact compared to the control sample (see Fig. S3 (c). It is imperative to state that the content of graphite is directly proportional to the structural integrity of the ensuing char and apparently the FR efficiency.

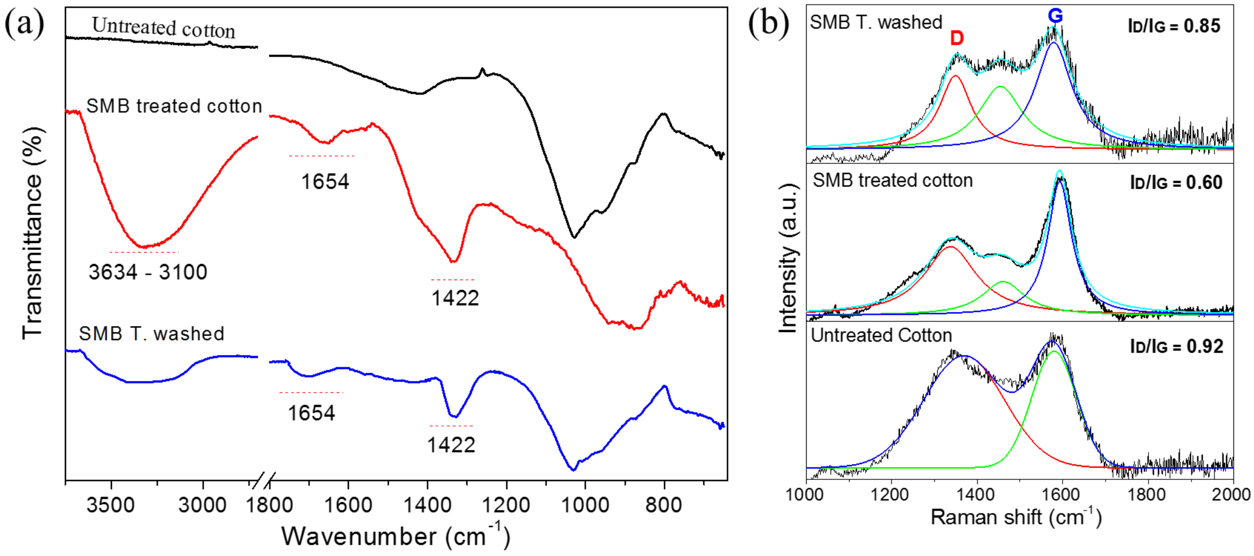


Figure 7. Char residues of untreated, SMB treated, and treated but laundered cotton fabrics after CCT: (a) FTIR spectra, and (b) Raman spectra.

3.6 Tensile properties

Tensile properties of the SMB treated, washed and the control sample was evaluated, and the data is shown in Table 1. The tensile strength of the control sample in the warp and the weft direction are 911N and 473N with the elongation at break of 32.9% and 21.3% respectively. The tensile strength of the SMB treated sample in warp and weft directions decreased marginally by ca. 2.1 and 1.5% respectively. Similar reductions were observed in the elongation at break in the weft and warp directions as shown in Table 1. The nominal reductions in the elongation at break and the tensile strength and could be attributed to the increasing amorphous regions in the fiber due to the presence of SMB crystals in the interstices of the fibers. However, after the soaping process, the reduction in tensile strength and the elongation at break was negligible compared to the control sample (see Table 1). The immaterial reduction in washed specimen could be attributed to the reduction in the amount of SMB crystals on the surface and in the interstices of the fibers as attested to by the reduction in weight after soaping.

Table 1. The tensile strength of control and SMB treated fabrics.

Sample	Tensile strength (N/mm^2) warp direction	Tensile strength (N/mm^2) weft direction	Elongation at break (%) in warp direction	Elongation at break (%) in weft direction
Control	911 ± 15	473 ±11	32.9 ± 3	21.3 ± 3
SMB T.	892 ± 21	466 ± 9	27.6 ± 5	19.5 ± 4
SMB T./W	901± 18	470 ±12	30.2 ± 3	20.1 ± 2

4 Conclusions

A simple approach to the FR finishing of cotton fabric was reported using hydrated sodium metaborate crystallized in-situ in the interstices and on the surface of the fibers. The thermal, FR and mechanical properties were evaluated. FTIR, XRD, and SEM result clearly confirmed the presence of SMB on and in the interstices cotton fibers. The FR performance evaluated by LOI and vertical flammability tests showed SMB as alternatively green and efficient FR for cotton fabrics. Cone calorimeter test showed a substantial reduction in peak heat release rate by 91.8 %. Similar reductions were achieved for THR, PCOP, and PCO_2P. TGA analysis showed that SMB is a thermally stable and active promoter of char due to the release of water molecules by SMB during the burning process, in addition to the glassy charring effect of B-OH groups. The surface morphology of treated fiber char residue demonstrates SMB as an intumescent FR which aided the preservation of the fabric structure of cotton without significant damages. Reductions in the tensile strength and the elongation at break of SMB treated cotton fabrics were generally negligible. The results demonstrate SMB as an effective FR for cotton fabric for practical applications that might not require repeated washing due to the apparent reduction in FR properties after laundry.

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