Cellulose (2020) 27:3501–3515
https://doi.org/10.1007/s10570-020-03020-0

ORIGINAL RESEARCH

A novel high-molecular-weight flame retardant for cotton fabrics

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Received: 28 October 2019 / Accepted: 23 January 2020 / Published online: 28 January 2020

Abstract A novel phosphorus-nitrogen based high-molecular-weight flame-retardant ammonium salt of *N*,*N*-bis(phosphonomethyl) polyacrylamide (FR-PA) was synthesized for cotton fabrics. The structure of FR-PA was characterized by nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, and ^{31}P NMR) as well as Fourier-transform infrared spectroscopy, and its viscosity average molecular weight was 3700. FR-PA could be grafted on cotton fabrics by using the dip–pad–cure method. The limiting oxygen index of the treated cotton fabrics reached 40.1%; after 50 laundering cycles, the cotton fabrics still retained an LOI of 28.5%. The treated fiber surface was smooth, as revealed by scanning electron microscopy, and the flame retardant was grafted on the cotton fibers, as determined by energy-dispersive X-ray spectroscopy. Thermogravimetric analysis showed that the treated cotton could leave a large amount of residue, and thermogravimetric infrared analysis indicated that the finished cotton released little flammable gas at high temperatures. Oxygen consumption cone calorimetry showed that the heat release rate and the total heat release of the treated cotton fabrics were significantly lower than those of the control cotton fabrics. Moreover, the stiffness and tensile strength of the treated cotton fabrics were also maintained.

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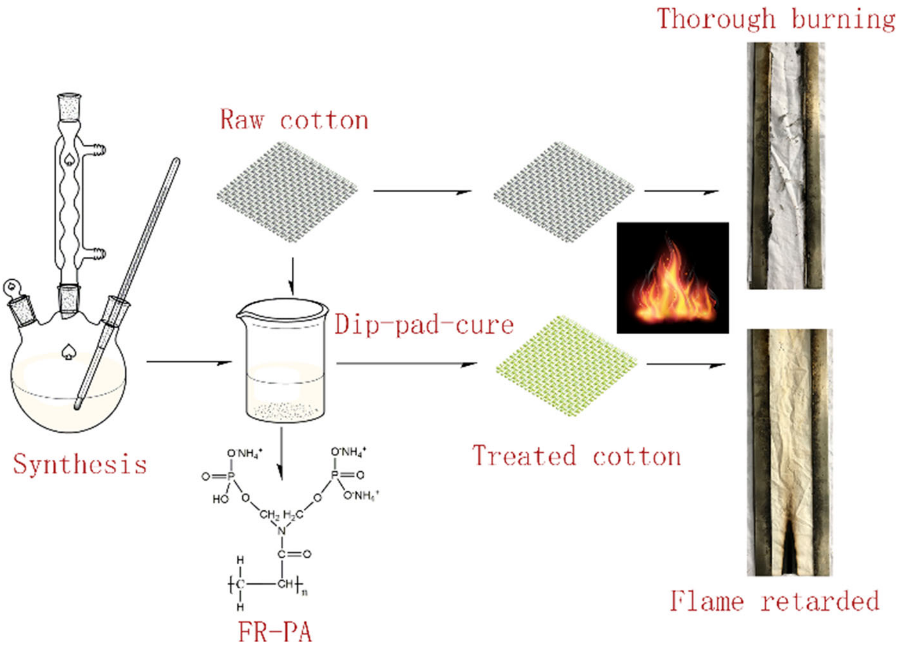
Graphic abstract



Keywords High-molecular-weight flame retardant · Cotton fabric · Polyacrylamide · Durability

Introduction

Cotton is widely used in apparel, home textiles, decoration, and other fields (Jia et al. 2017; Xie et al. 2013; Xu et al. 2019b). However, as a flammable material, cotton presents the risk of sparking a fire or spreading flames (Atakan et al. 2019); its limiting oxygen index is only about 18%. Thus, numerous studies have been conducted on methods of endowing cotton fabrics with flame retardancy (Chen et al. 2015; Gao et al. 2014; Huang et al. 2019; Liu et al. 2017; Salmeia et al. 2016).

Halogen or halogen-derivative flame retardants are important components of the earliest flame retardants because of their excellent flame retardancy (Lu and Hamerton 2002; van der Veen and de Boer 2012). However, the use of most halogen flame retardants has been stopped because of their toxicity (Chaudhry and Chapalamadugu 1991; Frederiksen et al. 2009; Wu et al. 2007). Research on halogen-free flame retardants mainly focus on phosphorus-based compounds (Green 1992, 1994; Xu and Wang 2016) and metal hydroxides, among others (Feng et al. 2017; Pietruszka and Brzozowski 2000; Pietruszka et al. 2000; Zhao 2010). In addition, graphene and micro-nanosized graphene oxide have been studied as flame retardants owing to their expansive property when heated (Alongi et al. 2019). Silicone compounds can form a three-dimensional polysiloxane network on the surface of cotton fabrics by the sol–gel method. The presence of this structure can reduce the flammability of cotton fabrics (Dutkiewicz et al. 2018).

Pyrovatex CP® and Proban® are very important flame retardants for cotton fabrics. Cotton fabrics finished with these two flame retardants exhibit excellent flame retardancy and durability (Poon and Kan 2015) but may release formaldehyde during use. To prevent the release of formaldehyde, several types of flame retardants with new reactive groups have been developed for cotton fabrics. One such flame retardant is the ethylene flame retardant, which can be grafted on cotton fabrics by ultraviolet curing (Xing et al. 2011). However, cotton fabrics treated with this type of flame retardant exhibit low flame retardancy. Compounds containing triazine have been considered as good charring agents and flame retardants because of the presence of the thermostable triazine ring. Some studies have shown that cotton fabrics treated with triazine flame retardants also exhibit antibacterial properties. However, the finished cotton fabrics cannot pass 50-standard-laundering cycle tests (Chang et al. 2011; Dong et al. 2017, 2018; Zhao et al. 2014). Bio-based nature flame retardants, such as deoxyribonucleic acid, hydrophobic protein, and phosphorus compounds, have also been reported (Alongi et al. 2013, 2015; Carosio et al. 2014; Manfredi et al. 2018); However, cottons treated with these flame retardants exhibit poor durability.

In our previous studies, several small-molecule flame retardants with the $–P=O(O^{-}NH_4^{+})_2$ group as a reactive group were synthesized for cotton fabrics (Huang et al. 2019; Tian et al. 2019; Wang et al. 2019; Xu et al. 2019b). The $–P=O(O^{-}NH_4^{+})_2$ groups can react with the –OH groups of the cotton fibers to form P(=O)–O–C covalent bonds, and the finished cotton fabrics can pass 50-standard-laundering cycle tests under the 1A test method per AATCC 61-2013 standard. However, under more stringent washing conditions, these cotton fabrics cannot pass 50-standard-laundering cycle tests such as the 2A test method per AATCC 61-2013 standard (with higher temperature and more steel balls than those of 1A). Therefore, further research on more durable flame retardants for cotton fabrics is needed.

Polyacrylamide is a water-soluble linear polymer with a large number of amide groups (Ghannam 1999). In the present study, a high-molecular-weight flame retardant ammonium salt of *N*,*N*-bis(phosphonomethyl) polyacrylamide (FR-PA) was synthesized and used in cotton fabric finishing. The ammonium phosphate groups in the flame retardants could react with the hydroxyl groups of the cotton fibers to form P(=O)–O–C covalent bonds (Jia et al. 2017; Zheng et al. 2018). Every FR-PA flame retardant molecule contains numerous reactive groups. A large number of P(=O)–O–C covalent bonds can form between each flame retardant molecule and cotton fiber. Only after all the P(=O)–O–C covalent bonds are hydrolyzed can the flame retardant molecules be washed out of the cotton fabric. Therefore, cotton fabrics treated with the FR-PA flame retardant can be expected to exhibit excellent durability.

Experimental

Materials

Cotton fabrics (100% woven cotton fabric, 129.51 g/m^2, 15.8 tex × 13.6 tex) were purchased from Chongqing Chaotianmen Market (China). Polyacrylamide was supplied by Shanghai Macklin Biochemical Co., Ltd. Dicyandiamide, absolute ethanol, and urea were purchased from Chengdu Kelong Chemical Co., Ltd. (Sichuan, China). Sodium hydroxide, hydrogen peroxide, phosphoric acid and formaldehyde were supplied by Chongqing Chuandong Chemical Co., Ltd. All reagents were used as received.

Synthesis of flame retardants

Polyacrylamide (1, 5 g), hydrogen peroxide (5 mL) (the goal was to degrade polyacrylamide), and distilled water (100 mL) were added to a 250 mL three-necked flask equipped with a magnetic stirring mixer, a thermometer, and a reflux condenser. The mixed liquid was heated to 100 °C, held for 60 min. After the mixed liquid was cooled to 50 °C, formaldehyde (2, 11.4 mL) was introduced into the three-necked flask, and the reaction lasted for 1 h at 50 °C. The phosphoric acid (3, 13.7 g) was then added and reacted for 3 h, and a slightly turbid viscous liquid was obtained. The solution was transferred to a 500 mL beaker. Subsequently, urea (4, 16.8 g) was added into the beaker, and the mixture was heated to 140 °C until the pH of the mixture was about 6. A faint yellow viscous liquid was obtained, purified with ethanol, and dried in an oven at 60 °C for 24 h. The synthesis reaction of the FR-PA is illustrated in Fig. 1a.

The FR-PA structure was characterized by proton nuclear magnetic resonance (^{1}H NMR), carbon-13 nuclear magnetic resonance (^{13}C NMR), and phosphorus-31 nuclear magnetic resonance (^{31}P NMR), as follows:

The FR-PA structure is represented by ^{1}H NMR (D_2O, 600 MHz) δ (ppm): 1.48 (s, CH, H_4), 2.08 (s, CH_2, H_1); 3.49 (s, $2CH_2$, H_2, H_3); No –OH groups or NH_4^{+} ions was detected because the reactive hydrogen atoms were replaced by deuterium by reaction with D_2O. ^{13}C NMR (D_2O, 600 MHz) δ (ppm): 35.8 (s, C_1, C_2, C_3), 41.9 (s, C_4), 179.5 (s, C_5), 162.8 (s, C_6), and ^{31}P NMR (D_2O, 600 MHz) δ (ppm): 0.22.

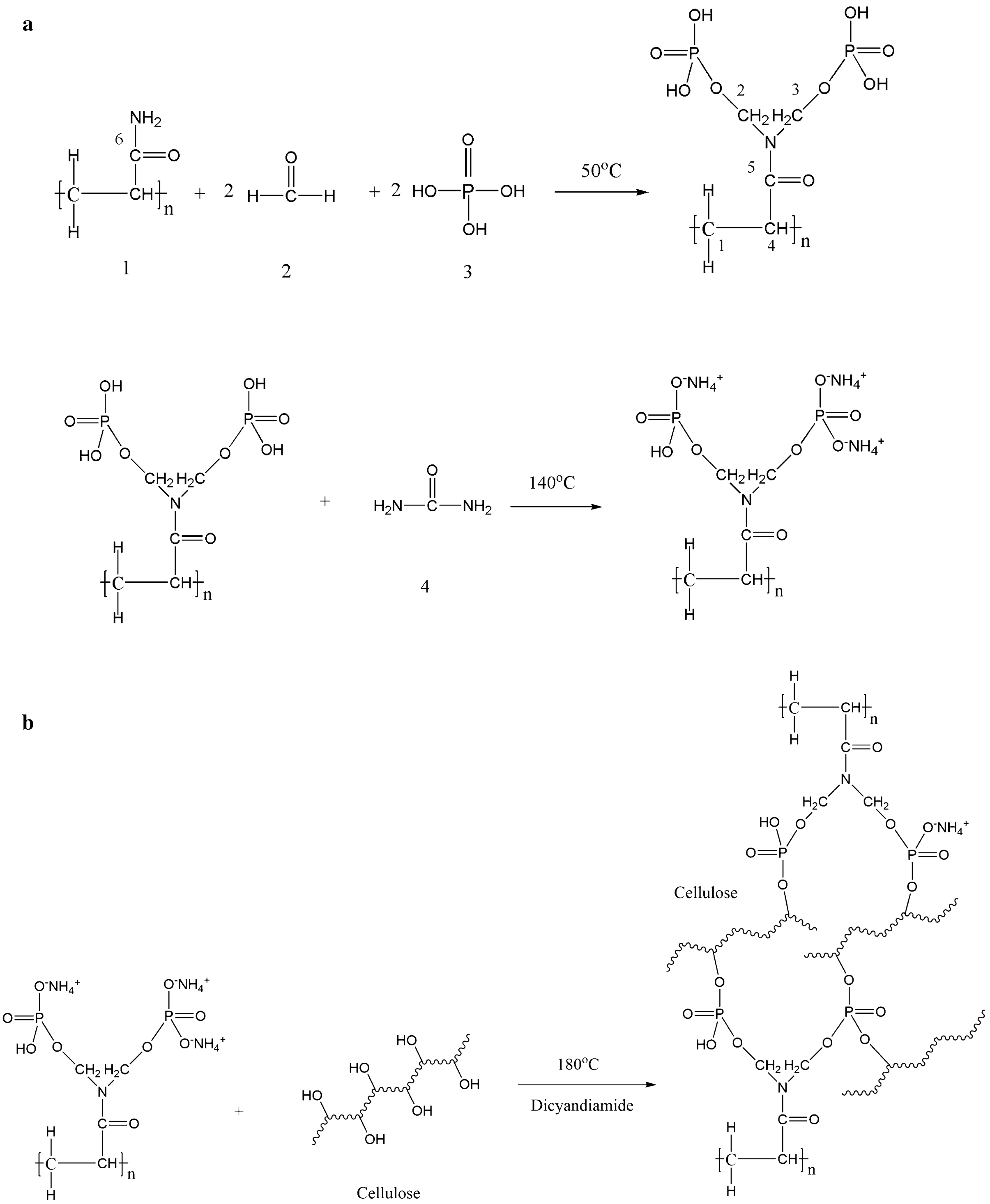


Fig. 1 **a** Synthesis of the FR-PA flame retardant and **b** preparation of cotton treated with the FR-PA flame retardant

Flame retardant finishing of cotton fabrics

The cotton samples were soaked in a 25 wt% sodium hydroxide solution for 5 min at 25 °C. They were then rinsed with distilled water until the cotton fabrics were neutralized. The samples were subsequently soaked into FR-PA solutions at varying concentrations, containing 5 wt% dicyandiamide as a catalyst at 70 °C for 40 min with a bath ratio of 1:20. The wet cotton fabrics were then padded with a padder, attaining a wet pickup of 100%. The samples were baked in an automatic continuous-shaping dryer at 180 °C for 5 min, washed with distilled water, and dried at 110 °C in an oven. The reaction between the FR-PA flame retardant and cellulose is presented in Fig. 1b). The weight gain rate (WG) of the cotton fabrics after treatment was calculated using Eq. (1), as follows:

$$\mathrm{WG} = (\mathrm{W}_2 - \mathrm{W}_1)/\mathrm{W}_1 \times 100\% \tag{1}$$

where W_1 and W_2 represent the weight of the cotton fabrics before and after treatment, respectively.

Measurements

The ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra of the FR-PA flame retardant were obtained using a Bruker 600 MHz liquid nuclear magnetic resonance spectrometer (USA). Tetramethylsilane was used as the internal standard and deuterium oxide (D_2O) was used as the solvent of the flame retardant sample.

The surface of the cotton fabric was observed using a Phenom Prox Holland scanning electron microscope (SEM). The test voltage was 10 kV, the working distance was 6–8 mm, and the magnifications were 1000×, 3000×, and 5000×. All samples were sheared into small pieces and coated with gold.

The elemental compositions and contents of the control and treated cotton fibers, after washing, as well as the carbon residue after combustion, were tested by energy-dispersive X-ray spectroscopy (EDX) (JEOL-6300F) using a high beam voltage (15 kV).

The infrared spectra of the control cotton, treated cotton and FR-PA flame retardant powders were analyzed with an infrared spectrometer (Spectrum GX) using a KBr pellet. The wavelength ranged from 4000 to 400 cm^{-1} with a 4.0 cm^{-1} resolution. The number of scans was 32.

The durability of the flame retardant against repeated laundering was tested with reference to the AATCC 61-2013 2A standard method and a more rigorous temperature. The washing temperature was set to 60 °C, and the number of steel balls was 50.

Vertical flammability test results were obtained using the YG815B vertical fabric flame retardant tester in accordance with the ASTM D6413-99 standard.

The limiting oxygen index (LOI) test was conducted using an M606B digital display oxygen index apparatus in accordance with the ASTMD2863-2000 standard.

The thermal properties of the cotton fibers were measured using the Pyris 1 TGA Thermogravimetric Analyzer (PerkinElmer, USA). Analysis was monitored on 5 mg samples that were heated from 40 to 700 °C with a heating rate of 20 K/min under nitrogen and air atmosphere and a flow rate of 60 mL/min.

Thermogravimetry–infrared (TG–IR) analysis was conducted on a Netzsch STA 409 PC thermal analyzer coupled with a Bruker Tensor 27 FTIR spectrometer via a tube. 5 mg of the cotton fiber powder was tested at a heating rate of 20 K/min under a nitrogen atmosphere at 40–700 °C and a flow rate of 60 mL/min. The wavelength range was 4000–600 cm^{-1} with a 4.0 cm^{-1} resolution and 4 scans.

Cone calorimetry (FTT 0007, UK) was employed to investigate the combustion behavior of the cotton fabrics (100 mm × 100 mm) under 35 $\mathrm{kW/m}^2$ of irradiative heat flux in accordance with the ISO 5660-1 standard.

The viscosity average molecular weight of the flame retardant was measured by using an Ubbelohde viscometer in accordance with the GB/T 12005.1-1989 standard test method. The viscosity average molecular weight (M) of the flame retardant was calculated using Eq. (2), as follows:

$$[\eta] = \mathrm{kM}^{\alpha} \tag{2}$$

The determination of the molecular weight of polyacrylamide by viscometry (GB/T 12005.10-92) specifies that the values of α and k for polyacrylamide are 0.80 and 0.00475, respectively.

The bending lengths of the cotton fabrics were evaluated using a YG (B) 022D fabric stiffness tester (Wenzhou Darong Textile Machinery Co. Ltd, Zhejiang, China) in accordance with the ASTM D 1388-96(2002) standard.

The tensile strengths of the cotton fabrics (25 mm × 180 mm) were measured using an electronic fabric tension tester (HD026N, Nantong Hongda Experiment Instruments Co. Ltd., China) in accordance with the ASTM 5035-2006 standard.

Results and discussion

Scanning electron microscopy–energy dispersive X-ray spectroscopy

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were employed to detect the effect of the flame retardant finishing on the surface morphology and elemental composition of the cotton fibers (Lu et al. 2018). The control cotton fibers (C), the cotton fibers treated with alkali (A), the cotton fibers treated with 30% FR-PA (T), and the treated cotton fibers after burning (B) were observed by SEM at different magnification levels. Electron microscopy images are presented in Fig. 2. The control cotton fibers appeared as flat, twisted structures with some furrows whereas the cotton fibers treated with alkali appeared as smooth, plump cylinders. No evident coating material was observed on the surface of the treated fibers. Many dense bubbles (Fig. 2j–l) were found on the surface of the fibers, which could have been caused by gases, such as ammonia spreading from the inside to the outside of the fibers during combustion. After combustion, the shape of the treated cotton fibers was retained because of the phosphoric acid released by the FR-PA flame retardant released phosphoric acid, which can promote the carbonization of cellulose during the combustion.

The elements on the surface of the control cotton fibers (C), cotton fibers treated with 30% FR-PA flame retardant (T), treated cotton fibers after 50 laundering cycles (LCs) (L), and treated cotton fibers after burning (B) were analyzed by EDX. The data are

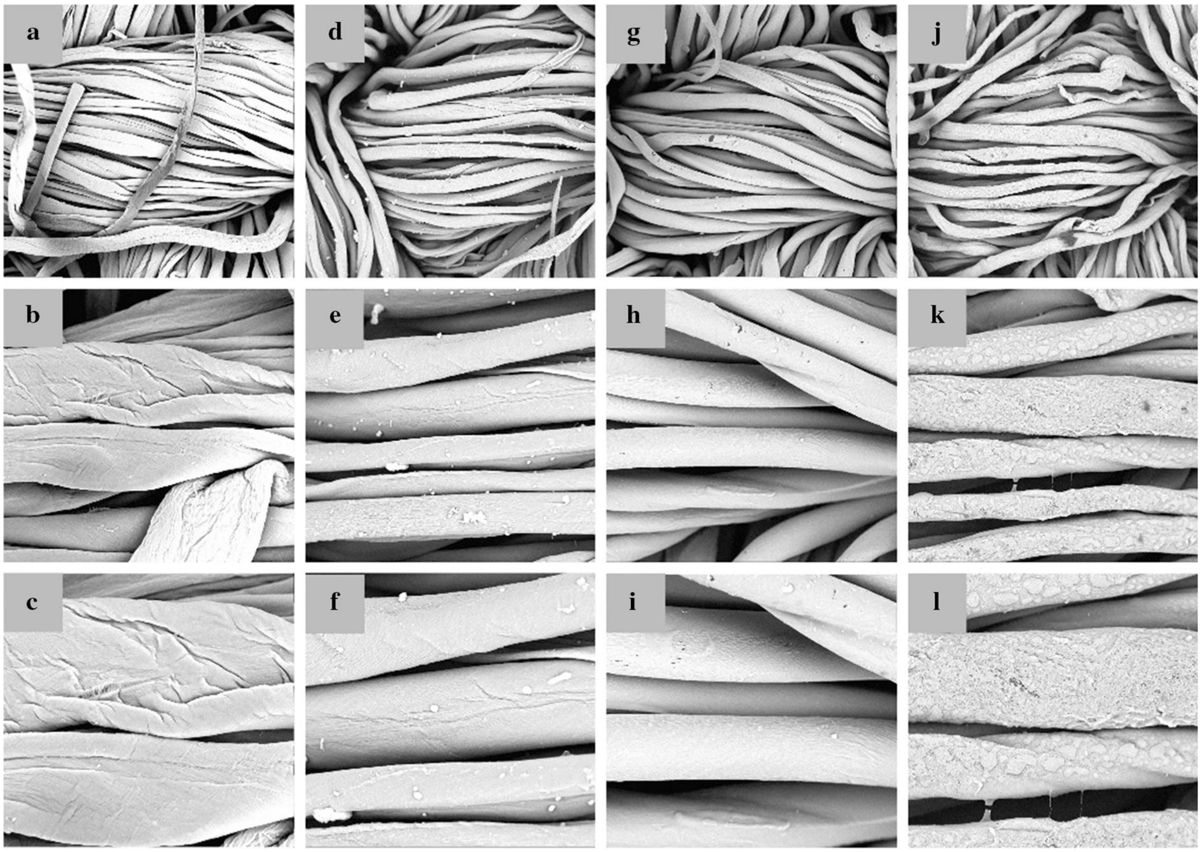


Fig. 2 SEM images of the control cotton fibers (**a**–**c**); cotton fibers treated with alkali (**d**–**f**); cotton fibers treated with 30% FR-PA flame retardant (**g**–**i**); and treated cotton fibers after burning (**j**–**l**) at the following magnification levels: 1000 (**a**, **d**, **g**, **j**), 3000 (**b**, **e**, **h**, **k**), and 5000 (**c**, **f**, **i**, **l**)

presented in Fig. 3 and Table 1. Phosphorus and nitrogen were found in T, L, and B but not in the control cotton fibers. These data showed that nitrogen and phosphorus were introduced into the treated cotton fibers.

Fourier-transform infrared spectroscopy

The FTIR spectra of the FR-PA flame retardant, the control cotton fiber, and the treated cotton fiber are presented in Fig. 4. For the FR-PA flame retardant, the wide absorption peak at 3500–3200 cm^{-1} is assigned to the stretching vibration absorption of the –OH groups. The peaks at 2863 and 1400 cm^{-1} are attributed to the stretching vibration absorption of $–CH_2$ and distortion vibration absorption of the C–H groups, respectively. The peaks at 1666 and 1303 cm^{-1} are assigned to the vibration absorption of C=O and C–N, respectively. The peaks at 900 and at 1165 cm^{-1} correspond to the vibration absorption of the P(=O)–O–C and P=O groups, respectively (Huang et al. 2019). The infrared spectroscopy results agreed with the structure of the FR-PA flame retardant.

For the treated cotton fiber, the peaks at 2896 and 1403 cm^{-1} belong to the stretching vibration absorption of the $–CH_2$ and distortion vibration absorption of the C–H groups, respectively. The peak at 1666 cm^{-1} is assigned to the vibration absorption of the C=O groups, and the multiple peaks at 1059 and 1025 cm^{-1} are assigned to the absorption of the C–O–C groups; these peaks are attributed to the C–O–C stretching vibration of the glucose ring. The peak at 891 cm^{-1} corresponds to the absorption of the P(=O)–O–C groups, and the peak at 1166 cm^{-1} corresponds to the absorption of the P=O groups. These results are consistent with the previously reported literature (Xu et al. 2019a; Zhao et al. 2016). The infrared spectroscopy results were consistent with the structure of the treated cotton fibers and suggested that the flame retardants were grafted onto the cotton fibers.

Durability, vertical flammability, and limiting oxygen index

Durability was measured at a more rigorous temperature (60 °C) than that specified in the AATCC 61-2013 2A standard (49 °C). The test data are presented in Fig. 5 and Tables 2 and 3. As shown in Fig. 5, the control cotton fabric burns violently, the afterflame time is 9 s, and the afterglow time is 6 s; only a small amount of ash remains. For the treated cotton fabrics, the length of the carbon frame decreased as the concentrations of the flame retardant increased. Specifically, even after 50 LCs, the cotton fabrics treated with 20% and 30% flame retardants had carbon frames measuring 85 and 69 mm in length, which were considerably shorter than that of the standard (150 mm).

As shown in Table 3, the LOI of the control cotton fabrics is only 18.1%, whereas those of the treated cotton fabrics are considerably higher; moreover, the treated cotton fabrics can resist more LC cycles when

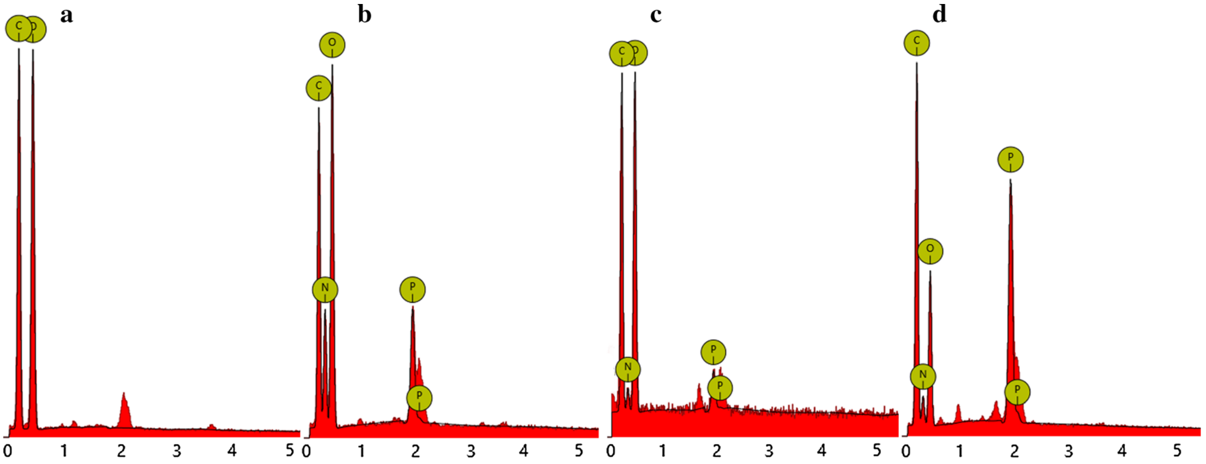


Fig. 3 EDX spectral analyses of the control cotton fibers (**a**); the cotton fibers treated with 30% FR-PA flame retardant (**b**); the cotton fibers treated after 50 LCs (**c**); and the treated cotton fibers after burning (**d**)

Table 1 EDX data (atomic percentages) of the control cotton fibers, cotton fibers treated with 30% FR-PA flame retardant, cotton fibers treated after 50 LCs and the treated cotton fibers after burning

Sample	C (%)	O (%)	P (%)	N (%)
Cotton	50.29 ± 0.46	49.71 ± 0.46	–	–
Treated cotton	31.06 ± 0.92	42.24 ± 0.47	1.10 ± 0.02	25.60 ± 1.23
Treated and washed cotton	40.16 ± 0.34.	40.15 ± 0.72	0.71 ± 0.06	18.98 ± 0.83
Treated cotton after burning	58.60 ± 2.72	20.16 ± 0.43	2.47 ± 0.43	18.77 ± 2.58

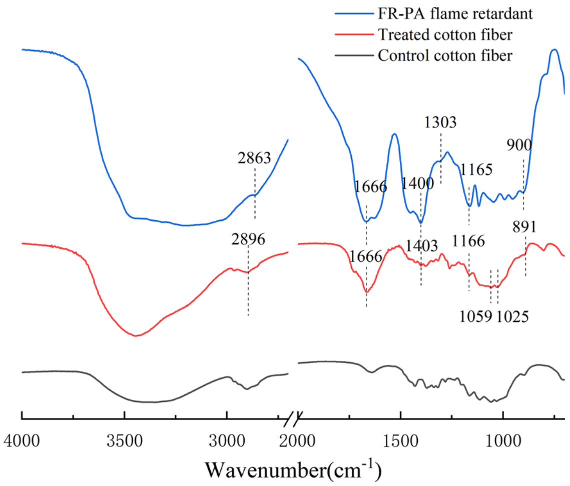


Fig. 4 Fourier-transform infrared spectra of the FR-PA flame retardant, control cotton fiber and treated cotton fiber

treated with high-concentration flame retardants. The cotton fabrics treated with 20% and 30% FR-PA can be considered as permanently washable.

The cotton fabrics treated with the FR-PA flame retardants exhibited high durability because the FR-PA flame retardants are high-molecular-weight compounds. Numerous P(=O)–O–C covalent bonds can form between each molecule of the flame retardant and cotton fiber. Only after all P(=O)–O–C covalent bonds were hydrolyzed could the flame retardant molecules be washed out of the cotton fabric. Therefore, the cotton fabrics treated with the high-molecular-weight flame retardant exhibited excellent durability.

Thermogravimetric analysis

The thermal oxidation stability of the flame-retardant cotton fiber in air and nitrogen was analyzed by TG

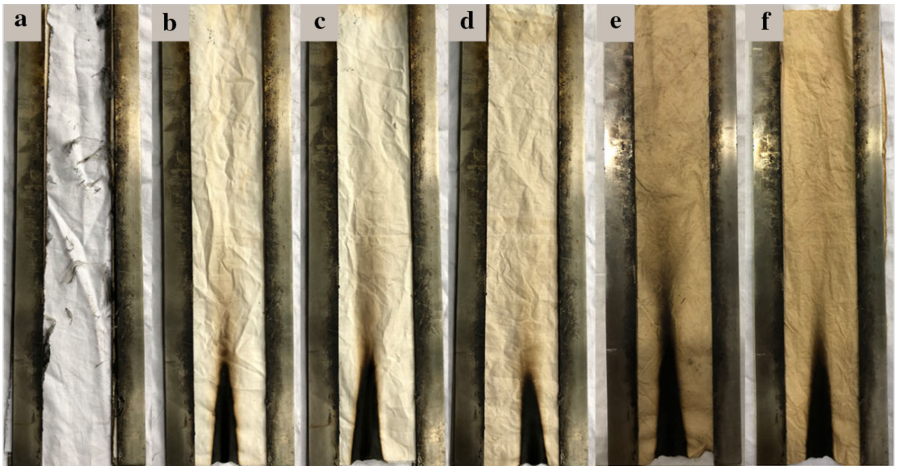


Fig. 5 Vertical flammability tests of the control cotton fabric (**a**); cotton fabric treated with 15% FR-PA flame retardant (**b**); cotton fabric treated with 20% FR-PA flame retardant (**c**); cotton fabric treated with 30% FR-PA flame retardant (**d**); cotton fabric treated with 20% FR-PA flame retardant and after 50 LCs (**e**); cotton fabric treated with 30% FR-PA flame retardant after 50 LCs (**f**)

Table 2 Vertical flammability test data

Samples	Concentration of the flame retardant	Afterflame time (s)	Afterglow time (s)	Char length (mm)
C(a)	–	9	6	0
T-15(b)	15%	0	0	64 ± 2
T-20(c)	20%	0	0	59 ± 2
T-30(d)	30%	0	0	56 ± 2
T-20-50Lc(e)	20%	0	0	85 ± 2
T-30-50Lc(f)	30%	0	0	69 ± 2

Table 3 LOIs of the treated cotton fabrics after varying numbers of laundering cycles

Samples	Concentration of FR	Weight gain (%)	Weight gain after 50 LCs (%)	LOI (%)					
				0 LCs	10 LCs	20 LCs	30 LCs	40 Cs	50 LCs
C	–	–	–	18.1	–	–	–	–	–
T-15	15%	21.0	15.6	33.6	32.8	30.9	27.5	26.8	26.2
T-20	20%	28.9	20.9	36.0	33.4	31.7	30.3	28.9	27.8
T-30	30%	33.3	25.1	40.5	35.9	33.3	31.5	29.6	28.5

analysis (TGA). Figure 6 presents the TGA curves and DTGA curves of the control cotton fibers and cotton fibers treated with 30% FR-PA flame retardant under air and nitrogen atmosphere. The corresponding parameters, namely, the 10% mass loss temperature ($T_{10\%}$), maximum mass loss rate (V_{max}), temperature at V_{max} (T_{max}), and char yield at 700 °C (CY_{700}) are listed in Table 4.

When the temperature was below 200 °C, both the control cotton fiber and treated cotton fiber underwent water evaporation at which stage both samples had highly similar weight-loss rates. The weight of the control cotton fiber decreased rapidly at 308.29–352.92 °C under air atmosphere. This stage corresponded to cellulose degradation. At this stage, the crystalline zone of the cellulose was degraded into levoglucosan, which was further degraded into combustible gases and water (Wang et al. 2019). The maximum mass loss rate of the control cotton fabric was 3.49%/°C, and the residue at 700 °C was almost 0%. Above 352.92 °C, the char was further oxidized to carbon monoxide and carbon dioxide. The cotton fibers treated with the FR-PA flame retardant was degraded earlier, compared with the control cotton fibers under air atmosphere, and the main degradation temperature was in the 255.95–282.51 °C range. This finding suggested that the FR-PA flame retardant can change the pyrolysis of the cotton fibers to achieve flame retardation by releasing phosphoric acid for catalysis of cellulose dehydration and formation of a carbon frame (Wang et al. 2017). The residue at 700 °C was 28.01%, which was considerably higher than that of the control cotton. The above results indicated that the FR-PA flame retardant can effectively improve the flame retardancy of the cotton fabric.

The degradation trends of the control cotton fiber and treated cotton fiber in nitrogen atmosphere were consistent with those in air atmosphere. The first step in the total degradation phase was still water evaporation. The weight of the control cotton fiber decreased rapidly from 312.33 to 352.85 °C and that of the treated cotton fiber quickly dropped from 268.79 to 281.60 °C. The maximum mass loss rate of the control cotton fabric was 2.71%/°C, and the residue at 700 °C was about 1.88%. The maximum mass loss rate of the treated cotton fiber was 0.80%/°C, and the residue at 700 °C was 56.28%, which was considerably higher. The above results showed that the FR-PA flame retardant can promote carbonization of cotton fibers to endow the cotton fabric with flame retardancy.

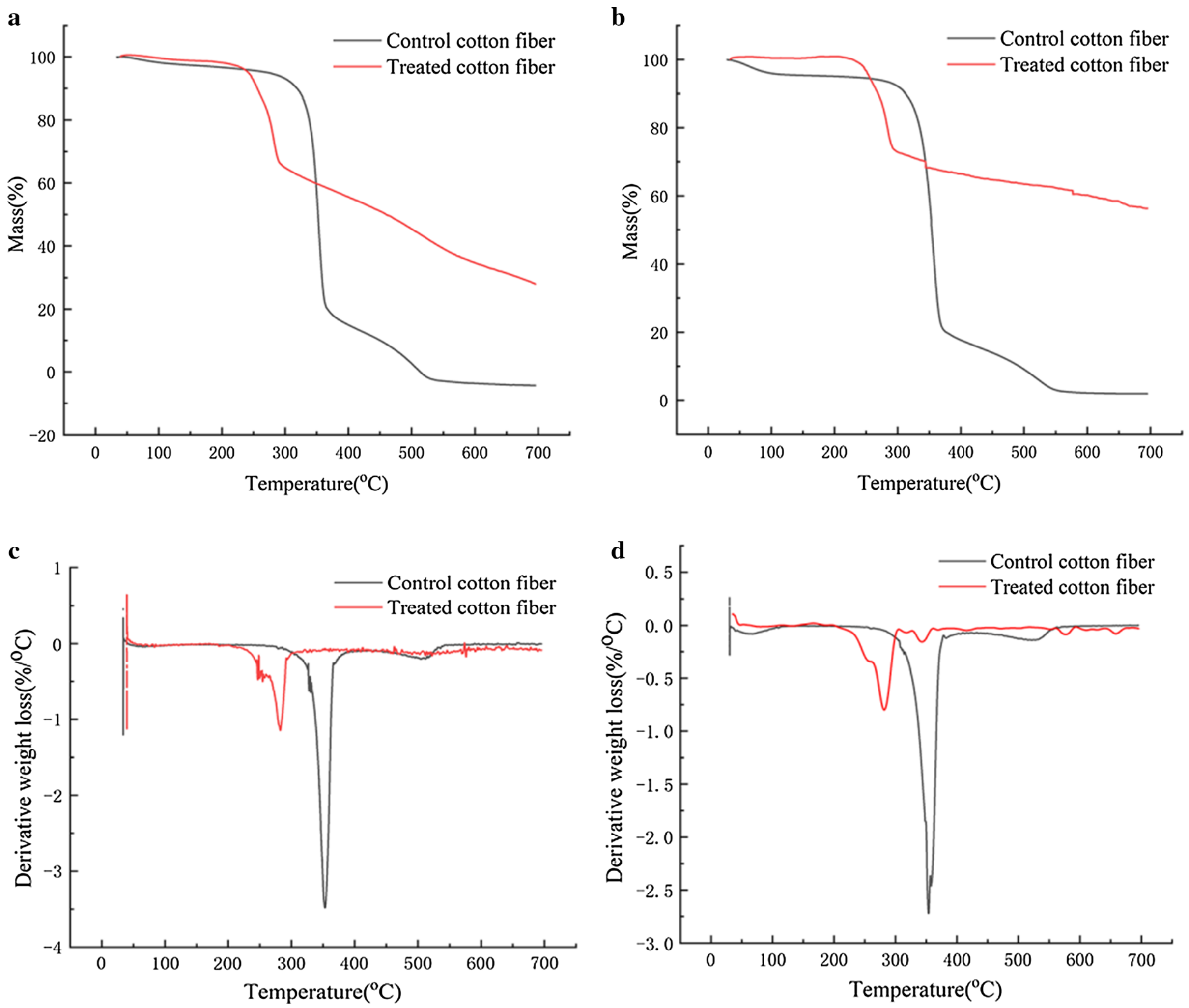


Fig. 6 Thermogravimetric analysis curves of the control cotton fiber and cotton fiber treated with 30% FR-PA flame retardant in air (**a**) and in nitrogen (**b**), derivative thermogravimetry analysis curves of the control cotton fiber and cotton fiber treated with 30% FR-PA flame retardant in air (**c**) and in nitrogen (**d**)

Table 4 Thermogravimetric analysis results for the control cotton fibers and cotton fibers treated with 30% FR-PA under air and nitrogen atmosphere

	Air atmosphere				Nitrogen atmosphere			
Sample	$T_{10\%}$ (°C)	V_{max} (%/°C)	T_{max} (°C)	Cy_{700} (wt \%)	$T_{10\%}$ (°C)	V_{max} (%/°C)	T_{max} (°C)	Cy_{700} (wt%)
Control cotton	308.29	3.49	352.92	0	312.33	2.71	352.85	1.88
Treated cotton	255.95	1.15	282.51	28.01	268.79	0.80	281.60	56.28

Thermogravimetry–infrared analysis

The thermal degradation products of the control cotton fibers and flame-retardant cotton fibers were analyzed by TG–IR spectroscopy. The three-dimensional diagrams of the thermal degradation of the control cotton and treated cotton samples under nitrogen atmosphere are shown presented in Fig. 7. The 3D TG–IR analysis

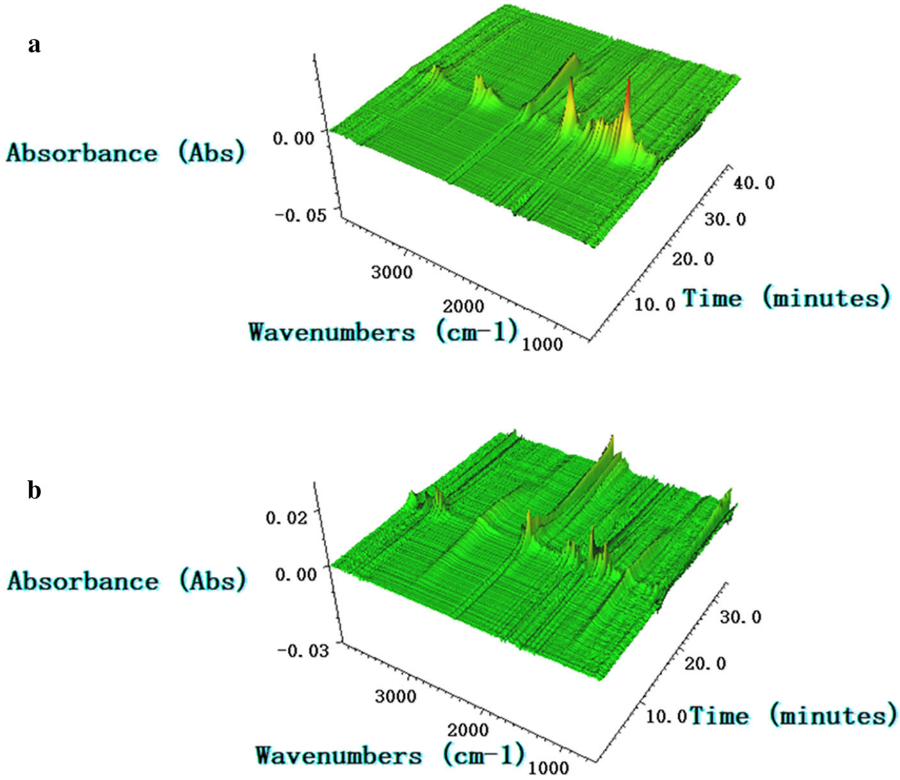


Fig. 7 Three-dimensional thermogravimetry–infrared spectroscopy results for the control cotton fiber (**a**) and treated cotton fiber (**b**)

spectra revealed that all absorption peaks of the treated cotton were weaker than those of the control cotton. Figure 8 presents the TG–IR spectroscopy results for the control cotton fibers and cotton fibers treated with 30% FR-PA flame retardant. As shown in the figure, the positions of the absorption peaks of both cotton fibers are highly similar. This similarity suggests that the thermal degradation products of the fabrics before and after treatment were basically the same. However, the absorption peaks of the control cotton are evidently stronger than those of the cotton treated with FR-PA. The wide peak at 3600–3200 cm^{-1} is assigned to the stretching vibration absorption of –OH. The stretching vibration peak at 2935 cm^{-1} belongs to the stretching vibration absorption of –CH$_2$. The cotton treated with FR-PA at this position shows almost no absorption peak, whereas the control cotton has a considerably higher peak. The absorption peaks at 1063 and 1741 cm^{-1} are attributed to the vibration absorption of the C–O–C bond and the C=O group respectively. The peaks at 2300 and 2185 cm^{-1} are attributed to the stretching vibration absorption of CO$_2$ and CO, respectively. The peak at 1512 cm^{-1} is assigned to the vibration absorption of the N–H of NH$_3$. The TG–IR results indicated that the treated sample only mildly released combustible hydrocarbon gas during

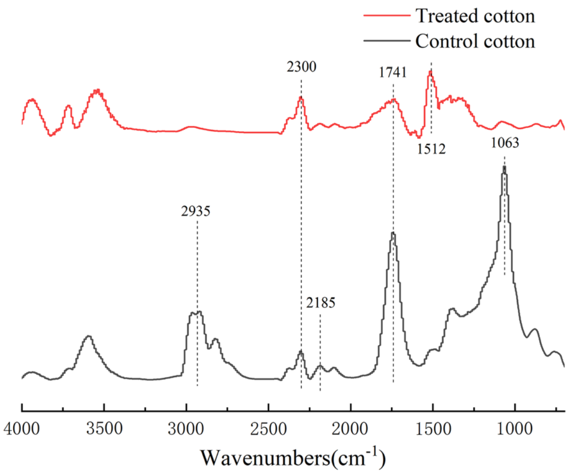


Fig. 8 Thermogravimetry–infrared spectroscopy results for the control cotton fiber and cotton fiber treated with FR-PA flame retardant

degradation; in addition, the flame retardant changed the degradation pathway of cellulose, suggesting that the cotton treated with FR-PA exhibits strong flame retardancy.

Cone calorimetry

The combustion performance of the samples was evaluated by cone calorimetry in the real environment. The test simulated the burning behavior of the cotton fabric exposed to 35 kW/m^2 heat flux. The test results are presented in Fig. 9 and Table 5.

The time-to ignition (TTI) of the control cotton was only 7 s, and the treated cotton was not ignited during the experiment (Table 5). The peak heat release rate (PHRR) and total heat release (THR) of the control cotton were 186.56 kW/m^2 and 2.88 MJ/m^2, respectively. Meanwhile, the PHRR of the treated cotton (12.88 kW/m^2) was far less than that of the control cotton. Similarly the THR of the treated cotton (1.44 MJ/m^2) was lower than that of the control cotton. These data suggested that the cotton treated with FR-PA flame retardant released less heat and had a lower heat release rate than those of the control cotton during burning. FGR, the ratio of PHRR to TPHRR, evaluates the fire risk of materials. As is generally known, the higher the FGR, the higher the fire risk of the material. Table 5 shows that the FGR value of the control cotton is 33 times that of the cotton treated with FR-PA flame retardant. A high CO$_2$/CO value indicates that the material burns sufficiently during combustion; thus, a low CO$_2$/CO value indicates that the material is difficult to burn. The results of the cone calorimetry, vertical combustion, and LOI tests showed that the treated cotton exhibited strong flame retardancy.

Determination of the molecular weight of the flame retardants

The viscosity of the synthetic flame retardant was evaluated using an Ubbelohde viscometer. The results are presented in Table 6 and Fig. 10. The parameters and what they represent are as follows: η, the viscosity of the solution; η_0, the viscosity of the pure solvent; t the time required for a solution to flow out of the Ubbelohde viscometer;, t_0, the time required for a solvent to flow out of the Ubbelohde viscometer; η_r, the relative viscosity; η_{sp}, the specific viscosity; c', the ratio of the solution concentration to the initial solution concentration; K, the proportional constant; α, the empirical parameters related to the molecular shape; M, the viscosity of the average molecular weight; and $[\eta]$, the intrinsic viscosity.

The average molecular weight of the flame retardants was 3700. The relative molecular weight of FR-PA flame retardant was lower than that of polyacrylamide because the FR-PA flame retardant was degraded with a small amount hydrogen peroxide; otherwise, if the polyacrylamide macromolecules

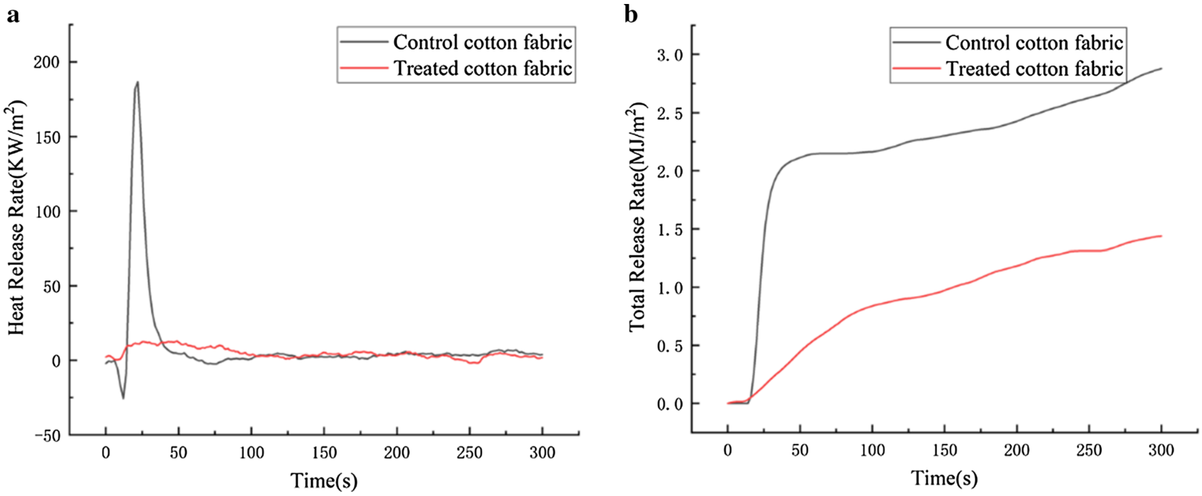


Fig. 9 Heat release rate (a) and total heat release (b) curves of the control cotton fabric and cotton fabric treated with 30% FR-PA flame retardant

Table 5 Cone calorimetry data for control cotton and treated cotton

Sample	TTI (s)	PHRR (kW/m^2)	Time to PHRR (s)	FGR (kW/(m^{2}s))	THR (MJ/m^2)	CO$_2$/CO	Residue (%)
Control cotton	7	186.56	22	8.48	2.88	77.86	0.66
Treated cotton	–	12.88	49	0.26	1.44	28.30	27.65

Table 6 Viscosity test record sheet

Samples	Time(s)				ηr	ηsp	$\frac{\eta sp}{c'}$	lnηr	$\frac{\ln\eta r}{c'}$
	t_1	t_2	t_3	Average					
Water	205.92	206.54	205.74	206.07	1	0	0	0	0
c′ = 1	312.10	312.87	311.81	312.26	1.515	0.515	0.515	0.415	0.415
c′ = 1/2	258.44	258.98	259.35	258.92	1.256	0.256	0.512	0.228	0.456
c′ = 1/3	239.79	241.86	242.31	241.32	1.171	0.171	0.513	0.159	0.477
c′ = 1/4	233.33	232.49	232.13	232.65	1.129	0.129	0.516	0.122	0.488
c′ = 1/5	225.78	227.36	229.64	227.59	1.104	0.104	0.520	0.099	0.495

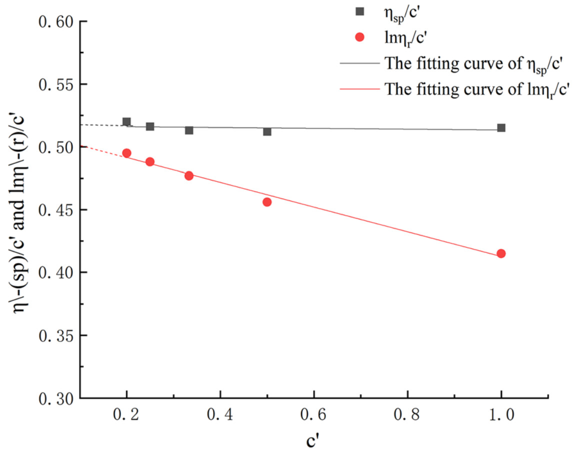


Fig. 10 Fitting curve of ηsp/c′ and ln ηr/c′

Table 7 Average bending lengths and average tensile strengths of the cotton fabrics

Sample	Bending length (mm)		Tensile strength (N/mm^2)	
	Warp	Weft	Warp	Weft
C	41.4	43.5	545	492
T-15	47.7	53.0	510	471
T-20	48.6	55.1	504	457
T-30	49.0	56.5	427	409

were not degraded, the flame retardant would be very high relative molecular mass, and the treated cotton fabrics would exhibit high stiffness. The flame retardant molecules prepared with this degraded polyacrylamide still exhibited high molecular weight.

Physical properties

The bending length and the tensile strength of the cotton fabrics were measured to determine the physical properties of the treated cotton fabrics. The results are listed in Table 7. As shown in the table, the bending length of the cotton fabrics increases with an increase in flame retardant concentration in both warp and weft directions. The treated cotton fabrics were sufficiently soft. The tensile strength of the cotton fabrics slightly decreased with an increase flame retardant concentration. The tensile strengths of the treated cotton fabrics were well sustained, which was attributed to the neutralization of the flame retardant.

Conclusions

A novel flame retardant FR-PA with an appropriate molecular weight was synthesized for cotton fabrics. The structure of the retardant was characterized by ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR, as well as FT-IR spectroscopy. The FR-PA viscosity average molecular weight is 3700. This FR-PA flame retardant can be firmly grafted onto the cotton fabric and endow cotton fabrics with excellent flame retardancy and durability.

Even after 50 LCs, the treated cotton fabric retained an LOI of 28.5% because the high molecular weight flame retardant was relatively difficult to wash out of the cotton fabrics. The TG and other tests showed the treated cotton fabrics had high flame retardancy. The treated cotton fabrics remained soft, and the tensile strength only decreased slightly. The results showed that the high-molecule FR-PA can endow cotton fabrics with excellent flame retardancy and satisfactory durability.

Funding This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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