



# A novel high durability flame retardant with phosphoric acid ester groups and a reactive ammonium phosphorus acid group for cotton fabrics

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Received: 22 July 2020 / Accepted: 15 December 2020 / Published online: 6 January 2021  
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**Abstract** A novel reactive flame retardant with two phosphoric acid ester groups and one ammonium phosphorus acid group, the ammonium salt of 2,7-bis(dimethoxyphosphoryl)-3,7-dimethyl-3-phosphonic acid (FR–LO), was synthesized. The treated cotton fabrics displayed a high flame retardancy and excellent durability because the FR–LO molecule contains two phosphoric acid ester groups without an ammonium ion that can be eliminated and decrease the flame retardancy. The cotton fabrics treated with 30% FR–LO had limiting oxygen indexes of 43.4, and 29.7 after 50 laundry cycles according to AATCC 61–2013 2A standard. Scanning electron microscope images and energy-dispersive X-ray spectroscopy showed that the treated cotton fibers retained their complete structure

after combustion, and nitrogen and phosphorus were present in the treated cotton fibers. Thermogravimetric and thermogravimetric-infrared analyses showed that the treated cotton produced more carbon residue and released fewer combustible gases during thermal decomposition. Microscale combustion calorimetry showed that the heat release rate and total heat release of the treated cotton during combustion were much lower than those of pre-treated cotton. The stiffness of cotton treated with FR–LO increased, and its tensile strength decreased compared with pre-treated cotton.

**Keywords** Cotton · Flame retardant · Linalool · Durability

**Supplementary information** The online version contains supplementary material available at (<https://doi.org/10.1007/s10570-020-03648-y>).

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## Introduction

Cotton fabrics have good hygroscopicity, anti-static properties, and comfort for personal wear (Sun et al. 2020; Zhu et al. 2020); however, cotton fabric burns easily and vigorously when ignited and can cause casualties and property damage (Atakan et al. 2019; Li et al. 2020). Therefore, cotton fabrics are often treated with flame retardants that typically contain halogens, phosphorus, nitrogen, boron, or silicon. Other specialty flame-retardant materials include graphite and alkaline earth metallic compounds (Molaba et al. 2016; Salmeia et al. 2016a). Halogen-containing flame

retardants are highly effective at capturing high-energy free radicals during thermal decomposition process, but they have been banned in many countries and regions because they release carcinogenic and toxic compounds (van der Veen and de Boer 2012). Boron-containing flame retardants often lack durability and are inefficient (Di Blasi et al. 2007), and while alkaline earth metal compounds have satisfactory flame resistance, they require high weight loadings, which affects the substrate properties (Costes et al. 2017; Li et al. 2010). Nitrogenous additives are often combined with other flame-retardant elements to improve their flame resistance (Xie et al. 2013; Zhang et al. 2017)

Recently, many researchers have investigated nanomaterials (e.g., clay, carbon nanotubes, and polyhedral oligomeric silsesquioxanes) as novel flame retardants (Decher and Hong 1991; Fabia et al. 2020; Fu et al. 2017; Jiang et al. 2018; Liang et al. 2013), because they can form continuous protective network layers that act as physical barriers to reduce flame spread (Kashiwagi et al. 2005). Although the heat release rate of treated samples is lower, other important fire parameters (e.g., time to ignition and total heat release) are not improved. Lignin is a kind of sustainable polymer with abundant reserves. Recently, it has been reported that lignin can be used as a synergistic agent to improve the flame retardancy of polymers (Lukawski et al. 2020; Song et al. 2011). But there is no evaluation of its durability. Phosphorous-containing flame retardants do not produce dust and have eco-friendly advantages, making them the most studied type of flame retardant (Nazir and Gaan 2020; Salmeia et al. 2016b). Proban and Pyrovatex CP are two typical organophosphorus flame retardants used in cotton fabrics (Horrocks 2013). However, cotton fabrics treated with these two flame retardants will release formaldehyde during usage. In recent years, many researchers have focused on the use of green flame retardants, and a wide range of source materials, including renewable biomass materials, have been investigated. Some bio-based substances such as deoxyribonucleic acid, casein, hydrophobin, and amino acids have potential applications as environment-friendly flame retardants (Alongi et al. 2013, 2014; Xu et al. 2019). However, cotton fabrics treated with these kind of flame retardants have poor durability.

In our previous research, we developed several ammonium organic phosphorus acid flame retardants (Huang et al. 2019; Jia et al. 2017; Tian et al. 2019; Wan et al. 2019a; Xu et al. 2019). The cotton fabrics treated with these flame retardants passed 50 laundering cycle tests under AATCC 61–2013 1A standard (40 °C, 10 steel balls), but they did not pass the AATCC 61–2013 2A standard (49 °C, 50 steel balls), because while the flame retardants contain many ammonium phosphorus acid groups, not enough hydroxyl groups of cellulose were exposed because of the high crystallinity of the cotton fibers. Therefore, during laundering, the ammonium ions were easily replaced by metal ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , and the flame retardancy of the treated cotton fabrics decreased greatly. So, if a flame retardant molecule contains several phosphoric acid ester groups (which do not combine with metal ions) and a few ammonium phosphorus acid groups that will react with cellulose, the cotton fabrics treated with this kind of flame retardants will have a high durability and may meet the AATCC 61–2013 2A standard.

Linalool is a colorless, oily liquid from biomass with two alkenes that can be functionalized with two phosphoric acid ester groups via an addition reaction, while the hydroxyl group of linalool can be used to introduce an ammonium phosphorus acid group. In this research, a novel flame retardant for cotton fabrics was synthesized from linalool, phosphoric acid, and dimethyl phosphite. It is expected that the cotton fabrics treated with this flame retardant will have high flame retardancy and excellent durability without producing formaldehyde.

## Experimental section

### Materials

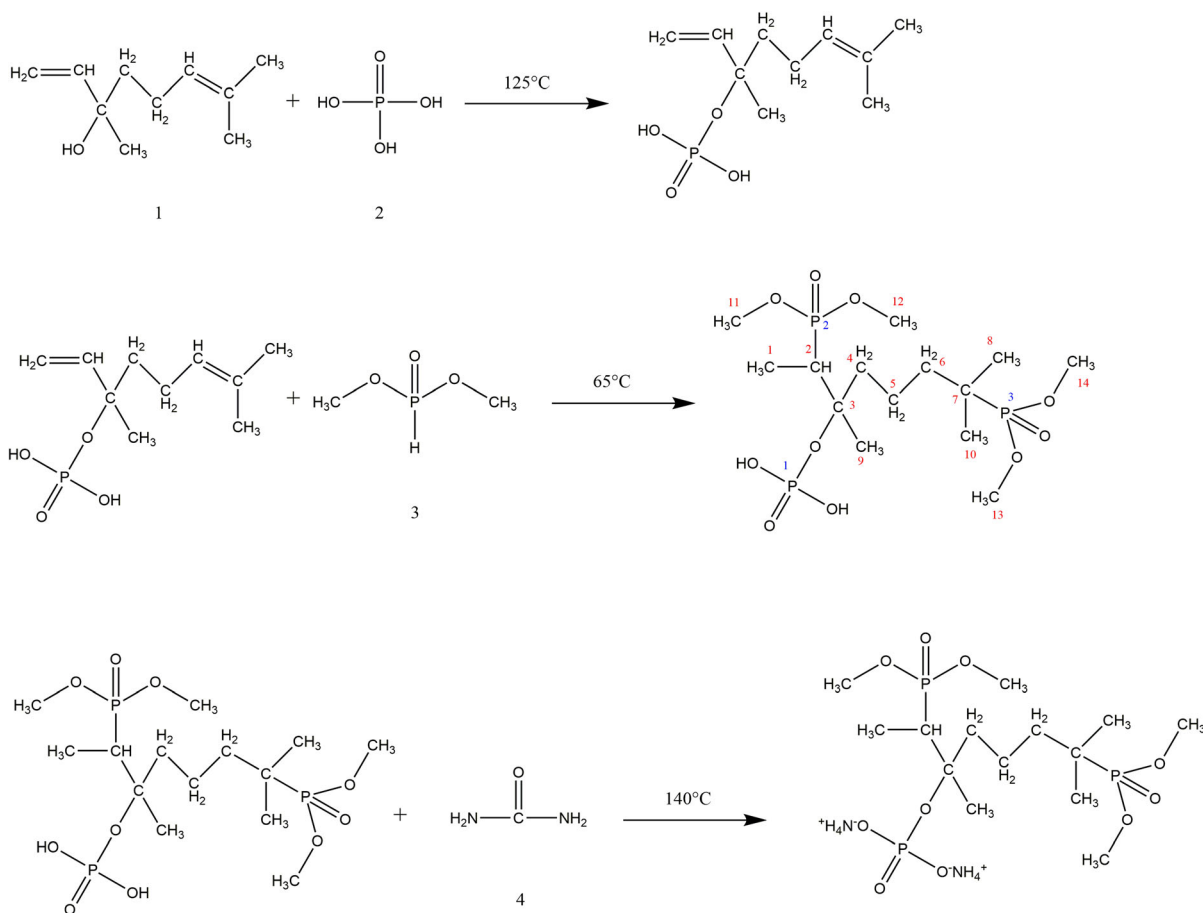
Cotton fabrics (159.91 g/m<sup>2</sup>) were obtained from Jinzhou Rongshun Textile Co., Ltd. (Hebei, China). Linalool and dimethyl phosphite were procured from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Phosphoric acid, sodium hydroxide, xylene and ethanol were purchased from Chongqing Chuan-dong Chemical Co., Ltd. (Chongqing, China). Urea and dicyandiamide were supplied by Chengdu Kelong Chemical Co., Ltd. (Sichuan, China). All reagents were used as received.

### Pretreatment of cotton fabrics

Cotton fabrics were dipped into a 25 wt% sodium hydroxide solution at 25 °C for 5 min with a bath ratio 1:20. Then, the wet cotton fabrics were washed with a large amount of water to remove excess sodium hydroxide. The pre-treated cotton fabrics were dried in an oven at 110 °C for later use. (The pretreatment of cotton fabric with sodium hydroxide solution can transform part of the crystalline cellulose into amorphous cellulose (mercerization), thereby increasing the number of reaction sites and improving the graft rate.)

### Flame retardant synthesis

The reactions used to synthesize the ammonium salt of 2, 7-bis(dimethoxyphosphoryl)-3,7-dimethyl-3-phosphonic acid (FR-LO) are illustrated in Scheme 1.



**Scheme 1** Reaction used to synthesize FR-LO

Linalool (1, 23.1 g, 0.15 mol), phosphoric acid (2, 16.7 g, 0.17 mol) and xylene (100 ml) were added to a 250 mL three-neck flask equipped with a magnetic stirrer, a thermometer, a Dean-Stark trap, and a reflux condenser. The mixture was heated to reflux at 125 °C for 4 h. At the end of the reaction, an obvious stratification occurred between the orange oily product and the light yellow solvent. The product was separated from the solvent by liquid separation. Then the intermediate, dimethyl phosphite (3, 33.0 g, 0.30 mol) and 50 ml distilled water were poured into a three-neck flask with a magnetic stirrer, a thermometer, and a reflux condenser. The reaction lasted for 3 h at 65 °C. Then, the product was poured into a large beaker. Urea (4, 18.0 g, 0.3 mol) was also added to the beaker, and the mixture was stirred at 140 °C until it reached a neutral pH. The crude product was purified by ethanol precipitation and dried in an oven at 60 °C.

The structure of FR–LO was characterized by proton nuclear magnetic resonance ( $^1\text{H}$  NMR), carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR), and phosphorus-31 nuclear magnetic resonance ( $^{31}\text{P}$  NMR) spectroscopy, as follows:

$^1\text{H}$  NMR results ( $\text{D}_2\text{O}$ , 600 MHz)  $\delta$  (ppm): 0.55, 0.67 (s, CH,  $\text{H}_2$ ), 2.72 (s,  $3\text{CH}_2$ ,  $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$ ); 3.03 (s,  $4\text{CH}_3$ ,  $\text{H}_1$ ,  $\text{H}_8$ ,  $\text{H}_9$ ,  $\text{H}_{10}$ ); 3.41 (s,  $4\text{O}-\text{CH}_3$ ,  $\text{H}_{11}$ ,  $\text{H}_{12}$ ,  $\text{H}_{13}$ ,  $\text{H}_{14}$ ); 4.93 ( $\text{D}_2\text{O}$ );  $^{13}\text{C}$  NMR results ( $\text{D}_2\text{O}$ , 600 MHz)  $\delta$  (ppm): 15.29 (s,  $\text{C}_1$ ,  $\text{C}_8$ ,  $\text{C}_9$ ,  $\text{C}_{10}$ ,  $\text{C}_{11}$ ,  $\text{C}_{12}$ ,  $\text{C}_{13}$ ,  $\text{C}_{14}$ ); 16.52 (s,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_6$ ), 57.24 (s,  $\text{C}_2$ ), 61.66 (s,  $\text{C}_3$ ,  $\text{C}_7$ );  $^{31}\text{P}$  NMR results ( $\text{D}_2\text{O}$ , 600 MHz)  $\delta$  (ppm):  $-0.63$  (s,  $\text{P}_1$ ); 4.70 (s,  $\text{P}_2$ ); 7.06 (s,  $\text{P}_3$ ). (Supplementary Material, Fig. S1, S2, S3).

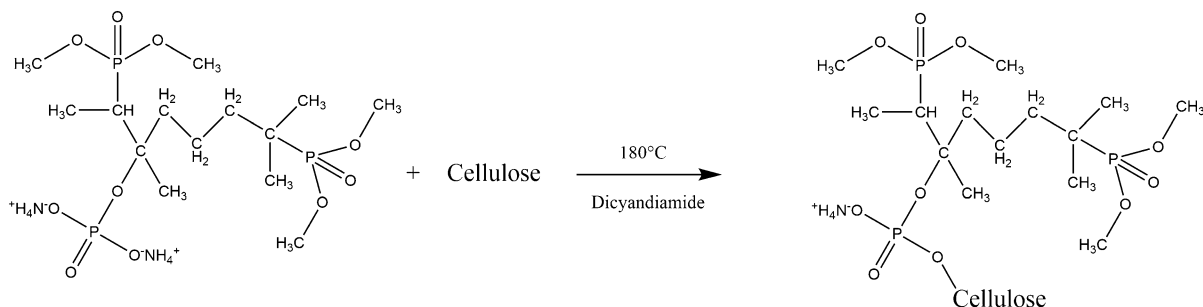
#### Flame retardant finishing of cotton fabrics

FR–LO solutions with different concentrations (15 wt%, 20 wt%, and 30 wt%) were prepared, and each solution contained 5 wt% dicyandiamide as a catalyst. Pretreated cotton fabrics were immersed in these solutions at  $70^\circ\text{C}$  for 40 min with a bath ratio 1:20. The cotton fabrics were then padded to reach a wet pickup of about 100% and baked in an automatic continuous-shaping dryer at  $180^\circ\text{C}$  for 5 min. Finally, the treated cotton fabrics were washed with distilled water, and dried at  $110^\circ\text{C}$  in an oven. The reaction between cellulose and FR–LO is illustrated by Scheme 2.

The weight gain (WG) of the cotton fabrics after treatment can be calculated by Eq. (1):

$$\text{WG} = (W_2 - W_1)/W_1 \times 100\% \quad (1)$$

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



**Scheme 2** Reaction between cellulose and the FR–LO

#### Measurements

##### Nuclear magnetic resonance (NMR)

The structural analyses of the FR–LO ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) were conducted on a Bruker AVIII 600 MHz liquid nuclear magnetic resonance spectrometer (USA) with deuterium oxide ( $\text{D}_2\text{O}$ ) as a solvent. The  $^{31}\text{P}$  chemical shifts are reported in  $\delta$  relative to external 85% aqueous phosphoric acid ( $\text{H}_3\text{PO}_4$ ).

##### Scanning electron microscope (SEM)

The surface morphologies of the control cotton fibers, the pre-treated cotton fibers and the cotton fibers treated with 30% FR–LO before and after combustion were observed using a Phenom Prox Holland SEM with magnifications of  $1000\times$ ,  $3000\times$ , and  $5000\times$ , and a voltage of 10 kV. All samples were sputtered with gold.

##### Energy-dispersive X-ray spectroscopy (EDS)

The elemental compositions and atomic contents of the pre-treated cotton fibers and the cotton fibers treated with 30% FR–LO before and after combustion and after 50 LCs were tested using an energy-dispersive X-ray spectroscopy (JEOL-6300F) with a voltage of 15 kV.

##### Fourier transform infrared spectroscopy (FT-IR)

The functional groups and chemical bonds of the pre-treated cotton fibers, the cotton fibers treated with 30% FR–LO and the FR–LO powders were analyzed with an FT-IR (PE Co., USA) at wavenumbers from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  and a resolution of  $4.0\text{ cm}^{-1}$ .

The potassium bromide tablet method was used in the infrared spectrum analysis of this experiment.

#### *Durability tests*

The durability of the cotton fabrics treated with different concentrations of FR–LO were tested according to the AATCC 61–2013 2A standard method (The washing temperature: 49 °C; the amount of detergent: 150 mL, 0.15%; the number of steel balls: 50; the washing time: 45 min, the effect of five typical hand or home washes on the fabric can be simulated in a 45-min test.)

#### *Limiting oxygen index (LOI) and vertical flammability tests (VFT)*

The flame retardancy of the pre-treated cotton fabric and the cotton fabric treated with different concentrations of FR–LO were tested using an M606B digital display oxygen index apparatus (Qingdao Shanfang Instrument Co. Ltd., China) according to the ASTM D2863-2000 standard, and a YG815B vertical fabric flame-retardancy tester (Nantong Sansi Electromechanical Science and Technology Co. Ltd., China) in accordance with the ASTM D6413-99 standard.

#### *Thermogravimetric analysis (TGA)*

TGA was conducted on a Pyris 1 TGA (PerkinElmer, USA). The mass losses of the pre-treated cotton and cotton treated with 30% FR–LO were measured using 3–5 mg samples heated from 40 to 700 °C at a heating rate of 20 K/min under a nitrogen atmosphere.

#### *TGA-FTIR*

TGA–FTIR analyses were conducted on a Netzsch STA 409 PC thermal analyzer coupled with a Bruker Tensor 27 FTIR spectrometer via a Teflon tube. The analyses were conducted using 3–5 mg samples heated from 40 to 700 °C at a heating rate of 20 K/min under a nitrogen atmosphere. The wavenumber range was 4000–600  $\text{cm}^{-1}$  with a 4.0  $\text{cm}^{-1}$  resolution and 4 scans.

#### *Microscale combustion calorimetry (MCC)*

The thermal properties of the cotton fabrics treated with different concentrations of FR–LO were measured on a FTT001 micro fire testing equipment (Fire Testing Technology Ltd, HL, UK) according to ASTM E1354 standard. Samples were heated in an atmosphere in which the ratio of nitrogen-to-oxygen was 4–1 from 100 to 700 °C at a heating rate of 1 K/s.

*Bending lengths and tensile strengths* The stiffness and tensile strengths of the cotton fabrics treated with different concentrations of FR–LO were evaluated using a YG (B) 022D fabric stiffness tester (Wenzhou Darong Textile Machinery Co. Ltd, Zhejiang, China) according to the ASTM D 1388–96(2002) standard and an electronic fabric tension tester (HD026N, Nantong Hongda Experiment Instruments Co. Ltd., China) according to the ASTM 5035-2006 standard, respectively.

*X-ray diffraction (XRD)* The XRD patterns of the pre-treated cotton and the cotton treated with 30% FR–LO were evaluated using a Rigaku XD-3 wideangle diffractometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China) at 36 kV and 20 mA. The diffractogram scattering angle ranged from 5 to 50° with a step size of 0.02° ( $\lambda = 0.154 \text{ nm}$ ).

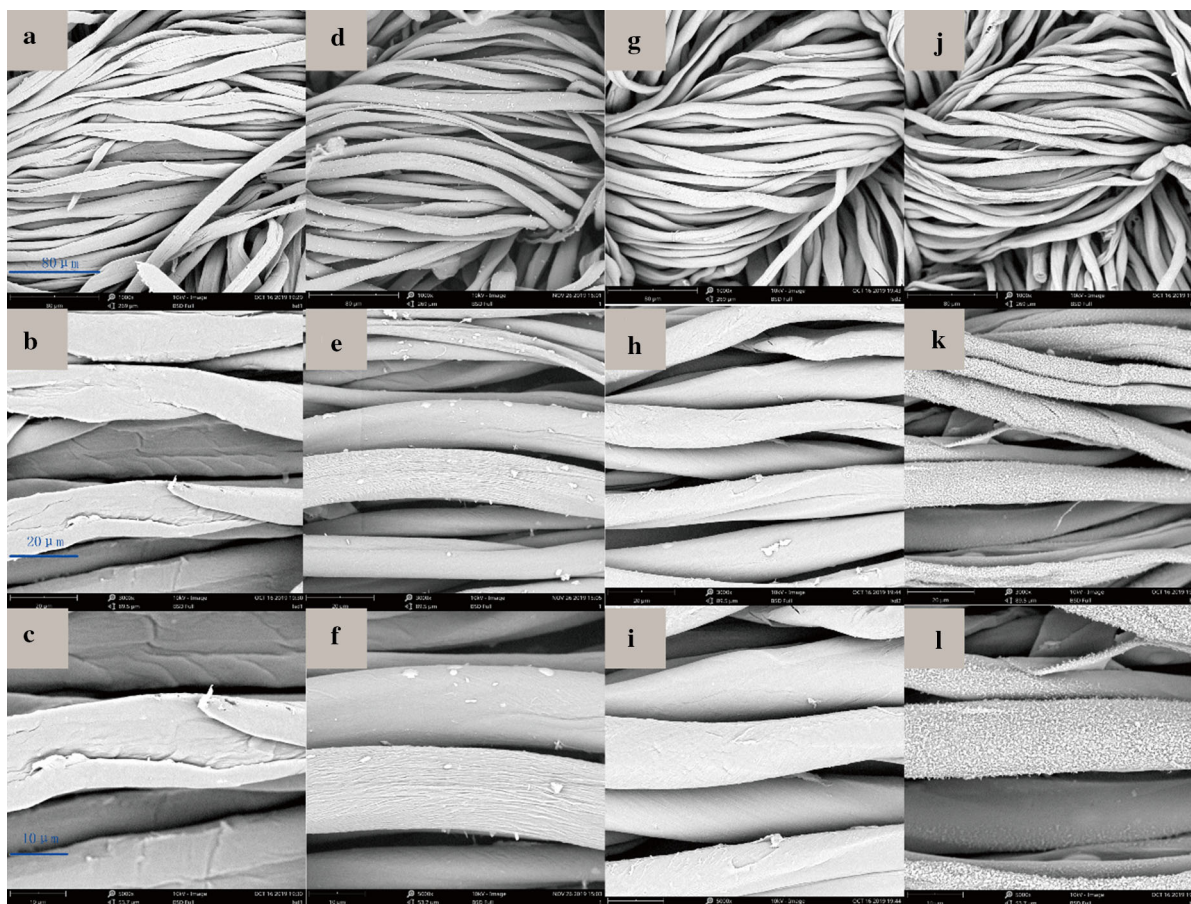
*X-ray photoelectron spectroscopy (XPS)* The elemental compositions of the pre-treated cotton and the cotton treated with 30% FR–LO were measured by X-ray photoelectron spectrometer (Thermo Fisher Scientific K-Alpha, USA) with a Al Ka excitation radiation ( $h\nu = 1253.6 \text{ eV}$ ). The working voltage is 15 kV. The test passing-energy is 50 eV, step length is 0.05 eV.

## **Results and discussion**

### **SEM–EDS**

The surface morphologies of samples were observed using SEM, and the corresponding micrographs are presented in Fig. 1. The control cotton fibers (Fig. 1 a, b, c) showed a spiral structure with many distinct folds (Jia et al. 2017), while the pre-treated cotton fibers (Fig. 1 d, e, f) had columnar structures, because the



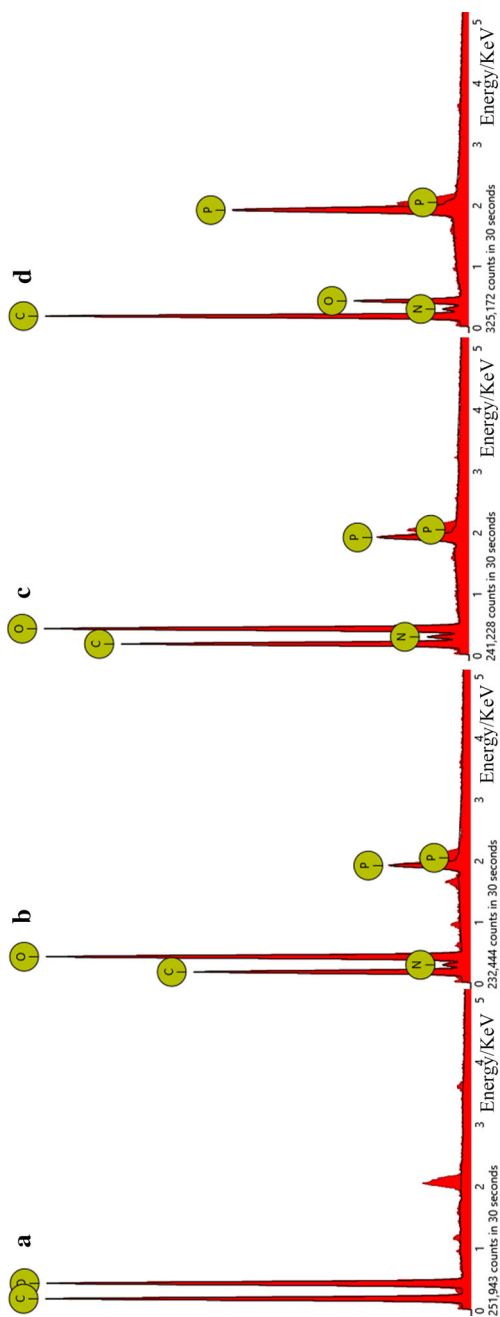


**Fig. 1** SEM images of the control cotton fibers **a, b, c**; pre-treated cotton fibers **d, e, f**; cotton fibers treated with 30% FR-LO **g, h, i**; and treated cotton fibers after combustion **j, k, l** at

magnifications of  $1000\times$  **a, d, g, j**,  $3000\times$  **b, e, h, k**, and  $5000\times$  **c, f, i, l**. Images with the same magnification share the same scale bars

cotton fabrics were modified through mercerization. (Tarbuk et al. 2014). The surface morphologies of cotton fibers treated with 30% FR-LO (Fig. 1 g, h, i) were similar to those of pre-treated cotton fibers, and no obvious coating was observed on the surfaces. This implied that FR-LO entered the inner spaces of the cotton fibers and grafted to cellulose (Huang et al. 2019). After combustion, the treated cotton fibers (Fig. 1 j, k, l) retained their complete structures and lots of bubbles remained on the cotton fiber surface. This was because FR-LO released phosphoric acid, which promoted formation of cellulose char during combustion (Zhao et al. 2016). Ammonia released by FR-LO during combustion diffused from the fiber interior to the exterior to form dense bubbles on the fiber surfaces (Feng et al. 2017).

The elemental compositions and atomic contents of samples were measured using EDS, and the corresponding data are recorded in Fig. 2 and Table 1. Only carbon and oxygen elements were detected in the pre-treated cotton fibers, and their atomic ratio matched that of cellulose (Klemm et al. 2005). In addition to carbon and oxygen, nitrogen and phosphorus were detected in fibers treated with FR-LO, treated fibers after 50 LCs, and treated fibers after combustion. The introduction of nitrogen and phosphorus in the cotton fibers showed that FR-LO was successfully grafted to the cotton fabrics, and the phosphorus content of the treated cotton fibers did not significantly decrease after 50 LCs. This demonstrated the excellent durability of the treated cotton fibers.



**Fig. 2** EDS spectra of the pre-treated cotton fibers **a**; cotton fibers treated with 30% FR-LO **b**; treated cotton fibers after 50 LCs **c**; and treated cotton fibers after combustion **d**

## FT-IR spectra

The FT-IR spectra of samples are shown in Fig. 3, and the data corresponding to the characteristic absorption peaks of each sample are listed in Table 2. The FT-IR spectra agreed with the structure of FR-LO. P = O (Thach-Mien et al. 2013), P–O–C (Hu et al. 2019), and P–N (Zhang et al. 2019) bonds were found in the spectra of FR-LO and of cotton treated with 30% FR-LO, but not in pre-treated cotton. These results were consistent with the EDS results and indicate that FR-LO was successfully grafted onto cotton fabrics. And the spectra of cotton treated with 30% FR-LO after 50LCs showed the esters could hydrolyze. The P–O–C bond at about 1060 is weaker than it was before washing.

## Vertical flammability, limiting oxygen index(LOI), and durability

The flame retardancy of cotton fabrics treated with different concentrations of FR-LO before and after laundering was analyzed by vertical flammability and LOI tests. The vertical flammability test images are shown in Fig. 4, and the parameters of the vertical flammability test and LOI tests are summarized in Table 3, 4, respectively. In the vertical flammability tests, the pre-treated cotton fabric burned down after the ignition source was removed, and smoldering lasted for 45 s without producing ash. However, the cotton fabrics treated with FR-LO did not burn, and there was no after-flame or after-glow. The length of the char frames decreased upon increasing the FR-LO concentration. The char lengths of the cotton fabrics treated with 20% and 30% FR-LO were only 39 mm and 38 mm, and after 50 LCs, they were 56 mm and 50 mm, respectively.

The LOI of the pre-treated cotton fabric was only 18.4. Compared with the pre-treated cotton fabric, the LOI of the cotton fabrics treated with various concentrations of FR-LO were greatly improved. The LOI of fabrics treated with 20% and 30% FR-LO, and after 50 LCs were still greater than 26, so the fabrics were considered to have permanent durability.

The fabrics treated with ordinary ammonium organic phosphorus acid flame retardant only passed the AATCC-61 2013 1A standard, while the one treated with FR-LO had a comparatively high durability and passed the AATCC-61 2013 2A standard.

**Table 1** EDS data (atomic percentages) of pre-treated cotton fibers, cotton fibers treated with 30% FR–LO, treated cotton fibers after 50 LCs and treated cotton fibers after combustion

Sample	C (%)	O (%)	P (%)	N (%)
Pre-treated	50.4 ± 0.3	49.6 ± 0.3	–	–
Treated 30%	45.0 ± 0.2	50.9 ± 0.2	3.0 ± 0.1	1.1 ± 0.1
LCs-50	45.6 ± 0.4	50.6 ± 0.4	2.6 ± 0.2	1.2 ± 0.1
Combustion	61 ± 3	20 ± 1	16.0 ± 0.5	3.0 ± 0.5

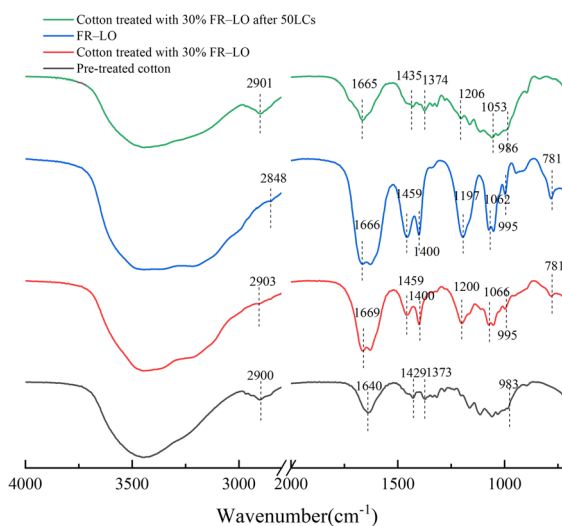
Pre-treated indicates cotton fibers treated in method 2.2; treated 30% indicates cotton fibers treated with 30% FR–LO; LCs-50 indicates treated cotton fibers after 50 LCs; Combustion indicates treated cotton fibers after combustion

This was because there were two phosphoric acid ester groups and only one ammonium phosphorus acid group, while the former flame retardants only had ammonium phosphorus acid groups and no phosphoric acid ester groups. The ammonium phosphorus acid groups that did not react with cellulose lost their ammonium ions and combined with metal ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  during washing, and the treated cotton fabrics quickly lost their flame retardancy; however, the phosphoric acid esters in the FR–LO did not lose their flame retardancy, and the cotton fabrics treated with FR–LO had excellent durability that was as good as Proban and Pyrovatex CP (Supplementary Material, Table S1). No formaldehyde was used to synthesize FR–LO, and the cotton fabrics treated with the FR–LO did not release formaldehyde during use, making FR–LO a promising candidate for replacing Proban and Pyrovatex CP.

## TGA

The thermal performance of pre-treated cotton and cotton treated with 30% FR–LO in nitrogen atmosphere was measured using TGA. The mass loss curves, the derivative thermogravimetry analyses (DTG) curves under a nitrogen atmosphere, and the corresponding data are shown in Fig. 5 and Table 5. The initial decomposition temperature of a material is generally considered to be the temperature at which 10% weight loss occurs. It could be seen from Fig. 5 that the pre-treated cotton and cotton treated with 30% FR–LO started to decompose at 349.7 °C, and 248.1 °C, respectively. Both of these substances underwent water evaporation, in which the cellulose lost its free and bound water before degradation. Pre-treated cotton rapidly degraded from 349.7–416.0 °C,

and the most rapid weight loss occurred at 361.2 °C. Within this temperature range, the cellulose degraded to levoglucosan, flammable hydrocarbons, carbonyl gases, CO, and CO<sub>2</sub> (Thach-Mien et al. 2014; Wan et al. 2019a, 2019b). At 700 °C, the residual weight was only 8.61%. The cotton fibers treated with 30% FR–LO underwent three-step degradation similar to the pretreated cotton fibers in which they degraded rapidly from 248.1–291.2 °C, and the fastest weight loss rate occurred at 283.2 °C. At 700 °C, the residual weight was still 37.24%. After FR–LO treatment, the thermal cracking process of cotton fabric changed significantly. The decomposition temperature of cotton treated with 30% FR–LO was lower than that of the pre-treated cotton because FR–LO easily decomposed into phosphoric acid at lower temperatures, and the presence of phosphoric acid promoted the char

**Fig. 3** FT-IR spectra of FR–LO, pre-treated cotton, and cotton treated with 30% FR–LO



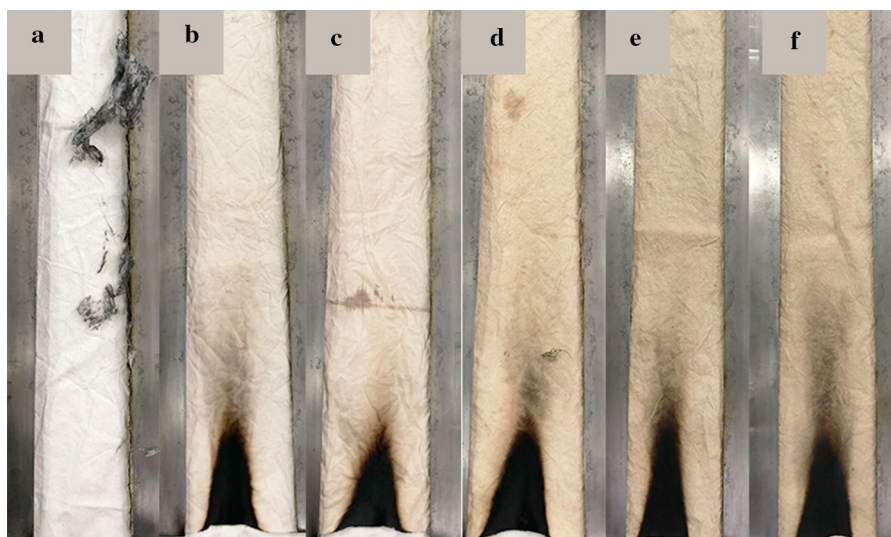
**Table 2** The characteristic peaks of pre-treated cotton, the FR–LO, and cotton treated with 30% FR–LO

Peak position	Pre-treated cotton( $\text{cm}^{-1}$ )	FR–LO( $\text{cm}^{-1}$ )	Cotton treated with 30% FR–LO( $\text{cm}^{-1}$ )	Cotton treated with 30% FR–LO after 50LCs( $\text{cm}^{-1}$ )
<i>Characteristic peak</i>				
–CH (Stretching vibration)	2900	2848	2903	2901
–OH (Bending vibration)	1640	1666	1669	1665
–CH <sub>2</sub> , –CH <sub>3</sub> (Bending vibration)	1429	1459	1459	1435
–CH (Bending vibration)	1373	1400	1400	1374
P = O (Bending vibration)	–	1197	1200	1206
P–O–C (Bending vibration)	–	1062	1066	1053
C–O (Bending vibration)	983	995	995	986
P–N (Bending vibration)	–	781	781	–

formation (Xu et al. 2019; Zheng et al. 2018), This is the reason for the difference in TGA spectrum. Therefore, the residual weight of cotton treated with 30% FR–LO was much higher than that of untreated cotton, showing that FR–LO endowed the cotton fabrics with flame retardancy.

#### TGA-FTIR

The pyrolysis products of pre-treated cotton and cotton treated with 30% FR–LO were analyzed by TGA-FTIR to explore the flame retardancy mechanism of FR–LO. Three- and two-dimensional spectra of the gaseous volatiles of pre-treated cotton and



**Fig. 4** Vertical flammability tests of the pre-treated cotton fabric **a**; cotton fabric treated with 15% FR–LO **b**; cotton fabric treated with 20% FR–LO **c**; cotton fabric treated with 30% FR–

LO **d**; cotton fabric treated with 20% FR–LO and after 50 LCs **e**; cotton fabric treated with 30% FR–LO after 50 LCs **f**

**Table 3** Vertical flammability test data of six kinds of cotton fabrics

Samples	Concentration of FR–LO	After-flame time (s)	After-glow time (s)	carbon frames length (mm)
Pre-treated (a)	0%	14 ± 1	45 ± 3	0
Treated 15% (b)	15%	0	0	45 ± 2
Treated 20% (c)	20%	0	0	39 ± 2
Treated 30% (d)	30%	0	0	38 ± 1
Treated 20%-50LCs(e)	20%	0	0	56 ± 2
Treated 30%-50LCs (f)	30%	0	0	50 ± 2

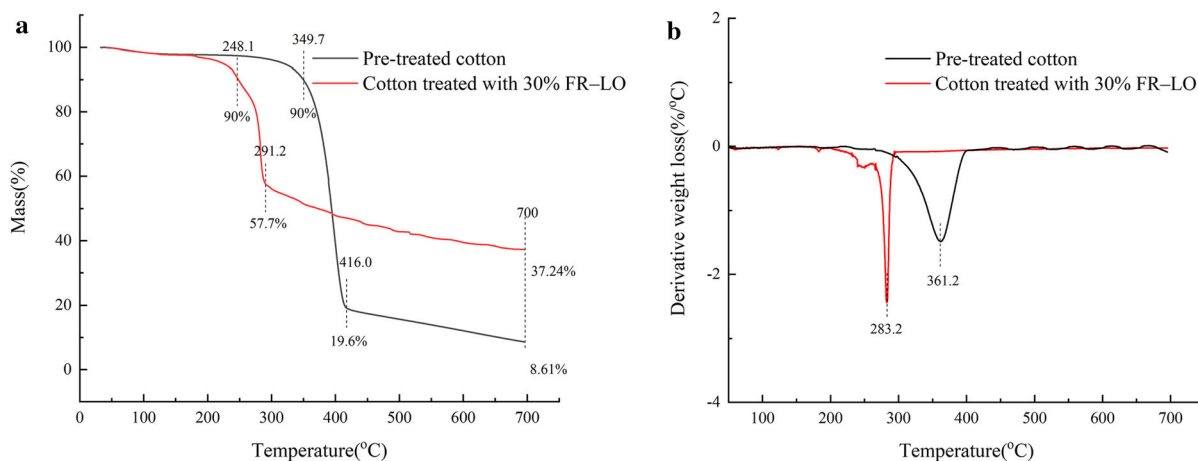
**Table 4** The weight gain rates of cotton fabrics treated with different concentrations of FR–LO and LOIs of the treated cotton fabrics after different numbers of laundering cycles

Samples	Concentration of FR	Weight gain (%)	LOI					
			0LCs	10LCs	20LCs	30LCs	40LCs	50LCs
Pre-treated	0%	–	18.4	–	–	–	–	–
Treated 15%	15%	13.0 ± 0.5	33.8	30.2	28.5	27.3	26.2	25.1
Treated 20%	20%	19 ± 1	39.3	33.3	30.3	29.8	29.4	28.5
Treated 30%	30%	22.7 ± 0.8	43.4	39.1	33.8	33.2	31.5	29.7

cotton treated with 30% FR–LO under a nitrogen atmosphere are presented in Fig. S4 and Fig. 6. The data corresponding to the characteristic absorption peaks of each sample are listed in Table 6. Both figures showed that the absorption peaks of most of gases released by treated cotton were much weaker than those of pre-treated cotton, except those at 2304 cm<sup>-1</sup> (CO<sub>2</sub>) and 1513 cm<sup>-1</sup> (N–H). The N–H stretching vibration was found in the gas released by the treated cotton but not in pre-treated cotton, which suggests that FR–LO decomposed and released NH<sub>3</sub> at high temperatures. In contrast to CO<sub>2</sub> and NH<sub>3</sub>, which are non-combustible gases, treated cotton released far fewer combustible gases such as hydrocarbons (C–H), carbonyl compounds (C = O), and ether compounds (C–O–C) at high temperatures than pre-treated cotton. The results showed that FR–LO mainly exhibited a condensed phase flame retardancy mechanism, which decomposed phosphorous-containing substances before accelerating the dehydration of cellulose. This reduced the release of combustible gases and diluted combustible gases by releasing ammonia gas (Liu et al. 2020).

#### Microscale combustion calorimetry

The thermal properties of the cotton fabrics treated with different concentrations of FR–LO were examined by microscale combustion calorimetry. The corresponding parameters, such as the total heat release (THR), peak heat release rate (PHRR), and temperature of maximum HRR ( $T_{max}$ ) are presented in Table 7 and Fig. 7. The PHRR of pre-treated cotton fabric during combustion was 365.4 W/g, and 19.1 kJ/g of heat was released during the entire combustion process. However, the PHRR values of cotton treated with 15%, 20%, and 30% FR–LO were only 107.3 W/g, 91.2 W/g, and 53.8 W/g, respectively. The THR values were also much lower than those of untreated cotton, with values of 8.8 kJ/g, 5.5 kJ/g, and 3.9 kJ/g, respectively. The values of PHRR and THR decreased upon increasing the FR–LO concentrations. The  $T_{max}$  values of cotton fabrics treated with FR–LO were lower than those of untreated cotton, which was consistent with the TGA results.



**Fig. 5** The mass loss curves **a** and the DTG curves **b** of the pre-treated cotton and cotton treated with 30% FR-LO in nitrogen

**Table 5** TGA results for the pre-treated cotton fibers and cotton fibers treated with 30% FR-LO under a nitrogen atmosphere

Sample	$T_{10\%}$ (°C)	$T_{max}$ (°C)	$T_{end}$ (°C)	$Rw_{700}$ (wt%)
Pre-treated	349.7	361.2	416.0	8.61
Treated 30%	248.1	283.2	291.2	37.24

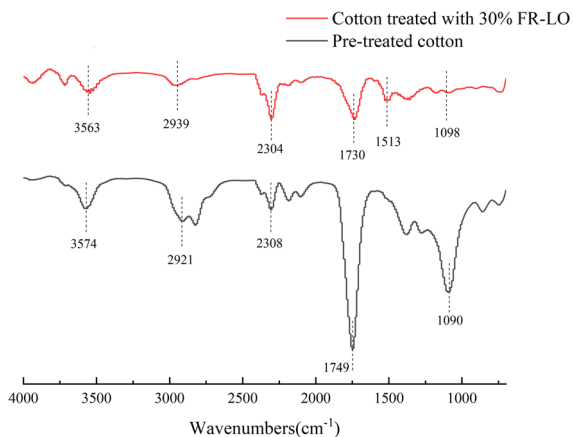
$T_{10\%}$  stands for the initial decomposition temperature;  $T_{max}$  stands for the temperature with the fastest weight loss rate;  $T_{end}$  stands for the temperature at the end of the rapid degradation phase;  $Rw_{700}$  stands for the residual weight at 700 °C

## Physical properties

To explore the stiffness and tensile strengths of the cotton fabrics treated FR-LO, the bending lengths and the tensile strengths of samples were tested, and the results are listed in Table 8. The bending lengths of the cotton fabrics increased upon increasing the FR-LO concentration, and at 30% FR-LO, the warp and weft bending lengths increased by 36% and 28%, respectively. The results indicated that the cotton fabrics treated by FR-LO were somewhat harder than pre-treated cotton, but they were still soft enough to be used in textiles. The tensile strengths of the cotton fabrics decreased upon increasing the FR-LO concentration. When 30% FR-LO was used, the warp and weft tensile strengths decreased by 33.1% and 28.4%, respectively, and the tensile strengths also decreased. Since FR-LO is neutral, the physical properties of the cotton fabrics treated with FR-LO did not significantly change. In addition, the bending lengths of the samples after 50 LCs were shorter than that of the treated samples and the tensile strengths of the samples after 50 LCs were stronger.

## XRD

In order to determine the effect of FR-LO on the crystal structure of cellulose, XRD analysis was used to test it, and the result is presented in Fig. 8. The peaks of raw cotton at 15.15° correspond to the (1–10) plane; the peaks at 16.88° are attributed to the (110) plane; the peaks at 22.88° are attributed to the (200) plane; and the peaks at 34.69° correspond to the (004) plane of cellulose I. After pretreatment with sodium hydroxide, the diffraction peak strength of the corresponding cellulose I decreases. In addition, new diffraction peaks appeared, the peak at 22.53° is probably a composite of the cellulose I (200) reflection and the cellulose II (020) reflections. The increased peak height at about 20 deg from I to II is due to adding some (1 1 0) cellulose II intensity to the (012) and (102) cellulose I peak. The peak shape and curve trend of the cotton treated with FR-LO is similar to that of pre-treated cotton, but the corresponding strength are all lower than that of pre-treated cotton. There was less cellulose in the sample as perhaps the primary cause of the lower peak compared with the

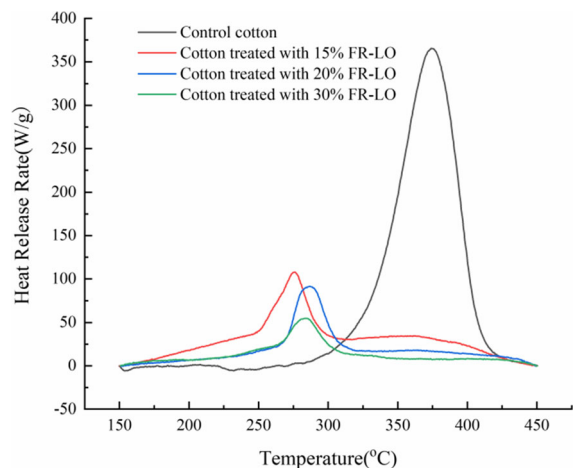


**Fig. 6** TGA-FTIR spectra of the pyrolysis products of pre-treated cotton and cotton treated with 30% FR-LO

pre-treated cotton. This result suggests that sodium hydroxide will cause the changed the allomorph of cellulose crystal while FR-LO will not.

#### XPS

XPS test results of pre-treated cotton and cotton treated with 30% FR-LO are shown in Fig. 9, 10 Table 9. As shown in Fig. 9, only C and O elements were detected in the pre-treated cotton while C, O, N



**Fig. 7** Heat release rate curves of the pre-treated cotton and cotton treated with 15%, 20%, and 30% FR-LO

and P elements were detected in the cotton treated with 30% FR-LO, which was consistent with EDS test. Further analysis of the P2p peak of cotton before and after finishing revealed that there was no P2p peak in the pre-treatment cotton, but there were two peaks in the cotton treated with 30% FR-LO,  $\text{PO}_2^{2-}$  at 133.4 eV and  $\text{P}(=\text{O})-\text{O}-\text{C}$  at 134.8 eV, respectively. The results showed that phosphorous in flame retardants could react with cellulose to form  $\text{P}=\text{O}$  and  $\text{P}-$

**Table 6** The peak positions of each characteristic peak of the pyrolysis products of pre-treated cotton and cotton treated with 30% FR-LO

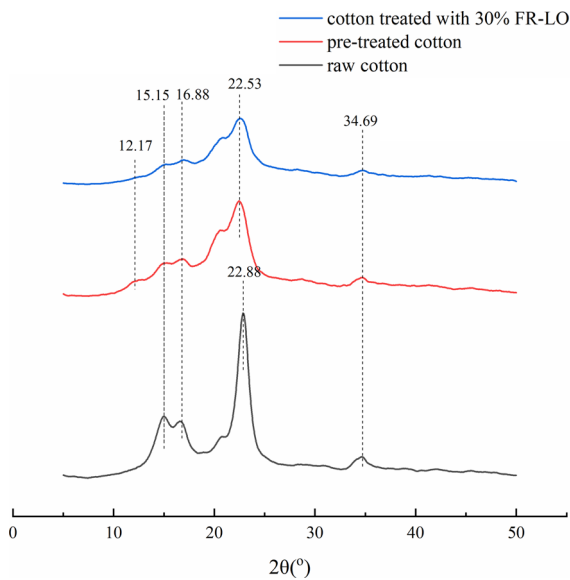
Peak position	Cotton treated with 30% FR-LO( $\text{cm}^{-1}$ )	Pre-treated cotton( $\text{cm}^{-1}$ )
<i>Characteristic peak</i>		
–OH (Stretching vibration)	3563	3574
C–H (Bending vibration)	2939	2921
$\text{CO}_2$	2304	2308
C = O (Bending vibration)	1730	1749
N–H (Bending vibration)	1513	–
C–O–C (Bending vibration)	1098	1090

**Table 7** Microscale combustion calorimetry data for pre-treated cotton and cotton treated with 15%, 20%, 30% FR-LO

	THR(kJ/g)	PHRR(W/g)	$T_{max}$ (°C)	$Rw_{700}$ (wt%)
Pre-treated	19.1	365.4	374.2	8.4
Treated 15%	8.8	107.3	275.6	20.9
Treated 20%	5.5	91.2	286.6	26.6
Treated 30%	3.9	53.8	282.9	36.8

**Table 8** Average bending lengths and average tensile strengths of the pre-treated cotton and cotton treated with 15%, 20%, 30% FR-LO and cotton treated with 15%, 20%, 30% FR-LO after 50LCs

Sample	Bending length (mm)		Tensile strength (N/mm <sup>2</sup> )	
	Warp	Weft	Warp	Weft
Pre-treated	33.3 ± 0.8	37.9 ± 0.6	481 ± 32	423 ± 38
Treated 15%	41.1 ± 0.1	46.6 ± 0.2	372 ± 30	328 ± 22
Treated 20%	44.5 ± 0.2	47.0 ± 0.1	341 ± 23	316 ± 42
Treated 30%	45.3 ± 0.1	48.6 ± 0.3	322 ± 30	303 ± 34
Treated 15%-50LCs	40.3 ± 0.3	44.5 ± 0.3	388 ± 25	349 ± 33
Treated 20%-50LCs	42.8 ± 0.2	45.8 ± 0.2	367 ± 29	338 ± 28
Treated 30%-50LCs	43.7 ± 0.2	47.7 ± 0.4	348 ± 21	319 ± 35

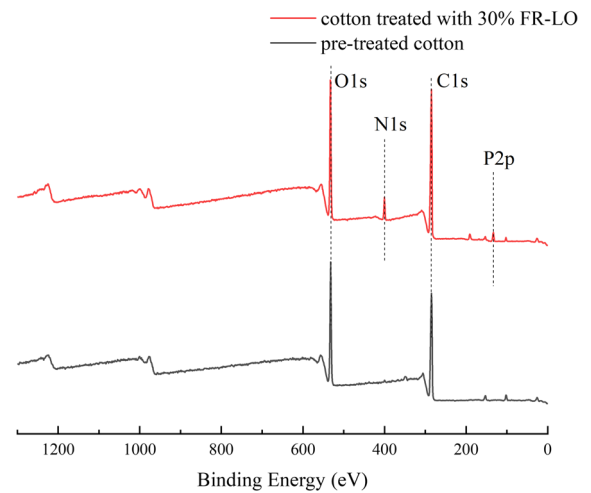


**Fig. 8** X-ray diffraction pattern of the raw cotton, pre-treated cotton and cotton treated with 30% FR-LO

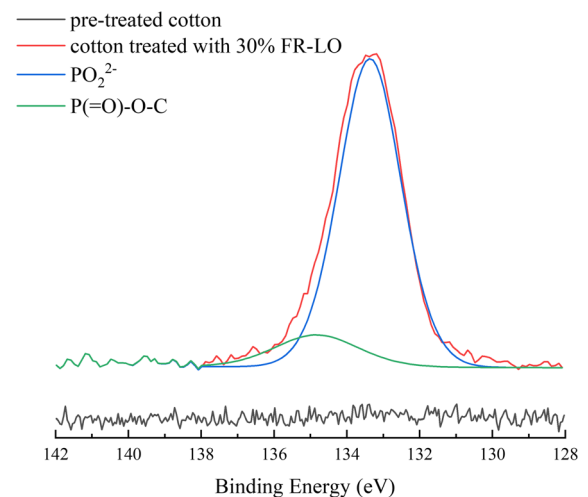
O–C bonds, which was consistent with the results of FT–IR analysis.

## Conclusion

In this work, a novel flame retardant with only one reactive ammonium phosphorus acid group and other phosphoric acid ester groups was synthesized without formaldehyde. The LOI of the cotton fabrics treated with 30% FR-LO reached 43.4 and remained at 29.7 after 50 LCs according to AATCC 61–2013 2A standard, and the treated cotton fabrics exhibited very high flame retardancy and excellent durability. The results of VFT and SEM results showed that the treated cotton maintained an intact structure and



**Fig. 9** XPS spectra of the pre-treated cotton and cotton treated with 30% FR-LO



**Fig. 10** Curve fitting the P2p peak of the pre-treated cotton and cotton treated with 30% FR-LO



**Table 9** XPS data (atomic percentages) of pre-treated cotton and cotton treated with 30% FR–LO

Sample	C (%)	O (%)	P (%)	N (%)
Pre-treated	70.1	29.9	–	–
Treated 30%	67.0	24.8	2.4	5.8

formed char after combustion. Thermal performance measurements such as TGA, TGA-FTIR and MCC showed that cotton treated with FR–LO decomposed in advance at high temperature and released only a small amount of combustible gases and heat compared with pre-treated cotton. Cotton treated with FR–LO had a slightly higher hardness and a lower tensile strength than pre-treated cotton. Replacing ammonium phosphorus acid groups with phosphate ester groups in the cotton fabric flame retardants greatly increased the durability of the treated cotton fabrics.

**Author contributions** SL: Software, data curation, writing—original draft, writing—review and editing, visualization, project administration. PW: Validation. YC: Formal analysis. CW: Investigation. GZ: Conceptualization, methodology, resources, supervision.

**Funding** This work was supported by the “Natural Funds for Chongqing” (cstc2019jcyj-msxmX0412) and the “National Natural Science Foundation of China” (Grant No.21905233).

#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Human and animal rights** This article does not contain any studies with human participants or animals performed by any of the authors.

**Informed consent** Informed consent was obtained from all individual participants included in the study.

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