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ORIGINAL PAPER

Synthesis and evaluation of an efficient, durable, and environmentally friendly flame retardant for cotton

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Abstract An efficient and durable formaldehyde-free flame retardant consisting of an ammonium salt of pentaerythritol tetraphosphoric acid (APTTP) was prepared by a solventless synthesis and characterized by Fourier-transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance. The flame retardancy of the treated cotton fabric was enhanced, as assessed by limiting oxygen index (LOI), vertical flammability, and cone calorimetry measurements. The collected results demonstrated that cotton fabrics treated with APTTP exhibited high flame retardancy and excellent durability. Cotton fabric treated with a 140 g/L APTTP solution showed a LOI of 43.8%, and this value reduced to 26.9% after 50 laundering cycles. No after-flame and after-glow phenomena were presented during vertical flammability tests for all cotton fabrics treated with different concentrations of APTTP. Cone calorimetry results revealed a significant reduction in the intensity of the heat release rate and total heat release peaks. X-ray diffraction revealed that the crystalline particles of cotton fibers treated with APTTP were slightly affected compared with those of control sample. FT-IR spectroscopy results revealed that APTTP was grafted on the cotton fibers. Scanning electron microscopy showed that the surface of the treated cotton fibers remained smooth, while thermogravimetric analysis confirmed that the treated cotton fibers easily decomposed to form char. It was proposed that the flame retardant mechanism of APTTP occurred in the condensation phase.

Keywords Cotton · Environmentally friendly flame retardant · Synthesis · Durability · Efficiency

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Introduction

Cotton fabrics are commonly used in clothing, carpeting, and bedding owing to their comfort, softness, and natural origin characteristics (Liu et al. 2012; Lv et al. 2016). However, cotton fabrics burn easily with a limiting oxygen index (LOI) value of ca. 18.0% (Dong et al. 2016; Yoshioka-Tarver et al. 2012). Therefore, numerous researchers have invested much effort in investigating the combustion and degradation mechanisms of pure and treated cotton to improve the flame retardancy of cotton fabrics (Shafizadeh and Bradbury 1979; Price et al. 1997; Wang et al. 2016; Nguyen et al. 2014).

During the combustion process of cellulose, an "activated" cellulose species ("Cellulose*") is formed in the early degradation stage at low temperatures prior flame combustion (Shafizadeh and Bradbury 1979; Price et al. 1997). Subsequently, there are two competitive processes at 300–400 °C, namely, depolymerization and dehydration. In depolymerization, cellulose chains end and volatile fuel-forming levoglucosan species (initiated by the scission of acetal bonds in the glycosidic units) are formed. On the other hand, dehydration reactions lead to thermally stable aliphatic structures (char I). As the temperature increases, these stable aliphatic structures (char I) are converted into aromatic structures (char II) at 400–600 °C, which are thermally stable up to 800 °C (Alongi and Malucelli 2015). Thus, it is hard to improve the thermal degradation properties of cellulose. On the basis of above issues, most flame retardants (FRs) recently designed for cotton focus on modifying the degradation mechanism of cellulose to favor the formation of char formation.

Most FRs for cotton are phosphorus-containing compounds releasing phosphorous acid upon heating, which promotes dehydration to form thermally stable char (Bourbigot 2008; Li et al. 2015; Zhou et al. 2015; Alongi et al. 2013b, c; Horrocks 1986, 2003, 2011). Pyrovatex® (i.e., *N*-methylol phosphonopropionamide derivatives) and Proban® (i.e., (hydroxymethyl) phosphonium salts) FRs having reactive hydroxymethyl species are widely used during cotton flame retardancy finishing because of their high flame resistance and the excellent durability of treated cotton fabrics. However, the presence of active hydroxymethyl causes the release of formaldehyde from the finished cotton fabrics (Horrocks 2011).

More recently, the continuous seeking of eco-friendly flame retardant finishing solutions has made renewable and environmentally benign materials such as deoxyribonucleic acid (DNA), chitosan (CH), and phytic acid (PA) as well as protein and casein to be considered as alternatives to traditional flame retardants for cotton. Thus, cotton fabrics treated with DNA (add-on of 19.0 wt%) showed LOI values up to 28 versus 18% of untreated cotton (Alongi et al. 2013a). This amount of added DNA (19 wt%) was able to retard the combustion of cotton under an irradiative flux of 35 kW/m^2 (Alongi et al. 2013b). This good performance was mainly produced by three components of DNA: First, the phosphate groups could release phosphoric acid that catalyzes the dehydration of cotton to form char. This char could prevent heat, fuel, and oxygen from being transferred from the flame to the polymer. Second, the deoxyribose units acted both as a carbon source and blowing agents with which a (poly)saccharide could dehydrate to form char and release water upon heating. Third, the nitrogen-containing bases, including guanine, adenine, thymine, and cytosine, released ammonia, which could further induce char development and produce non-combustible gases such as N_2, CO_2, and CO (Alongi et al. 2013a, 2014d). In a different study, DNA was combined with CH, which has been proven to be a promising carbon source that develops efficient and green FR coatings on cotton via a layer-by-layer (LbL) technique (Carosio et al. 2013). In addition, cationic CH and anionic PA have been reported to reduce flammability upon deposition on cotton fabrics via LbL assembly. PA first decomposes and provides CH species as a carbon source that can be turned into char by dehydration. This char is subsequently expanded by gases produced by the decomposition of the blowing agent CH. Eventually, the coating solidifies into a multicellular material that prevents the substrate from being achieved by the heat flowing from the fire (Laufer et al. 2012). Moreover, caseins and whey proteins were exploited as novel green flame retardants for cotton fabric owing to their high phosphorous content, which favors dehydration of cellulose to form char rather than depolymerization leading to the production of combustible species. The flame retardancy performance of these samples was indicated by the significant reduction of the heat release rate peak (27 and 45% lower for cotton samples treated with caseins and hydrophobins, respectively) at a heat flux of 35 kW/m^2 (Alongi et al. 2014a). Nevertheless, improving the durability of cotton fabrics coated with these FRs requires further study.

Besides the biomacromolecule-based coatings, nanotechnology approaches, including nanoparticle adsorption, LbL assembly, sol–gel methods, and dual-cure processes, which can form very thin layers of the nanomaterial on the fabric surface, have drawn the attention of the scientific community (Alongi and Malucelli 2015). Nanoparticle adsorption can be considered the first and fundamental attempt to deposit nanoparticles on cotton surfaces through a simple impregnation of the fabric material with the nanoparticle stable suspension. Despite the ionic reactions taking place between the nanoparticles and the substrate, nanoparticle adsorption has not yet achieved fabrics with the desired durability (Alongi et al. 2014b, 2015). This durability issue still remains unsolved for fabrics treated by innovative nanotechnology approaches. However, numerous interesting results have been achieved by employing sol–gel (Alongi et al. 2011a) and dual-cure processes (Alongi et al. 2011b, 2014c).

In our study, ammonium pentaerythritol tetraphosphoric acid (APTTP) was synthesized as a novel and efficient FR for cotton. Interestingly, the utilization of APTTP as a FR can overcome the three more important issues of flame retardancy of cotton: (1) the release of formaldehyde from FRs such as Pyrovatex® and Proban® (Horrocks 2011); (2) the employment of formaldehyde in the preparation of efficient FRs such hexamethylenediamine-N,N,N′,N′-tetra(methylphosphonic acid) (AHDTMPA) and ethylenediamine tetram-ethylenephosphonic acid (AEDTMPA) ammonium salts (Gao et al. 2015; Zheng et al. 2016); and (3) the poor durability of biomacromolecule-based coatings and FRs produced by nanotechnology approaches (Alongi and Malucelli 2015; Carosio et al. 2013). The synthesized APTTP exhibited very high flame retardancy efficiency, while providing cotton fabrics with excellent durability.

Experimental

Materials

A scoured and bleached cotton fabric with a density of 133.27 g/m^2 (580 × 350, 15.82 tex × 15.67 tex) was purchased from the Chaotianmen market in Chongqing, China. Phosphoric acid (85%) and aqueous ammonia were supplied by Chongqing Chuandong Chemical Co. Ltd. (Chongqing, China). Pentaerythritol and urea were obtained from Chengdu Kelong Chemical Reagent Co. Ltd. (Chengdu, China). Dicyandiamide was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All chemicals were of the reagent grade and were utilized without further purification.

Synthesis of ammonium of APTTP

Phosphoric acid (**1**, 23.052 g, 0.200 mol) and pentaerythritol (**2**, 6.807 g, 0.05 mol) were added to a beaker and heated at 120 °C. After 4 h, a viscous and buff liquid composed of pentaerythritol tetraphosphate ester **3** was obtained. Urea (**4**, 12.012 g, 0.200 mol) was subsequently added to the above liquid under magnetic stirring. The heated mixture reached 100 °C. After 1 h, the crude APTTP product **5** was obtained, and it was subsequently purified by precipitation using ethanol, filtered, and oven-dried at 100 °C. Scheme 1 shows an outline of the synthesis reactions. The characterizations of the APTTP are as follows:

FT-IR (KBr) (cm^{-1}): 3198 and 3139 (vs, N–H, O–H), 1353 (vs, P=O), 1045 (vs, P–O–C), and 990 (vs, P–OH).
^{1}H NMR (D_2O, 600 MHz) δ (ppm): 3.85 (s, 4CH$_2$, H$_1$, H$_2$, H$_3$, H$_4$) and 4.70 (s, deuterium oxide)—no signal peaks of –OH and –NH$_4^+$ groups were detected because of the replacement of two types of reactive hydrogen by deuterium.
^{13}C NMR (D_2O, 600 MHz) δ (ppm): 68.23 (4C, C$_1$, C$_2$, C$_3$, C$_4$) and 40.56 (1C, C$_5$).
^{31}P NMR (D_2O) δ (ppm): −11.01.

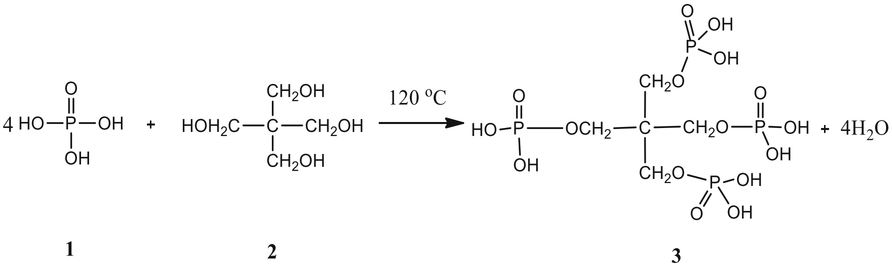
Flame retardant finishing of cotton fabrics

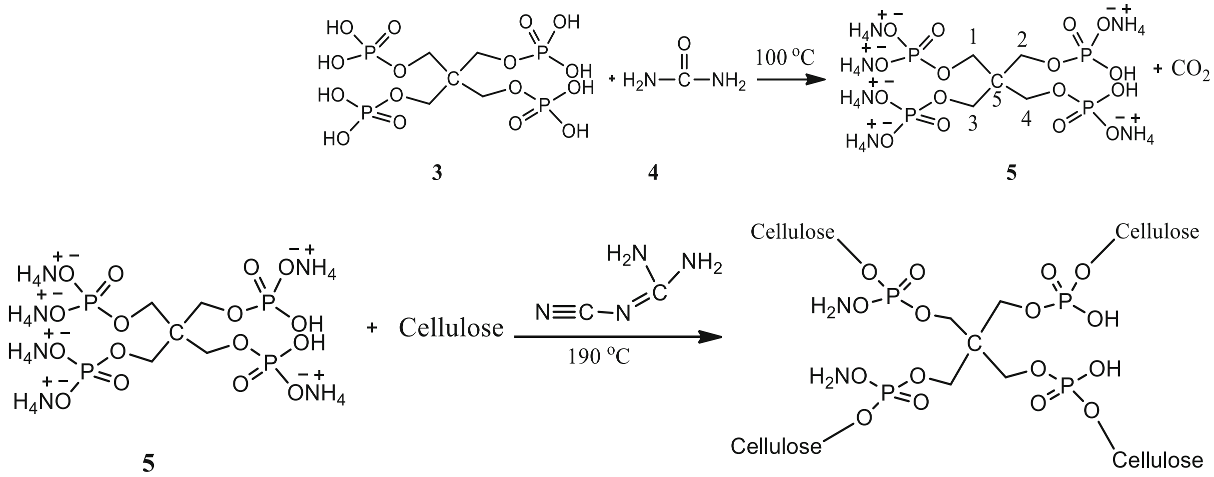
APTTP **5** was dissolved in deionized water to obtain solutions with varying concentrations. Dicyandiamide was added as a catalyst to improve the reactivity between APTTP and the cotton fiber at 50 °C. A low amount of ammonia water was added to fix the pH to 6.0. The cotton fabric was subsequently immersed in the solution with a bath ratio of 1:20 (w/v) at 70 °C for 40 min. The fabric was padded through the nip to come to an average wet pickup of 120%. Subsequently, the fabric was cured in an automatic continuous shaping and baking machine at 190 °C for 5 min. Finally, the fabric was rinsed and oven-dried at 60 °C. The finishing process was repeated twice to prepare the final APTTP-treated fabric (Scheme 2).

The weight gain (WG, wt%) of the treated cotton samples was calculated by the following equation:

$$\mathrm{WG}(\%) = [(W_f - W_i)/W_i] \times 100$$

Scheme 1 Synthesis of APTTP





Scheme 2 Grafting reaction between APTTP and cellulose in the cotton fiber

where W_f is the final weight of the fabric after the treatment, and W_i is the initial weight of the untreated fabric.

Characterization

The chemical structure of APTTP was characterized by obtaining its Fourier-transform infrared (FT-IR) spectra on a Spectrum GX infrared spectrometer (PE. Co., USA) in the wavenumber range of 500–4000 cm^{-1} with a resolution of 2.0 cm^{-1}. The FT-IR spectra of both the control and treated cotton fabrics were obtained at similar conditions. The ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectra of APTTP were obtained on a Bruker AV III 600 spectrometer (Germany).

LOI values of the control and treated cotton fabrics were obtained according to the ASTM D2863-2000 standard test method on a M606B digital oxygen index apparatus (Qingdao Shanfang Instrument Co., Ltd., Shandong, China).

The vertical flammability of the treated and untreated cotton fabrics was examined according to the ASTM D6413-99 standard test method on a YG815B vertical fabric FR tester (Nantong Sansi electromechanical Science & Technology Co., Ltd., China).

The AATCC 61-2006 standard test method was employed to evaluate the durability of the treated cotton fabrics after laundering at 49 °C by using a soaping fastness tester (Roaches Co., England).

Thermogravimetric (TG) analysis of the cotton fabrics before and after the treatment were performed on a Pyris 1 thermogravimetric analyzer (PerkinElmer, USA) from 40 to 600 °C (40–800 °C for experiments under air) at a heating rate of 20 K/min and under flowing N_2 (20 mL/min).

The surface morphologies of the cotton fabric samples were observed using a Hitachi S-4800 scanning electron microscope (Netherlands) with a voltage of 20 kV.

X-ray diffraction (XRD) was utilized to investigate the change in the crystal structure of the cotton fibers before and after the treatment. XRD was carried out using a Rigaku XD-3 wide-angle diffractometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China) at 36 kV and 20 mA. The diffraction angle ranged from 5° to 50° with a step size of 0.02° ($\lambda = 0.154$ nm).

Cone calorimetry (ASTM E 1354) was employed to investigate the combustion behavior of 100 mm × 100 mm × 0.3 mm cotton samples under an irradiative heat flux of 35 kW/m^2 in a horizontal configuration. The time to ignition (TTI, s), the time to flame-out (TTF, s), the total heat release (THR, kW/m^2), the heat release rate (HRR, kW/m^2), and the corresponding peak value (PHRR, kW/m^2) were measured. Moreover, the total smoke release (TSR, m^2/m^2) and the CO and CO_2 yields ([CO] and [CO_2], kg/kg) were evaluated.

The evolved gaseous products of untreated and treated cotton fabrics during thermal degradation were characterized by TG-IR by employing a Netzsch STA409PC thermal analyzer that was coupled with a Bruker Tensor27 spectrophotometer through a polytetrafluoroethylene pipe maintained at 200 °C. About 8.0 mg of the cotton samples was conducted under a nitrogen flow at a heating rate of 20 K/min.

Results and discussion

Flame retardancy and durability of a cotton fabric treated with APTTP

Table 1 displays the WG values of cotton fabrics treated with APTTP solutions at three different concentrations and their LOIs before and after the laundering cycles (LCs). As shown in Table 1, although the WG values of the fabrics treated with 80, 110, and 140 g/L APTTP solutions are not very high, i.e., 14.4, 16.8, and 22.4%, respectively, their LOI values were higher than that of the control sample (18%). The fabric treated with a 140 g/L APTTP solution reached a LOI of 43.8%. After 30 and 50 LCs, the LOIs still remained at 31.1 and 26.9%, respectively. Therefore, the cotton fabric treated with the 140 g/L APTTP solution could be invoked as a durable flame retardant fabric. After 30 LCs, the cotton fabric treated with a 110 g/L APTTP solution showed a LOI of 26.0% and therefore it could be used as a semi-durable FR fabric. These results suggested that APTTP, having a very high phosphorous content, is an effective and durable FR for cotton.

Similarly, vertical flammability tests were performed to determine the flame retardancy of the cotton fabrics before and after the treatment. The results of the samples after burning are shown in Fig. 1, and the corresponding afterflame time, afterglow time, and char length are collected in Table 2. As shown in Fig. 1, the original cotton fabric burned fast, leaving a very low amount of ash (Fig. 1a). In contrast, after 12 s of ignition, the fire flame extinguished immediately in the case of cotton fabrics treated with different concentrations of APTTP, and narrow chars were retained at the end of the cotton fabrics (Fig. 1b–d). As shown in Table 2, the char lengths of the 80-, 110-, and 140-g/L-APTTP-treated fabrics were 49, 40, and 33 mm, respectively. In addition, after 50 LCs, the 140-g/L-APTTP-treated cotton fabric showed a char length of 62 mm, thereby further revealing the excellent durability and flame resistance properties of treated cotton samples.

Based on the LOI and vertical flammability test results, the 140-g/L-APTTP-treated cotton fabric sample showed excellent durability and efficient flammability characteristics. Therefore, additional investigations (detailed below) on the physical properties and characterization were conducted on this sample.

Table 1 LOIs and WGs of APTTP-treated cotton before and after LCs

Concentrations of APTTP (g/L)	WG (%)	LOIs (%)						
		0 LCs	5 LCs	10 LCs	20 LCs	30 LCs	40 LCs	50 LCs
80	14.4	34.0	32.0	29.4	25.8	24.0	22.7	20.1
110	16.8	38.8	34.3	32.9	28.0	26.0	24.1	22.5
140	22.4	43.8	41.5	38.7	33.9	31.1	29.0	26.9

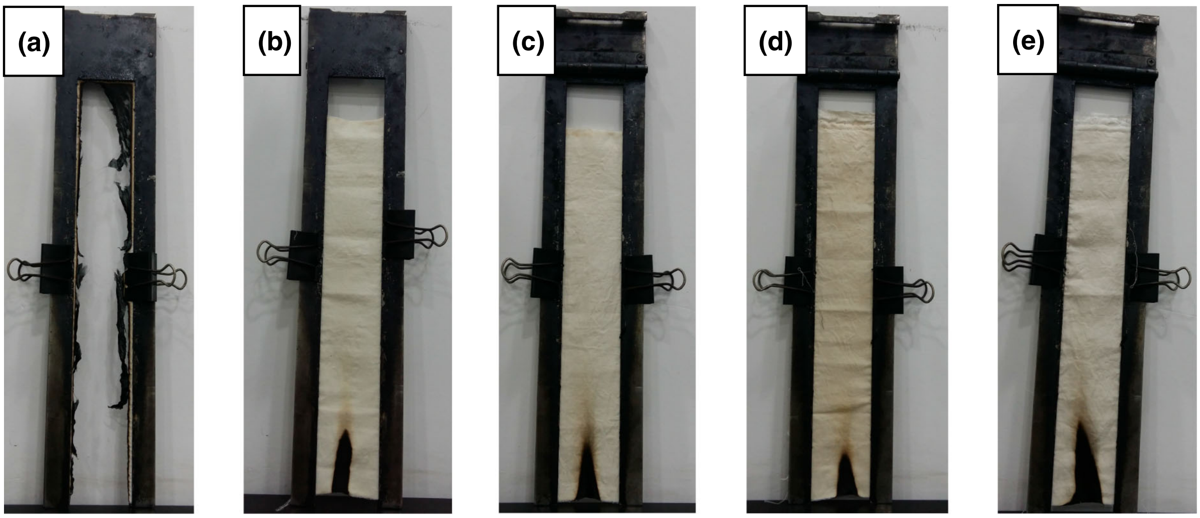


Fig. 1 Vertical flammability test results of the original cotton fabric (**a**), and APTTP-treated samples (**b**) 80 g/L, (**c**) 110 g/L, (**d**) 140 g/L, and (**e**) 140 g/L after 50 LCs

Table 2 Vertical flammability test results of the control and treated samples under different concentrations of APTTP

Samples	WG (%)	After-flame time (s)	After-glow time (s)	Char length (mm)
Control sample	0	12	5	0
80 g/L	14.4	0	0	49
110 g/L	16.8	0	0	40
140 g/L	22.4	0	0	33
140 g/L after 50 LCs	9.7	0	0	62

FT-IR and TG analysis

Figure 2 presents the FT-IR spectra of the control and treated samples. As shown in Fig. 2, additional absorption peaks were observed for the treated cotton fiber as compared to the control fibers. Thus, the peaks at 1243 and 835 cm^{-1} were assigned to the stretching vibrations of the P=O and P–OH groups of APTTP (Zheng et al. 2016), respectively. The strong peak at 1020 cm^{-1} was attributed to the P–O–C bond formed by the reaction between APTTP and cellulose (Zheng et al. 2016). In addition, a strong peak at 1706 cm^{-1} was observed and ascribed to the C=O group generated via oxidation of the C–O–C bond in cellulose (Gao et al. 2015). These results imply that APTTP was actually grafted onto the cotton fibers by covalent bonds.

Figure 3a depicts the TG results of the control and APTTP-treated cotton fibers under nitrogen atmosphere. Cotton usually pyrolyzes under nitrogen

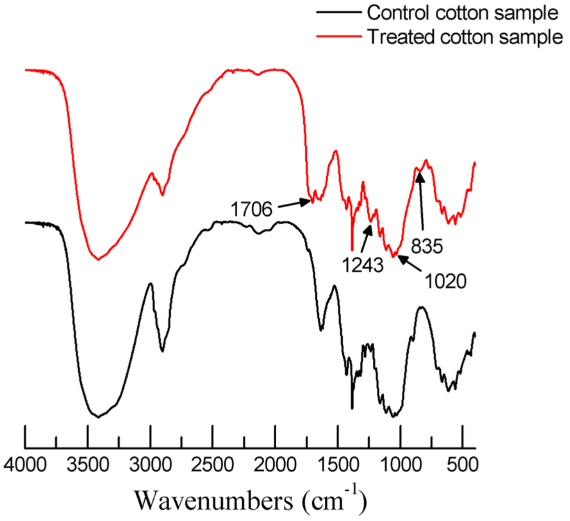


Fig. 2 FT-IR spectra of the control and treated samples

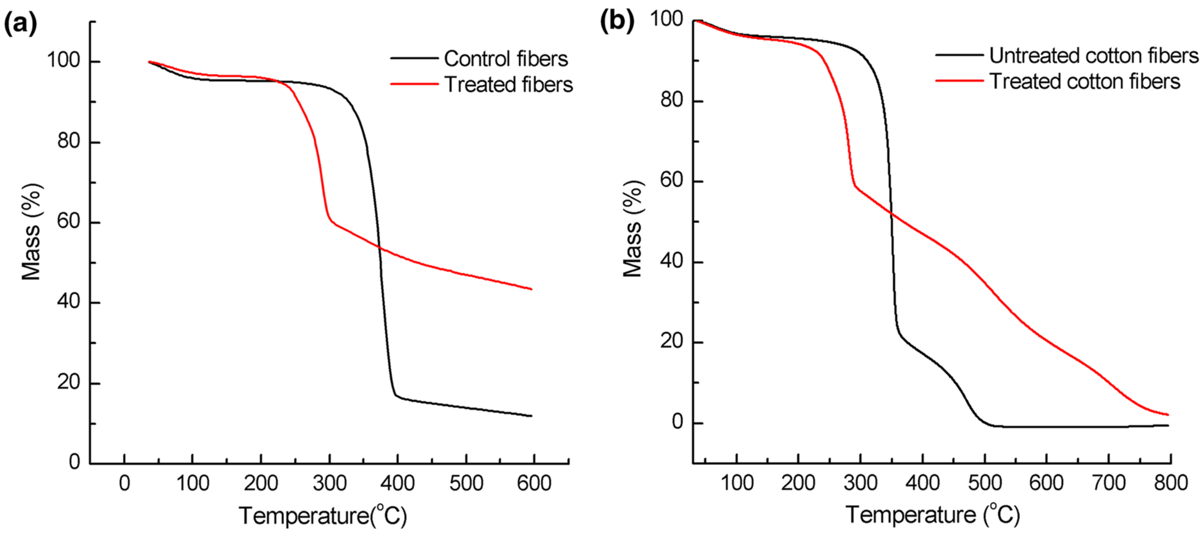


Fig. 3 TG analysis of cotton samples for determining their combustion characteristics under N_2 (**a**) and air (**b**)

following two alternative pathways, namely, the decomposition of the glycosyl units to char at lower temperatures and the depolymerization of the units to volatile products containing levoglucosan at higher temperatures (Alongi et al. 2014b). The decomposition temperature varied from 320 to 395 °C in the case of the original cotton sample, while this range was 219–298 °C in the case of the modified cotton fibers. These results suggest that the decomposition temperature of the treated cotton fiber decreases by approximately 100 °C as compared with the control sample. In addition, after this degradation process, the treated cotton fibers showed a remaining residue of 43.5%, which was greater than that of the control sample (11.8%). These results indicated that APTTP could change the pyrolytic process of the cotton fibers to efficiently form char, thereby rendering this compound an efficient FR finishing reagent. On the basis of the decrease of the decomposition temperature and the increase of residues of APTTP-treated cotton fabric, it was supposed that APTTP could catalyze the dehydration of cotton and form char, thus decreasing the amount of flammable gases. Hence, it was considered that APTTP enhances flame retardancy of cotton by condensation phase.

The thermo-oxidative stability of the untreated and APTTP-treated cotton fabrics was also assessed using TG analysis under air, and the results are presented in Fig. 3b. Cotton degradation in air usually consists of three steps. The first stage at 300–400 °C involves two competitive pathways: the formation of aliphatic chars and volatile products. In the second step at 400–800 °C, some aliphatic chars is converted to aromatic chars, while some char is oxidized to CO and CO_2 simultaneously. During the final step at ca. 800 °C, the remaining chars and hydrocarbon are further oxidized to CO and CO_2 (Alongi et al. 2013a). In the decomposition process, APTTP favors the formation of stable char, with the residue of the treated fibers being significantly higher than that of pure cotton (21.3 vs 0.13%) at 600 °C.

Surface morphologies of cotton fibers

Figure 4 shows Scanning electron microscopy (SEM) images of the control and treated cotton fibers. As shown in Fig. 4, the control fibers showed a planar structure with curly edges (Fig. 4a, b). The surfaces of the treated cotton fibers showed nearly the same morphology as the untreated sample (Fig. 4c, d). In the case of the treated cotton fibers with a WG of 22.4%, no additional materials were observed on their surface, thereby implying that APTTP has likely penetrated the inner space of the cotton fibers. The shapes of the treated cotton fibers were maintained well after burning (Fig. 4e, f). Protuberances appeared in some areas, although the treated cotton fibers did not show any cracks after burning, which could be ascribed to the presence of N (with intumescent flame retardancy properties) in the APTTP molecule.

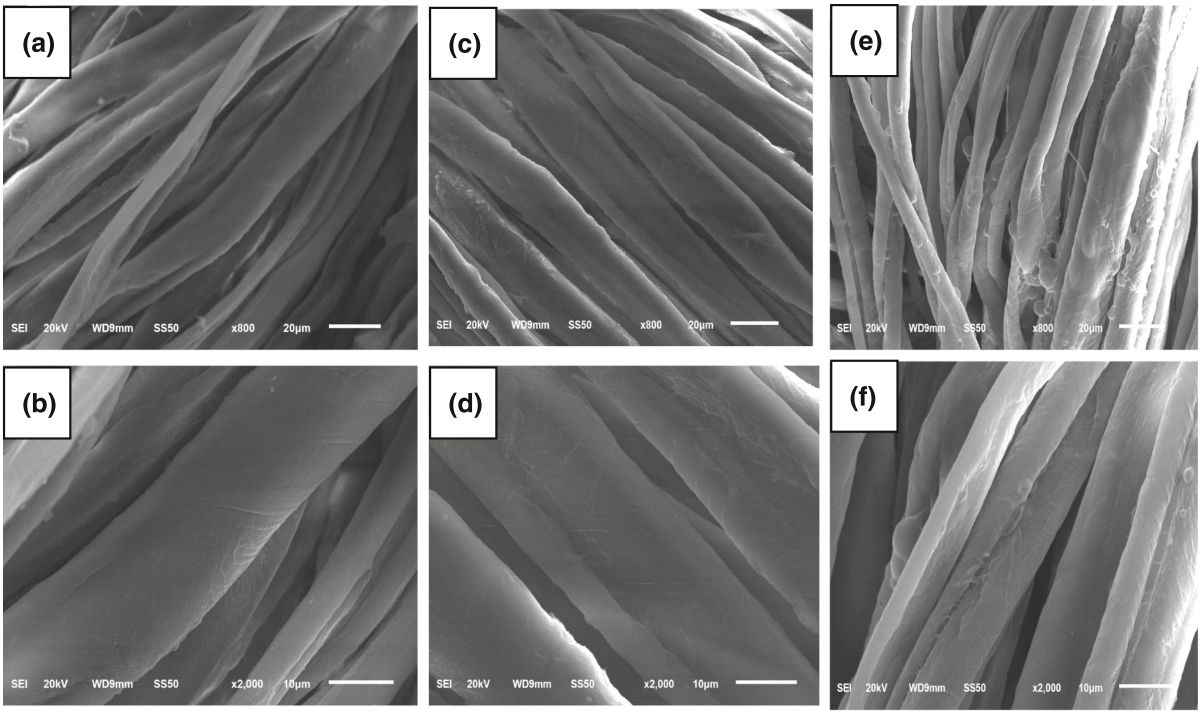


Fig. 4 SEM images of the original cotton fibers (**a**, **b**); treated cotton fibers (**c**, **d**); and treated cotton fibers after burning (**e**, **f**). *Scale bars* are 20.0 µm in **a**, **c**, and **e** and 10.0 µm in **b**, **d**, and **f**

XRD and stiffness of cotton fibers before and after treatment

Figure 5 shows the XRD profile of the cotton fibers before and after the finishing treatment. The diffraction peaks at 15.06°, 16.47°, and 22.88° corresponded to the (1–10), (110), and (200) planes of untreated cotton fibers (Zheng et al. 2016). The diffraction angles of the APTTP-treated fibers were nearly similar to those of the untreated cotton fibers. The intensity of diffraction peaks of the treated cotton fibers was slightly lower compared with those of the untreated sample. This result may be attributed to the slight decrease of the cellulose component in the total mass of the modified fibers as a result of the APTTP grafting process on the cotton fibers. This result suggested that the crystalline particles may be only slightly affected during the APTTP finishing process. In addition, the treated cotton fabrics still feel soft.

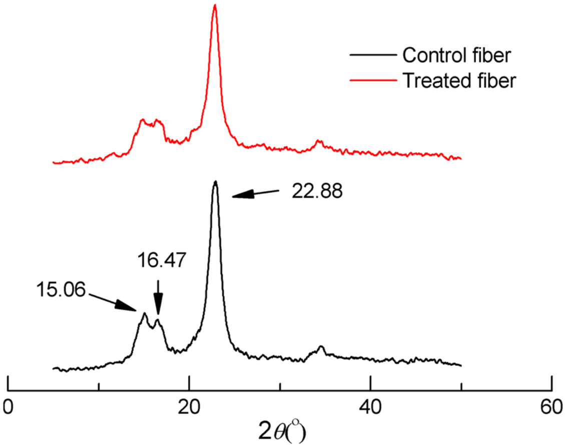


Fig. 5 XRD profiles of the cotton fibers before and after finishing

Flammability of the cotton fabrics

Cone calorimetry was used to further evaluate the flame retardancy of the APTTP-treated cotton fabric. The HRR and THR results for untreated and treated cotton fabrics are shown in Fig. 6. As seen in Fig. 6a, the untreated cotton fabric generally exhibited significantly higher HRR values than the APTTP-treated cotton fabrics. Table 3 shows some cone calorimetry data for the untreated and treated cotton fabrics. The THR and the corresponding PHRR values were

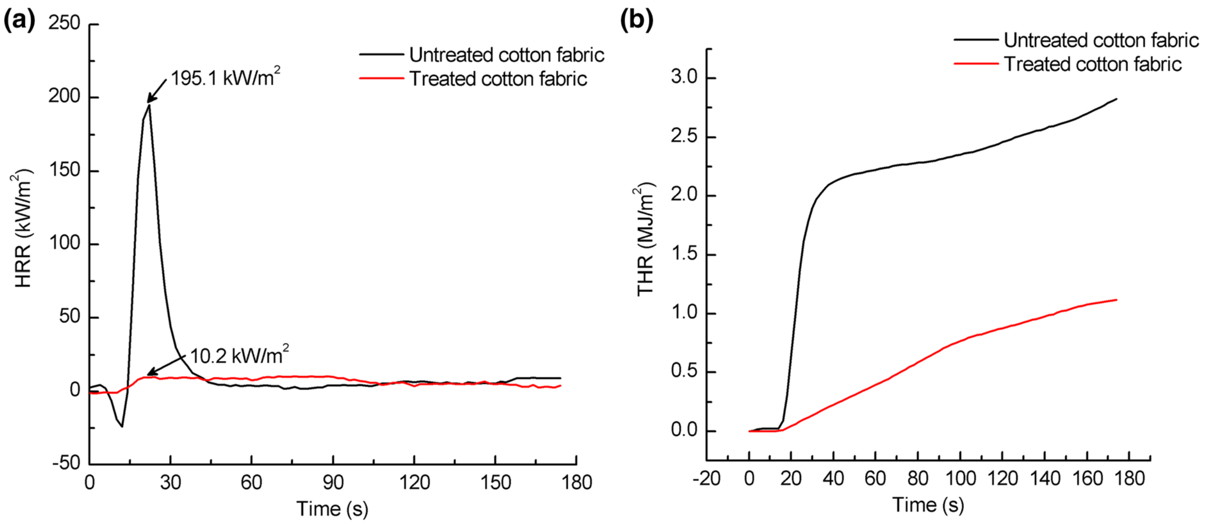


Fig. 6 HRR (**a**) and THR (**b**) curves for the untreated and APTTP-treated cotton fabrics

Table 3 Cone calorimetry data for the untreated and treated cotton fabrics

Samples	TTI (s)	TTF (s)	Residue (%)	$[CO_2]/[CO]$	TSR (m^2/m^2)
Untreated cotton	6	23	7.4	86	3.15
APTTP-treated cotton	–	–	32.0	23	24.7

significantly affected by the treatment. The treated cotton fabric showed a PHRR of 10.2 kW/m^2, which is significantly lower than that of control cotton fabric (195.1 kW/m^2). When compared with the control sample, the treated cotton fabric's PHRR and THR values greatly decreased (94.8 and 59.2%, respectively). These lower PHRR and THR values of the treated cotton fabric demonstrated that, once the flame source is removed, the treated cotton fabric self-extinguishes more easily as compared to the untreated cotton fabric. Because of the lower heat release from the burning portion of the treated cotton fabric, it is harder for fire to spread from the burning portion to the unburned part adjacent to the site of flaming combustion (Yang et al. 2010; Laufer et al. 2012). As shown in Table 3, the TTI of the control cotton fabric sample was only 9 s, and it burned heavily for 23 s after ignition (TTF). The combustion behavior of the treated cotton fabric was dramatically affected. Thus, no flame was observed during the test, and therefore, TTI and TTF were not recorded. In addition, the amount of residue (32.0%) was significantly greater than that of control sample because of the formation of phosphorous acid, which favors char formation, in agreement with the TG results. The TSR of the ATTP-treated cotton fabric was greater than that of untreated cotton fabric, which is maybe due to the incomplete combustion of treated cotton fabric.

In addition, the CO_2/CO ratio is often considered an indicator to assess the combustion efficiency, with this ratio being positively correlated with the combustion efficiency. As shown in Table 3, the CO_2/CO ratio for the treated cotton fabric was 23 (versus 86 of the control sample). Thus, the CO_2/CO ratio declined by a factor of 4 for the treated cotton fabric. This result indicates that APTTP is efficient in hindering combustion to generate combustible volatile species, thereby favoring the formation of char (Grancaric et al. 2015).

TG-IR analysis of the cotton fabrics

In order to further investigate the thermal degradation mechanism and the toxicity level of APTTP-treated cotton, the degradation products of the control and APTTP-treated cotton fabrics were collected and

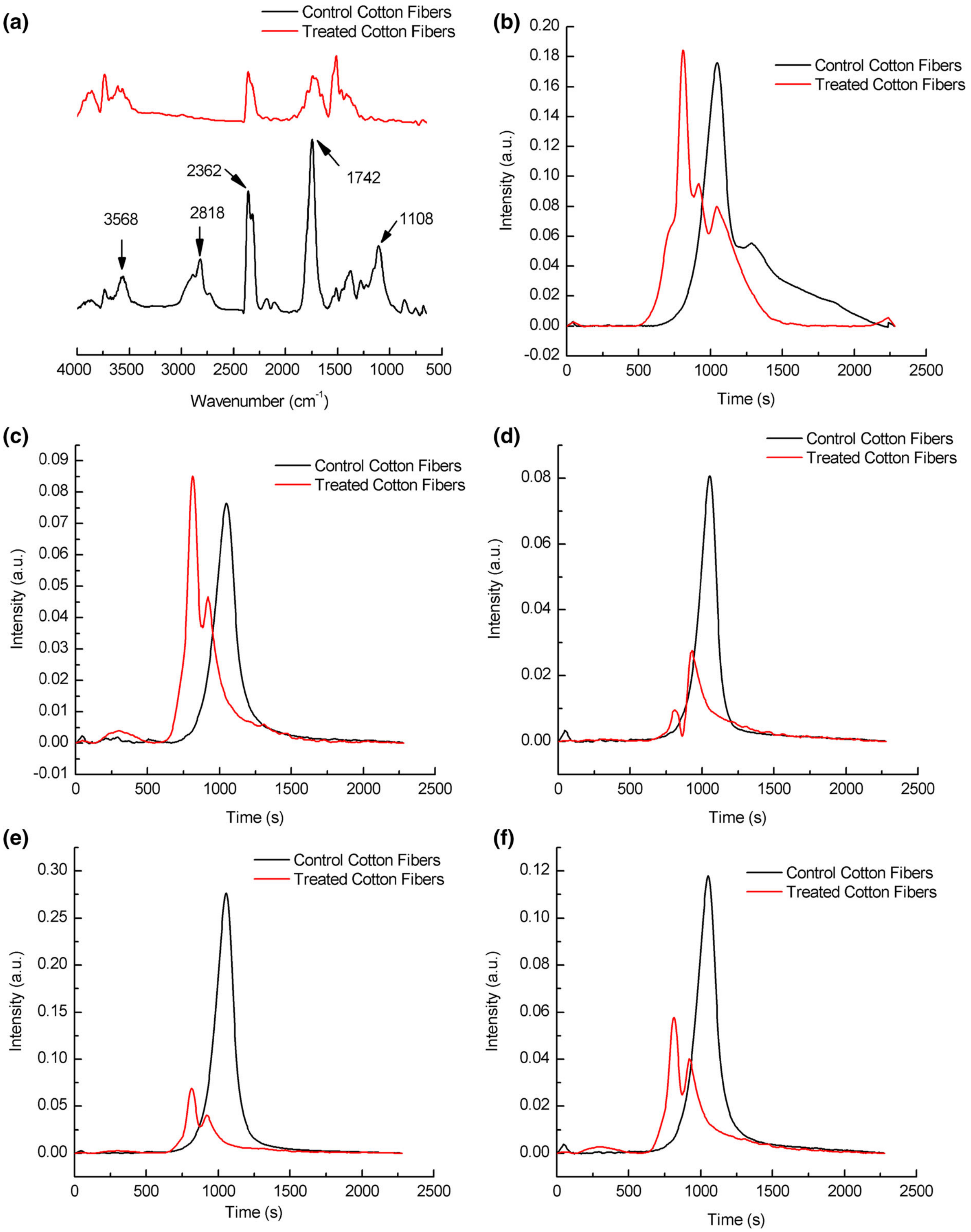


Fig. 7 TG-IR spectra of total pyrolysis products of control and treated cotton fibers **a**; Intensity of characteristic peaks for pyrolysis products **b** CO_2, **c** H_2O, **d** hydrocarbons, **e** carbonyl compounds, **f** ethers

monitored by TG-IR analysis. Figure 7a exhibits the TG-IR spectra of the total products evolved during the entire degradation processes of the control and APTTP-treated cotton fabrics in a nitrogen atmosphere. Intuitively, for the products obtained by pyrolysis, no new absorption peaks appeared for the APTTP-treated cotton fibers compared with those of control cotton fibers. The result indicates that no new toxic species was produced in this process. In contrast, it can be observed that the graft of APTTP does not alter the position of IR absorption peak significantly, implying the similar decomposition products for the control and treated cotton fibers. Furthermore, most degradation products are characterized by TG-IR. The peak at 3568 cm^{-1} is ascribed to the vibration absorption of O–H group, suggesting the release of water vapor (Huang and Wang 2009). The peak at 2818 cm^{-1} is attributed to the vibration absorption of C–H bond derived from hydrocarbons (Dong et al. 2012). The sharp peak at 2362 cm^{-1} is due to the absorbance of CO_2 (Gaan et al. 2009). The intense peak at 1742 cm^{-1} is due to the vibration absorption of C=O derived from carbonyl compounds (Chen et al. 2013), and the absorption peak at 1108 cm^{-1} is ascribed to C–O–C bonds derived from ethers (Ghosh et al. 2011).

The absorption intensity of the selected degradation products for the control and treated cotton fabrics versus time are shown in Fig. 7b–f. As can be seen, the degradation products comprise two categories: one is inflammable species, such as H_2O and CO_2; the other is flammable species, such as hydrocarbons, carbonyl compounds, and ethers. From Fig. 7b–c, the absorption intensity of CO_2 and H_2O for the treated cotton fibers reach a maximum at a lower temperature compared with those of control cotton fibers, in agreement with the decrease of decomposition temperature for treated cotton fibers in TG analysis. In addition, the maximum absorption intensities of flammable products for control cotton fibers is much higher than those of treated cotton fabric in Fig. 7d–f. The lower amounts of hydrocarbons, carbonyl compounds and ethers of APTTP-treated cotton indicates less fuel required to supply a continuous flame (Wang et al. 2015). It was supposed that APTTP favors dehydration to form char instead of flammable species, which prevent heat and fuel from the flame.

Conclusion

An efficient and environmentally friendly FR (APTTP) having reactive $-P{=}O(O^{-}{-}NH_4^{+})_2$ groups was successfully synthesized. The cotton fabric treated with 110 g/L of APTTP could be used as a semi-durable FR fabric, while the cotton fabric treated with 140 g/L of APTTP could be employed as a durable FR fabric. The flame on the treated cotton fabric extinguished once the fire source was removed, whereas the control cotton was consumed completely. TG results demonstrated that the decomposition temperature of the treated cotton fibers decreased by approximately 100 °C and the remaining residues significantly increased as compared with those of the control fibers. SEM images revealed that the APTTP-treated cotton fibers had nearly the same morphology as the original cotton fibers, while the XRD results indicated that the APTTP finishing process may have slightly affected the crystalline particles. The remarkable decrease in PHRR and THR of the treated cotton fabric demonstrated that APTTP is efficient in hindering fire spreading by favoring the formation of char. In addition, TG-IR results show the flame retardant APTTP decreased absorption intensity of flammable species and its flame retardancy mechanism occurred by condensation phase. The cotton fabric treated with APTTT exhibited high flame retardancy and durability characteristics.

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