

Highly flame-retarding cotton fabrics with a novel phosphorus/nitrogen intumescent flame retardant

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Abstract—A novel phosphorus/nitrogen intumescent flame retardant, namely 6-chloro-4-(diethylamino phosphorate phosphoryl chloride)-2-(sodium 4-aminobenzenesulfonate)-1,3,5-triazine (APPCABT), has been synthesized and characterized by elemental analysis, FT-IR, ¹H-NMR and ³¹P{H}-NMR spectroscopies. To investigate the flame-retarding properties of the treated cotton fabrics, APPCABT was applied to the chemical treatment of the cotton fabrics surface. The flame-retarding performance of the treated samples with APPCABT was evaluated by limiting oxygen index (LOI). The thermal degradation behavior of the treated samples was studied using thermogravimetric analysis (TGA). The surface morphology of the treated samples was observed by scanning electron microscopy (SEM). These results show that APPCABT is both an intumescent flame retardant with high efficiency and an excellent char-forming agent for the flame-retarding treatment of cotton fabrics.

Keywords: Phosphorus/Nitrogen, Intumescent Flame Retardant, Triazine, Cotton Fabrics, Flame-retarding Property

INTRODUCTION

Cotton fabrics (CFs) have been widely used in both civilian and military fields due to their excellent properties [1,2]. However, CFs are easily flammable materials, whose limiting oxygen index is about 18% [3].

To decrease the combustibility of CFs, most researchers have focused on the development of the flame-retarding treatment of CFs. Phosphorous-containing compounds are good halogen-free flame retardant for CFs, which have been used to substitute for the halogenated ones [4-7]. As compared to the phosphorus-containing compounds, the phosphorus-nitrogen-containing compounds have been currently considered the most ideal halogen-free flame retardants and defined as a type of novel intumescent flame retardant, which are broadly applied for the flame-retarding treatment for a large number of easily flammable materials such as cotton fabrics, polyurethane foam, and epoxy resin, etc [8-10]. This is because (i) the phosphorus-based compounds can effectively inhibit the flammability of CFs by promoting the phosphorylation and enhancing the formation of the protective char layer during combustion [11,12], and the phosphorylation further prevents the pyrolytic process and the formation of the toxic gas during flaming [13]; (ii) a constant content of the phosphorus atom is combined with the additional nitrogen atom, resulting in the generation of the phosphorus-nitrogen synergism [14]; (iii) nitrogen in an intumescent system is usually used as gas source, which may strongly promote the cross-linking with carbon and produce the incombustible gases during decomposition [15]; furthermore, the gases produced above can dilute the concentration of the flammable gases and form the foamed-char layers,

which serve as the superiorly protective barriers against flaming and heating [16,17]. In addition, the triazine compounds have been well known as a flame-retarding material and a good charring agent owing to the presence of the thermostable triazine ring and the tertiary nitrogen atom [18,19].

As a continuation of our study on the phosphorus/nitrogen intumescent flame retardants [20], we recently investigated the synthesis, characterization, and flame-retarding property of a novel phosphorus/nitrogen intumescent flame retardant for cotton fabrics. In this work, a new flame retardant [namely, 6-chloro-4-(diethylamino phosphorate phosphoryl chloride)-2-(sodium 4-aminobenzenesulfonate)-1,3,5-triazine (APPCABT)], has been prepared and structurally characterized by elemental analysis, FT-IR, ¹H-NMR, as well as ³¹P{H}-NMR spectra. The flame retardancy, the thermal degradation behavior, and the surface morphology of the treated CFs with APPCABT were studied by limiting oxygen index (LOI), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). These results show that APPCABT is both an intumescent flame retardant with high efficiency and an excellent char-forming agent for the flame-retarding treatment of CFs.

EXPERIMENTAL

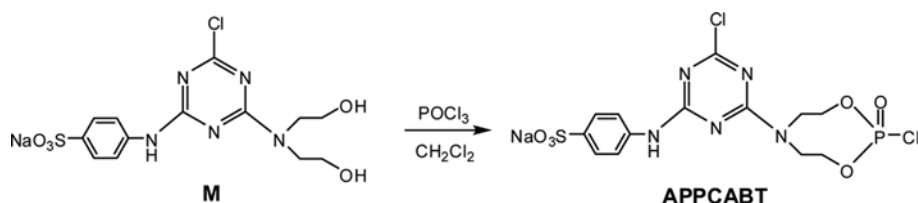
1. Materials and Measurements

Cyanuric chloride and phosphorus oxychloride were purchased from Alfa Chemical Co, Ltd (Zhengzhou, China). Triethylamine, diethanol amine, sodium carbonate, and sodium sulfanolate were obtained from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). All the chemicals were used without further purification. The intermediate M [namely, (6-chloro-4-(dihydroxyethylamino)-2-(sodium 4-aminobenzenesulfonate)-1,3,5-triazine)] was prepared according to the reported literature [21]. 100% Cotton fabrics with the density of 184 g/m² were supplied by Santai Fire Resistant Products Co.,

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Scheme 1. Preparation of the target product APPCABT.

Ltd. (Jinan, China). Melting points were uncorrected and determined on a YRT-3 apparatus (Nanjing temperature Connaught Equipment Co., Ltd., China). FT-IR spectra were recorded from KBr pellets in the range 4,000–400 cm^{-1} on a Nicolet 670 IR spectrometer (Thermo Corp., Madison, WI, USA). ^1H -NMR and $^{31}\text{P}\{\text{H}\}$ -NMR spectra were conducted using $\text{DMSO}-d_6$ as the solvent at room temperature on a Bruker Avance 400 MHz spectrometer (Bruker Biospin International AG, Switzerland). Elemental analyses were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer International AG, USA).

2. Synthesis of APPCABT

To the dichloromethane solution of the intermediate M (0.03 mol) was slowly added the phosphorus oxychloride (0.03 mol) at the room temperature. After the reaction temperature added to 35 $^{\circ}\text{C}$, triethylamine was dropwise added to the reaction mixture to keep the pH at 8–9. The reaction process was monitored by TLC on silica gel eluting methanol : toluene = 4 : 3 (v : v). After the reaction was completed, the white solid was filtered, washed with dichloromethane two times, and dried at room temperature under vacuum to give the white powder. The yield was 77.2%. M.p. >250 $^{\circ}\text{C}$; ^1H -NMR (400 MHz, $\text{DMSO}-d_6$, TMS): δ/ppm 10.10 (s, 1H, NH), 7.65–7.53 (m, 4H, C_6H_4), 4.03–3.56 (m, 8H, $\text{NCH}_2\text{CH}_2\text{O}$); $^{31}\text{P}\{\text{H}\}$ -NMR (161.9 MHz, $\text{DMSO}-d_6$, 85% H_3PO_4): δ/ppm = –1.18 (s); FT-IR (KBr): ν/cm^{-1} = 3417 (N–H), 3,109, 3,065, 2,966, and 2,939 (C–H), 1,580 and 1,415 ($\text{C}=\text{N}$), 1,622, 1,535, and 1,502 ($\text{C}=\text{C}$), 1,188 and 1,039 (S=O), 1,300 ($\text{P}=\text{O}$), 1,128 and 1,006 (P–O–C), as well as 795 and 567 (P–Cl); Anal. Calcd. (%) for $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}_5\text{NaO}_6\text{PS}$: C 31.72, H 2.66, N 14.23; found (%): C 31.51, H 2.91, N 14.06.

3. Flame-retarding Study of Cotton Fabrics Treated with APPCABT

The flame-retarding properties of cotton fabrics were determined in the following. Limiting oxygen index (LOI) tests were measured on a HC-2 analyzer (Jiangning Analysis Instrument Company, China) with strips of cotton fabrics (15.0 × 5.0 cm) according to GB/T5454–1997. Thermogravimetric analysis (TGA) was performed on ZCT-A thermal analyzer (Perkin-Elmer International AG, USA) in the region of 25–600 $^{\circ}\text{C}$ in air atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$, and sample weight was in the range of 5–10 mg. Scanning electron microscopy (SEM) was performed on a Hitachi X650 instrument (Hitachi Company, Japan) at room temperature, and all the samples were sputtered with platinum before SEM analysis.

4. Flame-retarding Treatment of Cotton Fabrics with APPCABT

First, CFs were washed in water with 0.5% (w/w) NaOH solution and then dried. Then, aqueous flame-retarding finishing bath was prepared by various concentrations of APPCABT at 90 $^{\circ}\text{C}$, in which the liquor ratio was 1 : 20. Sodium sulfate as a neutral salt was added to the reaction bath and the pH was adjusted using sodium carbonate. The above-mentioned process was completed for about

1.5 h. Finally, CFs was washed in the tap water and dried at 60 $^{\circ}\text{C}$ in an oven.

RESULTS AND DISCUSSION

1. Synthesis and Characterization of APPCABT

As shown in Scheme 1, the intermediate M was obtained from cyanuric chloride, $p\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, and $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ as starting materials [21], and then the target product APPCABT was successfully synthesized by reaction of M with 1.0 equiv. POCl_3 using acid-binding agent Et_3N in CH_2Cl_2 .

The molecular structure of APPCABT was determined by FT-IR, ^1H -NMR and $^{31}\text{P}\{\text{H}\}$ -NMR spectra. Compared with the FT-IR spectrum of intermediate M that gave the following absorption peaks—3,488 and 3,347 cm^{-1} ($\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$ of p -aminobenzenesulfonate and diethanolamine moieties), 3,114, 3,002, 2,930, and 2,863 cm^{-1} ($\nu_{\text{C-H}}$ of diethanolamine moiety), 1,581 and 1,428 cm^{-1} ($\nu_{\text{C=N}}$ of triazine ring), 1,627, 1,553, and 1,495 cm^{-1} ($\nu_{\text{C=C}}$ of benzene ring), 1,189 and 1,040 cm^{-1} ($\nu_{\text{S=O}}$ of sulphonate group) [21,22]—that of APPCABT presented similar characteristic absorption bands as follows: 3,417 cm^{-1} ($\nu_{\text{N-H}}$), 3,109, 3,065, 2,966, and 2,939 cm^{-1} ($\nu_{\text{C-H}}$), 1,580 and 1,415 cm^{-1} ($\nu_{\text{C=N}}$), 1,622, 1,535, and 1,502 cm^{-1} ($\nu_{\text{C=C}}$), 1,188 and 1,039 cm^{-1} ($\nu_{\text{S=O}}$) (as shown in Fig. S1 for Supporting Information). This demonstrated that the successful incorporation of triazine ring, p -aminobenzenesulfonate, and diethanolamine units into the as-obtained product APPCABT [23,24]. Note that a clearly distinct feature of the FT-IR spectra of M and APPCABT was that the absorption peaks at 3,347 cm^{-1} ($\nu_{\text{O-H}}$) disappeared, whereas the new peaks at 1,300 cm^{-1} ($\nu_{\text{P=O}}$), 1,128 and 1,006 cm^{-1} (P–O–C), as well as 795 and 567 cm^{-1} ($\nu_{\text{P-Cl}}$) appeared [25], further indicating that the target product APPCABT was successfully synthesized.

Fig. 1 shows the ^1H -NMR (a) and $^{31}\text{P}\{\text{H}\}$ -NMR (b) spectra of APPCABT, respectively. As shown (a), the ^1H -NMR spectrum of APPCABT gave the proton signals with the following peaks: 10.10 ppm (1H of NH), 7.65–7.53 ppm (4H of C_6H_4), 4.03–3.56 ppm (8H of $\text{NCH}_2\text{CH}_2\text{O}$). The appearance of the characteristic proton signals of amino group, benzene ring, and diethylene moiety in APPCABT indicated the successful attachment of p -aminobenzenesulfonate and diethanolamine with cyanuric chloride to afford the corresponding product. Especially, in the ^1H -NMR spectrum of APPCABT, a key characteristic was that the hydroxyl proton signals in the range from 4.87 to 4.83 ppm in that of M (where the signals labeled as “f” was assigned to the H atoms of the hydroxyl group according to the H–D exchange by addition of D_2O as displayed in Fig. S2 for Supporting Information) absolutely disappeared. This demonstrated that the hydroxyl H atoms of the $\text{N}(\text{CH}_2\text{OH})_2$ group in M reacted totally with the Cl atoms of $\text{P}(\text{O})\text{Cl}_3$ to obtain the target product APPCABT. In addition, the $^{31}\text{P}\{\text{H}\}$ -NMR spectrum of APP-

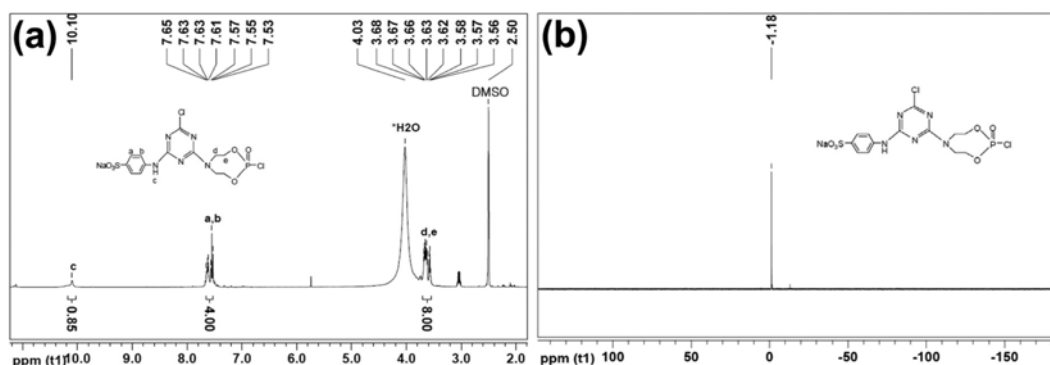


Fig. 1. ^1H -NMR (a) and ^{31}P -NMR (b) spectra of APPCABT in $\text{DMSO}-d_6$, respectively.

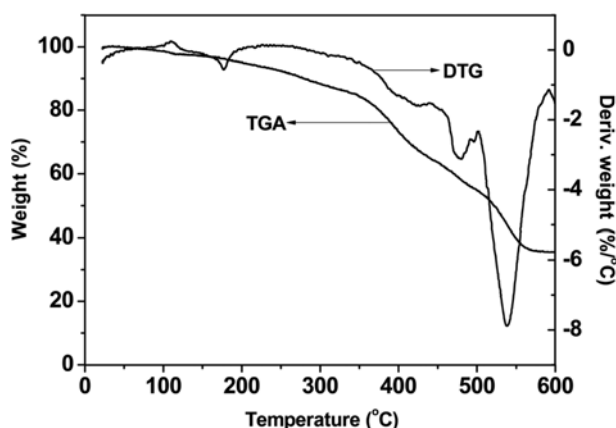


Fig. 2. TGA and DTG curves of APPCABT in air.

CABT exhibited a single phosphorus signal at -1.18 ppm as displayed in Fig. 1(b), further indicating that the target product APPCABT was successfully prepared.

All of the above facts led us to conclude that the target product APPCABT had been surely synthesized.

2. Thermal Stability of APPCABT

Fig. 2 shows TGA and DTG curves of APPCABT in air while Table 1 gives the corresponding data. From Fig. 2 and Table 1, it is evident that APPCABT showed good thermal stability. Its initial decomposition temperature was 201.7°C . From its TGA and DTG curves, it mainly underwent two-step thermal degradation processes, where the first step was 478.0°C and the second one was 538.0°C , which may be attributed to the scission of the phosphate ester bonds and the formation of the char layer [24]. According to the char residue data in Table 1 and TGA curves in Fig. 1, the char residue of APPCABT was 37.0% at 600.0°C . These results indicated that APPCABT had excellent thermal stability and high char residues, which

Table 1. TGA and DTG data of APPCABT in air

Sample	T_{onset} ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)		Residue at 600.0°C (%)
		Stage 1	Stage 2	
APPCABT	201.7	478.0	538.0	37.0

T_{onset} : Initial decomposition temperature (based on 5% weight loss)

T_{max} : Maximum weight-loss temperature

may be attributed to the presence of the benzene ring and the triazine ring containing tertiary amino groups [22]. Furthermore, the TGA and DTG data of APPCABT relative to those of intermediate M [21] indicated that APPCABT had higher thermal stability and charring stability than M, which may be attributed to the certain synergistic interaction between phosphorus and nitrogen atoms in its molecular structure.

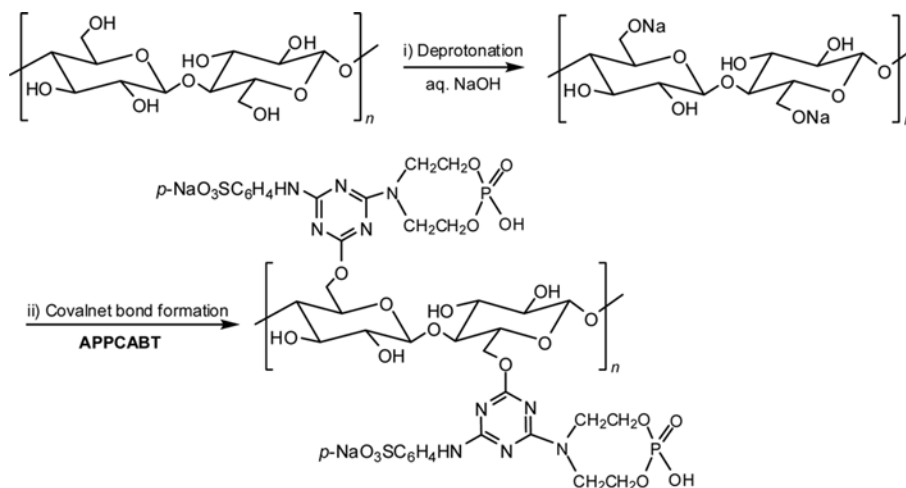
3. Flame Retardant Performance of Cotton Fabrics by LOI Test

From Table 2, pure CFs were a type of easily flammable polymeric material with the LOI value of only 17.5%. However, the flame retardancy should be significantly improved when the covalent bond is coupled between the C6 position oxygen of the cellulose unit in CFs and the C6 position carbon of the triazine ring in the APPCABT, probably resulting from the chemical finishing of CFs surface with APPCABT as shown in Scheme 2 [26]. To prove the proposed chemical treatment of CFs surface with APPCABT, the FT-IR spectrum of the treated CFs with APPCABT was studied and it gave the following characteristic absorption peaks (as displayed in Fig. S3 for Supporting Information): 3413 cm^{-1} ($\nu_{\text{N-H}}$ and $\nu_{\text{O-H}}$), 1573 and 1423 cm^{-1} ($\nu_{\text{C=N}}$ of triazine ring), 2963 and 2907 cm^{-1} ($\nu_{\text{C-H}}$ of diethanolamine moiety), 1615 and 1528 cm^{-1} ($\nu_{\text{C=C}}$ of benzene ring), 1164 and 1057 cm^{-1} ($\nu_{\text{S=O}}$ of sulphonate group), 1311 cm^{-1} ($\nu_{\text{P=O}}$), 1119 and 905 cm^{-1} (P-O-C), and 617 cm^{-1} ($\nu_{\text{P-OH}}$). These demonstrated that CFs surface should be treated with APPCABT through the P-O-C covalent bonds (Scheme 2).

From Table 2, the LOI value of the treated CFs with APPCABT was from 17.5% to 28.2% as the amount of APPCABT coated onto CFs was increased in the range of 0-25%. Note that the rise of the corresponding LOI value was low when the amount was increased from 10% to 25%. Considering the cost of flame retardant and the pollution of the environment, we therefore selected 10% add-on as the optimal amount of APPCABT coated on CFs. It is worth noting that the LOI value of the treated CFs with 10 wt% add-on of intermediate M reached 26.1% [21], whereas the one of the treated CFs with only 10 wt% add-on of APPCABT could reach 27.9%. This demonstrated that APPCABT had better flame retardancy than M

Table 2. LOI data of the untreated and treated CFs with APPCABT at different add-on

Add-on (wt%) of APPCABT	0	5	10	15	25
LOI (vol%)	17.5	25.2	27.9	28.1	28.3



Scheme 2. The proposed chemical treatment of CFs surface with APPCABT.

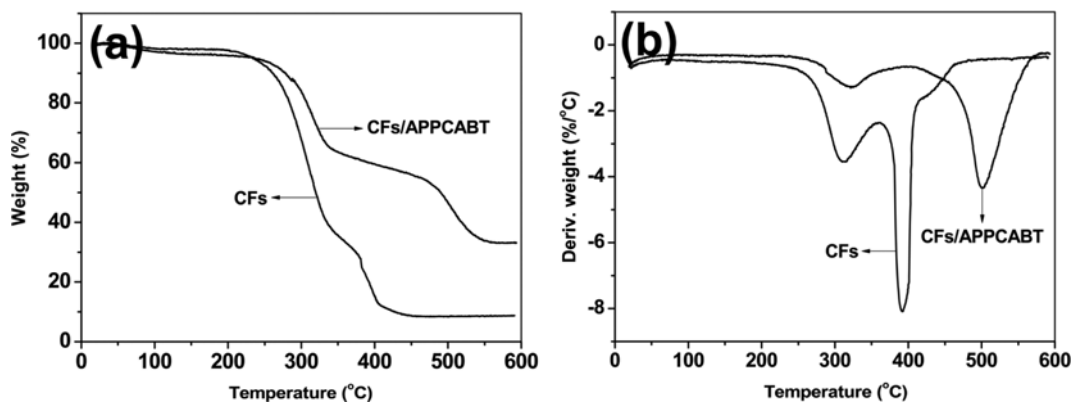


Fig. 3. TGA (a) and DTG (b) curves of the untreated and treated CFs with APPCABT, respectively.

for the treated CFs, possibly due to the presence of the phosphorus-nitrogen synergistic effect in flaming system of the treated CFs with APPCABT.

4. Thermal Decomposition behavior of Cotton Fabrics by TGA Analysis

Fig. 3 displays TGA (a) and DTG (b) curves of the untreated and treated CFs with 10 wt% add-on of APPCABT in air, whereas Table 3 lists the corresponding data. From Fig. 3 and Table 3, the initial decomposition temperatures of the untreated and treated CFs with APPCABT were 225.1 °C and 235.4 °C, respectively. The TGA and DTG curves and the char residue data clearly indicate that the untreated and treated CFs underwent two-step thermal degradation

stages. For the pure CFs, it had a minor thermal weight-loss stage at 310.8 °C and a major one at 391.8 °C, which had the merely char residues of 8.8% at 600.0 °C. For the treated CFs with APPCABT, it had a minor thermal weight-loss stage at 323.3 °C and a major one at 500.7 °C, which had the char residues of 33.1% at 600 °C. The char forming ability of the treated CFs with APPCABT was remarkably improved relative to that of the treated CFs with intermediate M with the char residues of 23.0% at 600 °C [21]. These results indicated that APPCABT not only changed the thermal degradation behavior of CFs but also promoted the char layer formation of CFs surface. Moreover, the treated CFs with APPCABT showed the higher char residues than those with intermediate M [21], indicating that the phosphorus-nitrogen synergistic effect in APPCABT has significant contribution to the char-forming and flame-retarding properties of CFs.

5. Surface Morphology of Cotton Fabrics after LOI Test by SEM

Fig. 4 shows the surface morphologies of the untreated and treated CFs with APPCABT before and after the LOI tests. For pure CFs, the surface morphology before flaming was intact and smooth (Fig. 4(a)), whereas the char layer after burning was completely destroyed and very loose (Fig. 4(c)). For the treated CFs with APPCABT, while the surface morphology before flaming was almost intact and rough

Table 3. TGA and DTG data of the untreated and treated CFs with 10 wt% APPCABT

Samples	T_{onset} (°C)	T_{max} (°C)		Residue at 600.0 °C (%)
		Stage 1	Stage 2	
CFs	225.1	310.8	391.8	8.8
CFs/APPCABT	235.4	323.3	500.7	33.1

T_{onset} : Initial decomposition temperature (based on 5% weight loss)

T_{max} : Maximum weight-loss temperature

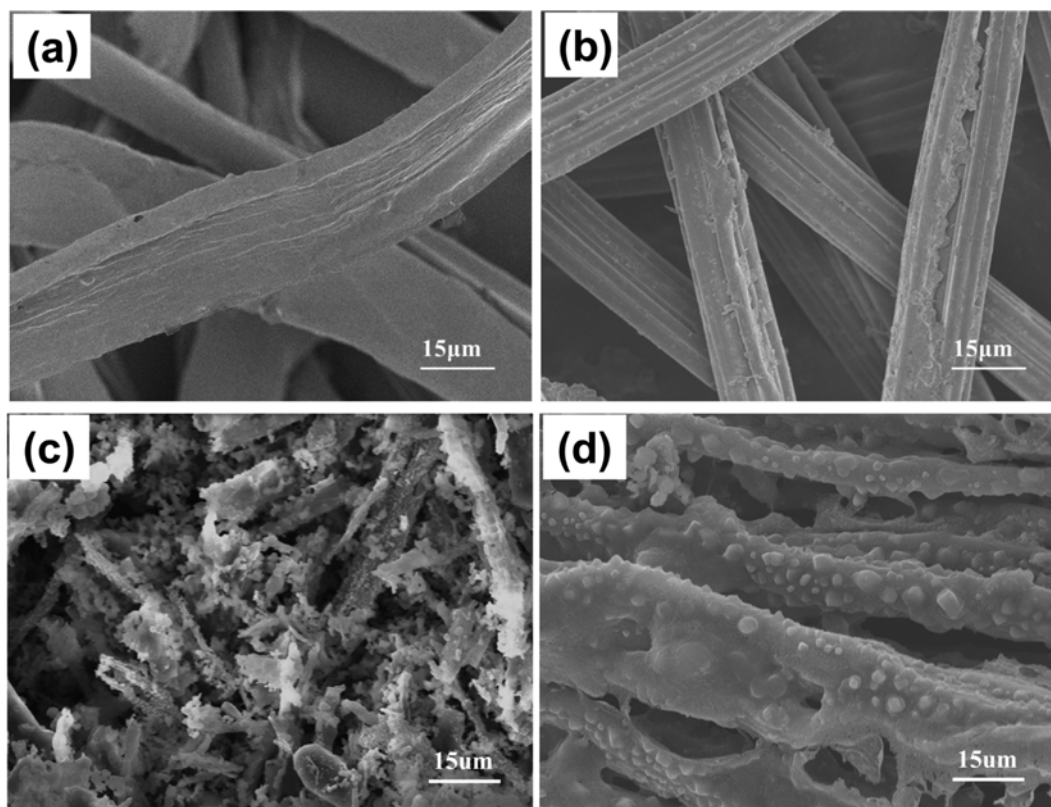


Fig. 4. SEM images of the untreated CFs (a) and (c), and the treated CFs with APPCABT (b) and (d) before and after LOI tests, respectively.

(Fig. 4(b)), the char layer after flaming was still compact and continuous, and especially showed an intumescent and cross-linked microstructure (Fig. 4(d)), which could effectively prevent the heat and oxygen transmission during combustion [27]. These indicated that the high-quality char layer formed during combustion of the treated CFs with APPCABT played an important role in protecting the inside of CFs and in blocking the propagation of the combustion reaction [28], which was in agreement with the good flame retardancy and the high char-forming property of the treated CFs with only 10 wt% add-on of APPCABT for LOI and TGA tests.

CONCLUSIONS

A novel phosphorus/nitrogen intumescent flame retardant (APPCABT) has been successfully prepared and characterized by elemental analysis, FT-IR, ^1H -NMR as well as $^{31}\text{P}\{\text{H}\}$ -NMR spectra. The influence of the phosphorus-nitrogen synergistic effect of APPCABT on the flame-retarding performance, thermal degradation behavior, and surface morphology of CFs has been investigated by LOI, TGA, and SEM in detail. The LOI tests show that APPCABT is effective in flame-retarding finishing of CFs, in which the LOI values of the treated CFs with only 10 wt% APPCABT can reach 27.9%. The TGA results indicate that the treated CFs with 10 wt% APPCABT have not only high initial temperatures but also good char-forming abilities during the thermal degradation process, where the corresponding char residues reach 33.1% at 600.0 °C. The SEM observations indicate that the surface morphology of the treated CFs with 10 wt% APPCABT after flaming is compact and

continuous, and is further intumescent and cross-linked. Therefore, the target product APPCABT, which is regarded as a novel phosphorus/nitrogen intumescent flame retardant, has high flame retardancy and good char-forming ability for cotton fabrics.

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Supporting Information

Highly flame-retarding cotton fabrics with a novel phosphorus/nitrogen intumescent flame retardant

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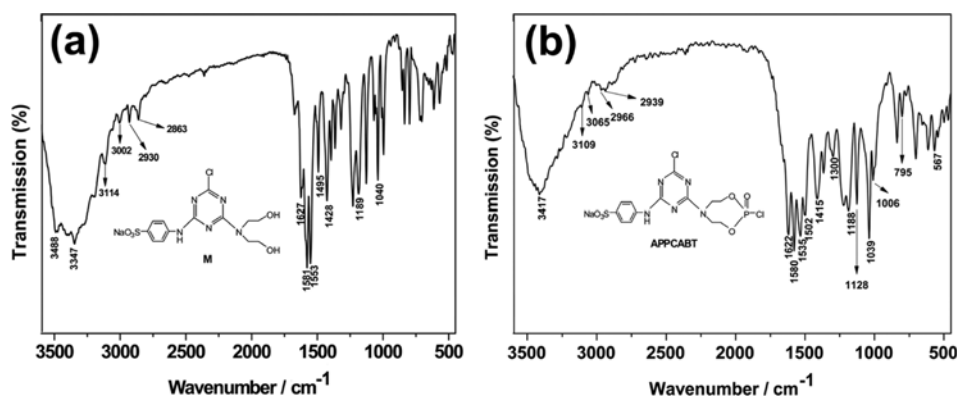


Fig. S1. The FT-IR spectra of intermediate M (a) and APPCABT (b) in KBr disk, respectively.

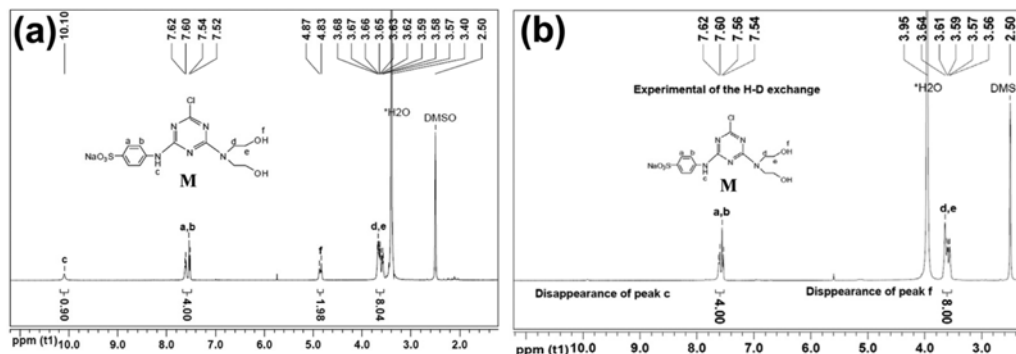


Fig. S2. The ¹H-NMR spectra of intermediate M in DMSO-*d*₆ (a) and in DMSO-*d*₆ + D₂O (b), respectively.

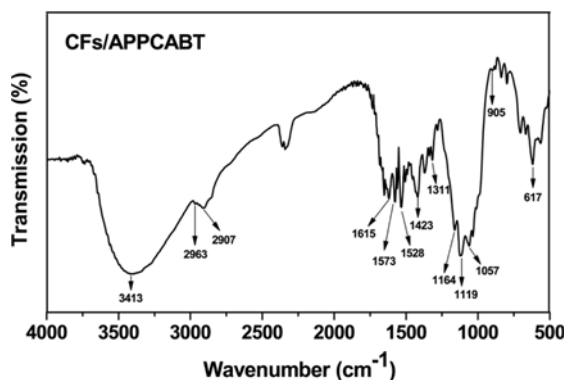


Fig. S3. The FT-IR spectrum of CFs surface treated with APPCABT.