

Combustion behaviors of cotton fabrics treated by a novel nitrogen- and phosphorus-containing polysiloxane flame retardant

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Abstract A novel flame-retardant agent, nitrogen- and phosphorus-containing polysiloxane [(IB-co-N-MDPA)PDMS] was synthesized, and it was employed on cotton fabrics. Cone calorimeter testing showed that the treated cotton fabric with (IB-co-N-MDPA)PDMS became less flammable with longer time to ignition and lower value of HRR, THR, EHC and mass loss. Thermogravimetric analysis demonstrated that (IB-co-N-MDPA)PDMS improved the thermal and thermo-oxidative stability of cotton fabric with fewer flammable volatiles, and more char is produced during combustion. Scanning electron microscopy showed that the surface of treated cotton fabric after combustion was covered by a compact char layer which indicated that (IB-co-N-MDPA)PDMS favored the formation of char as evidenced by the FTIR of residues. Furthermore, EDS analysis results demonstrated that the concurrent presence of Si and P in flame retardant effectively enhance the flame retardancy of cotton fabric with the remarkable amount of Si and P elements that were still present on the surface of fibers after combustion.

Keywords Flame retardancy · Cotton fabric · Cone calorimeter · Thermal analysis

Introduction

Cotton, as a kind of natural resource, has been the most versatile material for clothing, house furnishing, and many industrial and military goods, due to its superior water absorbance and breathability [1, 2]. However, one foremost defect of cotton is its high flammability which can lead to fire disaster and bring damage to lives and properties of human beings [3, 4]. Therefore, conferring a flame-retardant behavior to cotton fabrics has been an essential and challenging issue in textile industry and attracting more attention than ever before due to strict safety requirements [5–7].

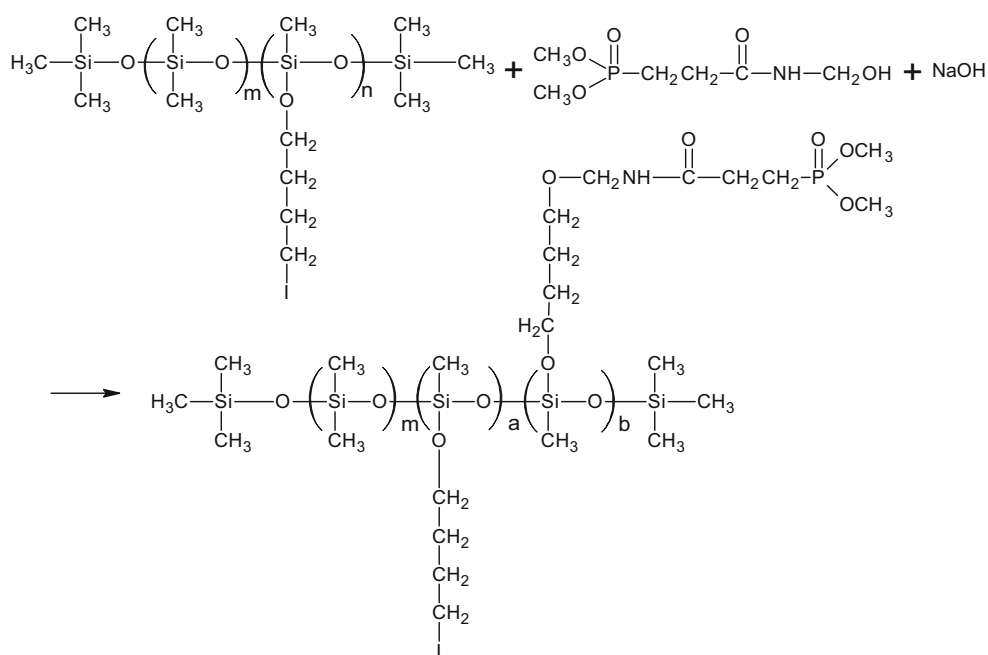
Application of flame retardant is the most commonly used method to inhibit the flammability of cotton fabrics. Halogenated compounds containing chlorine and bromine have been developed as effective flame retardants for cotton fabrics attributed to their excellent inhibiting effect. Nevertheless, many countries and regions all over the world have restricted or completely phased out the employment of halogen-based flame retardants because they generate toxic gases [8, 9]. Consequently, researches for alternatives have been motivated, and new environmentally acceptable alternatives have been synthesized both at academic and industrial levels [10–13].

Organophosphorus compounds, especially the major industrial compounds known as Proban and Pyrovatex, have been established as excellent flame retardants because they have positive effects on flame-retardant properties of cotton fabrics [14]. These flame retardants can phosphorylate C(6) of the glucose monomer, inhibiting the formation of levoglucosan and promoting the dehydration process, which accelerate the formation of an inorganic carbonaceous fire residue [15]. The residual char acts as a protection layer blocking the transportation of heat. Furthermore, the phosphorous–nitrogen systems have attracted

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Scheme 1 Preparation of (IB-*co-N*-MDPA)PDMS

much attention due to synergistic effect of P–N rendering better flame retardancy to cotton fabrics [16].

Recently, silicone-based compounds have been proposed as promising new flame retardants for cotton fabrics. These flame retardants possess good thermal stability, low fire hazard, and biological compatibility [17, 18]. It is elucidated that these compounds produce siliceous char layer which delays the spread of fire and causes a remarkably larger reduction in materials' flammability during combustion [19, 20], especially coupled with other flame-retardant elements [18, 21–24]. Therefore, silicone-based compounds have great potential as flame inhibitors for cotton fabrics, and it is of interest to develop eco-friendly new flame retardants containing Si, P, and N elements [25, 26].

In this study, a novel flame-retardant agent, nitrogen- and phosphorus-containing polysiloxane [(IB-*co-N*-MDPA)PDMS] was prepared, and it could be combined to cotton fabrics with covalent bond due to the activity group. The combustion properties of treated cotton fabric were evaluated by cone calorimeter. The thermal decomposition behavior of cotton fabrics was investigated by thermogravimetric (TG) analysis. In addition, morphologies and structure of the residues were investigated by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR). Furthermore, the composition of elementals conferring flame retardancy to cotton fabrics was analyzed using energy-dispersive X-ray spectrometer (EDS).

Experimental

Materials

Scoured and bleached 100 % plain woven cotton fabric (14.75tex × 14.75tex, 122 g m⁻²) was supplied by Weifang Qirong Textiles Co., Ltd.

Poly(4-iodobutoxy) methylsiloxane was self-made in our laboratory. N-methyl-3-(dimethoxy dibenzoyloxyphosphoryl) acrylamide was supplied by Yixing Xingfeng Chemical Factory (China). Sodium hydroxide was purchased from Tianjin Bodi Chemical Co., Ltd (China).

Preparation of (IB-*co-N*-MDPA)PDMS

(IB-*co-N*-MDPA)PDMS was synthesized using N-methyl-3-(dimethoxy dibenzoyloxyphosphoryl) acrylamide, sodium hydroxide, and poly(4-iodobutoxy) methylsiloxane as raw materials. The reaction equation is shown in Scheme 1. The structure of (IB-*co-N*-MDPA)PDMS was characterized by the FTIR and ¹H NMR.

FTIR (KBr) (cm⁻¹): 1050 (vs. O = P–OCH₃), 1660 (vs. C = O), 3340 (vs. Si–O, N–H).

¹H-NMR: δ = 0.09–0.14 (OSiCH₃), δ = 4.69 (OCH₂), δ = 3.7–3.8 (CH₂I), δ = 2.5–2.6 (O–CH₂CH₂), δ = 2.2–2.4 (CH₂CH₂I), δ = 7.15–7.30 (–NH).

Table 1 Effect of (IB-co-N-MDPA)PDMS on flame retardancy of cotton fabric

Add-on/%	LOI/%	Char length/cm	After-flame time/s	After-glow time/s
0	18.0	–	–	–
22.1	28.2	6.1	4.0	0

Preparation of treated cotton fabrics

The cotton fabrics were impregnated in finishing bath containing (IB-co-N-MDPA)PDMS and urea at room temperature for 30 min, and then passed through a laboratory-scale padder with two dips and two nips, to wet pick up 100 %. Then the samples were subjected to several times home laundering and drying cycle. After that, the samples were dried at 100 °C for 3 min and cured at 160 °C for 4 min.

The amount (mass% owf) of flame retardant added on cotton fabric was calculated as follows:

$$\text{add-on}\% = \frac{W_f - W_b}{W_b} \times 100\% \quad (1)$$

W_b and W_f represent the mass of cotton fabrics before and after flame-retardant treatment, respectively.

Characterization

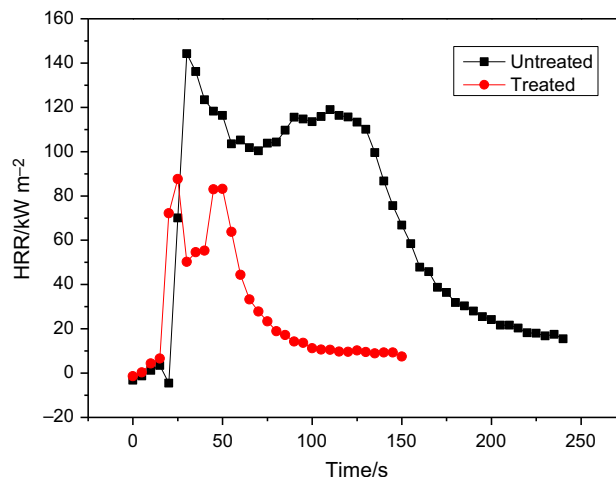
The structure of (IB-co-N-MDPA)PDMS was verified by ^1H NMR spectrum (JEOL LA500, Japan). FTIR analysis was carried out on a Nicolet 5700 FTIR apparatus (Thermo Nicolet Corporation, USA) using the KBr pellet technique.

Limited oxygen index (LOI) tests were carried out on a digital display oxygen index instrument LFY-606 according to GB/T 5454-2009. The vertical burning test was carried out on CZF-3 instrument according to GB/T 5455-2009.

A FTT0007 cone calorimeter (Fire Testing Technology Ltd.) was used to investigate the combustion of cotton fabrics following ISO 5660. The experiments were conducted under a heat flux of 30 kW m^{-2} . The instrument allows for the determination of time to ignition (TTI, s), total heat release (THR, kW m^{-2}), heat release rate (HRR, kW m^{-2}), the relative peak (PHRR, kW m^{-2}), effective heat combustion (EHC, MJ kg^{-1}), and CO and CO_2 yield (kg kg^{-1}). The parameters calculated were fire performance index (FPI, $\text{s m}^2 \text{ kW}^{-1}$) and CO_2/CO ratio.

TG was performed using TGA851 thermal analyzer (Mettler-Toledo International Inc.) at a heating rate of 10 °C min^{-1} with a continuous nitrogen and air flow rate of 20 mL min^{-1} from 25 to 700 °C.

The surface morphology of the residue of the treated cotton fabrics after combustion was investigated by a JSM-6010LA SEM instrument (Japan Electron Optics Laboratory Co., Ltd). A sputter coater was used to pre-coat

**Fig. 1** HRR curves of samples

conductive gold onto the surface before observing the microstructure at 10-kV beam voltage.

EDS analysis was performed by a JSM-6700F instrument (Japan Electron Optics Laboratory Co., Ltd) and a OXFORD-INCA X-ray spectrometer EDS (Oxford instruments).

Results and discussion

Flame-retardant performance

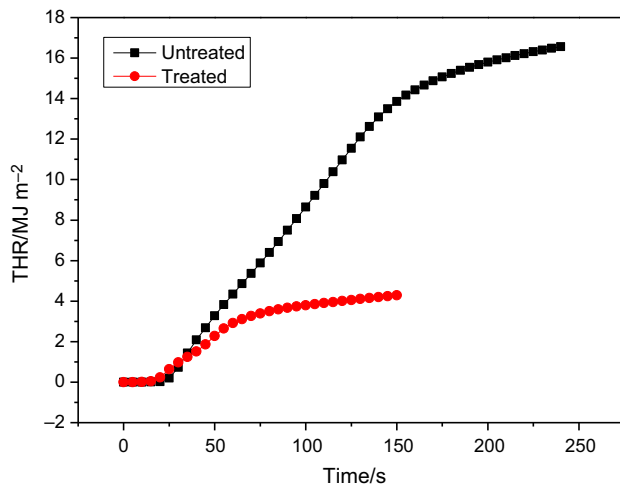
The flammable properties of cotton fabrics were investigated, and the results are presented in Table 1. It can be seen that (IB-co-N-MDPA)PDMS increased the LOI value of cotton fabric from 18.0 to 28.2 %. The vertical burning test results demonstrated that the untreated cotton fabric was completely destroyed, while the treated cotton fabric obtained shorter char length (6.1 cm), shorter after-glow time (4.0 s) and no after-flame. It can be concluded that (IB-co-N-MDPA)PDMS enhanced the flame retardancy of cotton fabric.

Combustion behaviors

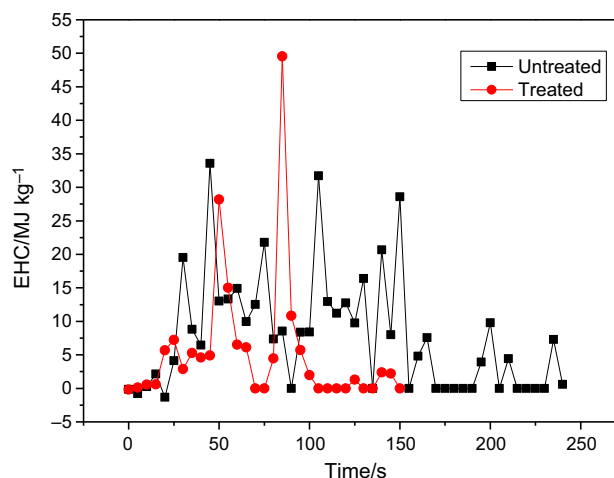
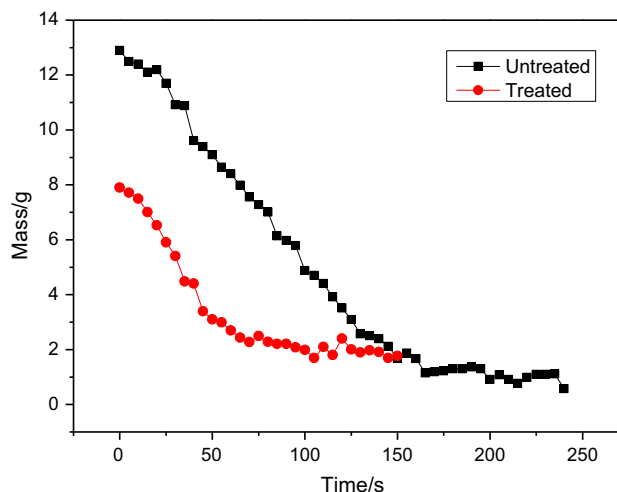
To investigate the combustion properties of treated cotton fabrics with (IB-co-N-MDPA)PDMS, cone calorimeter testing was conducted. Figure 1 shows the heat release rate

Table 2 Combustion data by cone calorimeter

Sample	TTI/s	PHRR/kW m ⁻²	FPI/s m ² kW ⁻¹	Average EHC/MJ kg ⁻¹	CO/kg kg ⁻¹	CO ₂ /kg kg ⁻¹	CO ₂ /CO
Untreated	2	144.23	0.01	12.57	0.10	2.33	23.30
Treated	15.6	87.63	0.18	6.60	0.10	1.53	15.30

**Fig. 2** THR curves of samples

(HRR) curves of untreated and treated cotton fabrics, and it can be seen that untreated cotton fabric is easily flammable with a peak heat release rate (PHRR) of 144.23 kW m⁻², while the flammability of treated cotton is inhibited with a lower PHRR of 87.63 kW m⁻² as collected in Table 2. TTI of treated cotton fabric is 13.6 s longer than that of untreated one (2 s) as shown in Table 2. Consequently, the FPI (ratio between TTI and PHRR) value of treated cotton fabric obtains a large increase which indicates better flame retardancy. In comparison with untreated cotton fabric, the total heat release (THR) of treated cotton fabric is reduced as shown in Fig. 2. The reduction in THR is associated with the formation of char layer which can provide protection to cotton fabric. For the cotton fabric treated with (IB-co-N-MDPA)PDMS, the heat released from volatiles is reduced obviously as confirmed by EHC curves of cotton fabrics (Fig. 3). Mass loss is also an important parameter which can reflect the flammability of materials. From Fig. 4, we can know that the mass loss of treated cotton fabric is lower than untreated one. Furthermore, it has been demonstrated that CO₂/CO ratios play an important role on combustion of materials, and lower CO₂/CO ratios mean inefficiency of combustion [27]. Compared with that of untreated cotton fabric (23.30), the CO₂/CO ratio of treated one is lower (15.30). All of these indicate that (IB-co-N-MDPA)PDMS enhance obviously combustion properties of cotton fabrics.

**Fig. 3** EHC curves of samples**Fig. 4** Mass curves of samples

Thermal behaviors

Thermal degradation properties of untreated and treated cotton fabrics have been investigated by TG analysis in nitrogen atmosphere. The results are shown in Fig. 5a, b, and the corresponding data are presented in Table 3. As shown in Fig. 5a, b, the thermal degradation of untreated and treated cotton fabric in nitrogen undergoes only one step as already have been demonstrated [28] with a maximum mass loss at 379 and 327 °C, respectively. Under

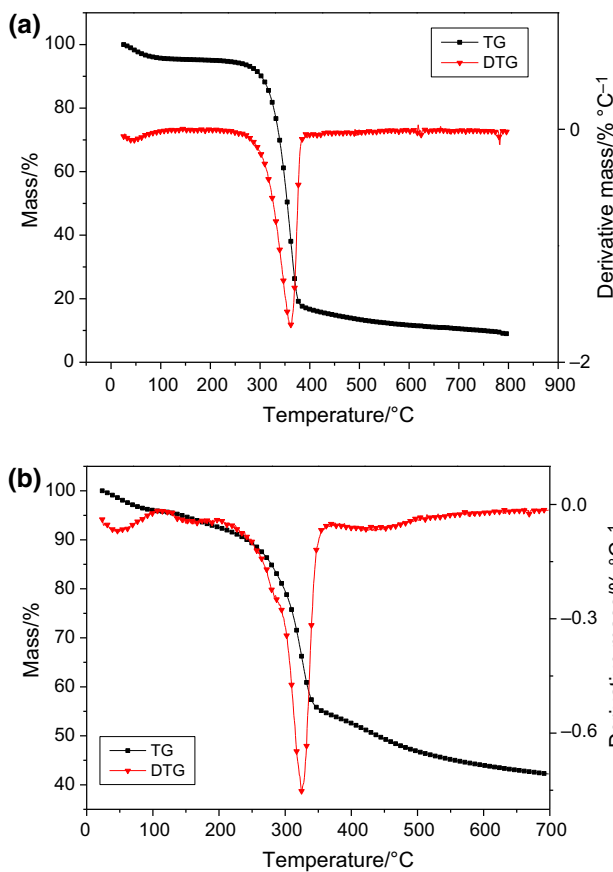


Fig. 5 a TG and DTG curves of untreated cotton fabric in nitrogen, b TG and DTG curves of treated cotton fabric in nitrogen

Table 3 Data of TG and DTG curves of the cotton fabrics in nitrogen

Add-on %	$T_{onset}/$ °C	$T_{max}/$ °C	Residue at $T_{max}/$ %	Residue at 700 °C/ %
0	300	379	22.2	10.5
22.1	227	327	57.8	42.4

nitrogen atmosphere, cotton fabrics degrade by decomposition of cellulose at lower temperature to volatile species and dehydration to char. It is noted that (IB-co-N-MDPA)PDMS decreases the initial depolymerization temperature of cotton from 300 to 227 °C as shown in Table 3. The untreated cotton fabric degrades mainly in the range of 300–379 °C with 77.8 % mass loss, while the treated one degrades in the range of 227–327 °C with 33.3 % mass loss. The residue of untreated cotton fabric at 700 °C is 10.5 %, while it is 42.4 % for treated cotton fabric. It clearly demonstrates that (IB-co-N-MDPA)PDMS promotes the dehydration of cellulose producing more char which is helpful to inhibit the transformation of heat. The reason is that (IB-co-N-MDPA)PDMS a kind of phosphorus-containing flame retardant can form phosphoric and

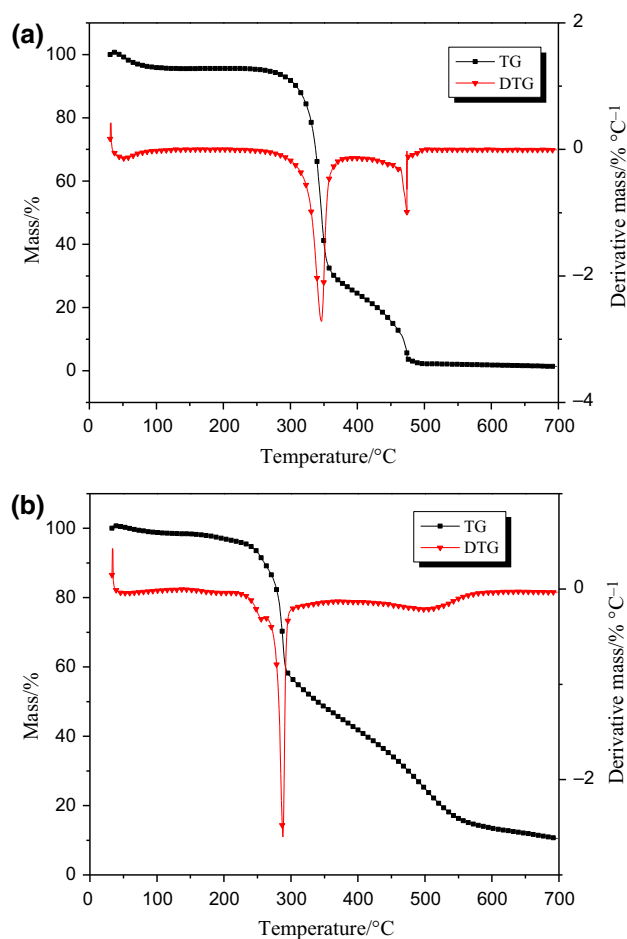


Fig. 6 a TG and DTG curves of untreated cotton fabric in air, b TG and DTG curves of treated cotton fabric in air

Table 4 Data of TG and DTG curves of the cotton fabrics in air

Add-on %	$T_{onset}/$ °C	$T_{max}/$ °C	Residue at $T_{max}/$ %	Residue at 700 °C/ %
0	296	478	3.4	1.3
22.1	238	553	15.9	10.5

polyphosphoric acid in combustion. Moreover, it has been established that silicon-containing inhibitors can form silica char which works as a physical barrier and favors the char formation during combustion as have mentioned before.

The thermo-oxidative stability of untreated and treated cotton fabrics have also been assessed by TG analysis in air atmosphere as shown in Fig. 6 and Table 4. Compared with thermal degradation in nitrogen, cotton fabrics degrade by three steps in air [28]. The first step (at 296–361 °C for untreated fabric and 238–292 °C for treated fabric) involves two competitive pathways, which

mainly yield aliphatic char and volatile products. Within the second step (at 361–478 °C for untreated fabric and 292–553 °C for treated fabric), aliphatic char is further converted to aromatic char due to carbonization and yields CO and CO₂ due char oxidation. During the last step (above 478 °C for untreated fabric and 553 °C for treated fabric), the char is further oxidized mainly to CO and CO₂. It can be concluded that (IB-co-N-MDPA)PDMS favors the char formation and reduces volatile products at lower temperature which is helpful to enhance the thermo-oxidative stability of cotton fabric. Furthermore, fewer amounts of char of treated cotton fabric is oxidized in the last stage with a char residue of 10.5 % at 700 °C comparing with that of untreated ones due to the formation of

phosphoric acid, polyphosphoric acid, and silica char as demonstrated in nitrogen atmosphere.

The results from TG analysis demonstrate that (IB-co-N-MDPA)PDMS has a significant effect on thermal and thermo-oxidative stability of cotton fabric due to synergistic effect arise from P, N, and Si elements especially at higher temperature range.

Char structure

The morphologies of treated cotton fabric with (IB-co-N-MDPA)PDMS before and after burning have been assessed by SEM, and the results are shown in Fig. 7. It can be seen that, compared with the treated cotton fabric before

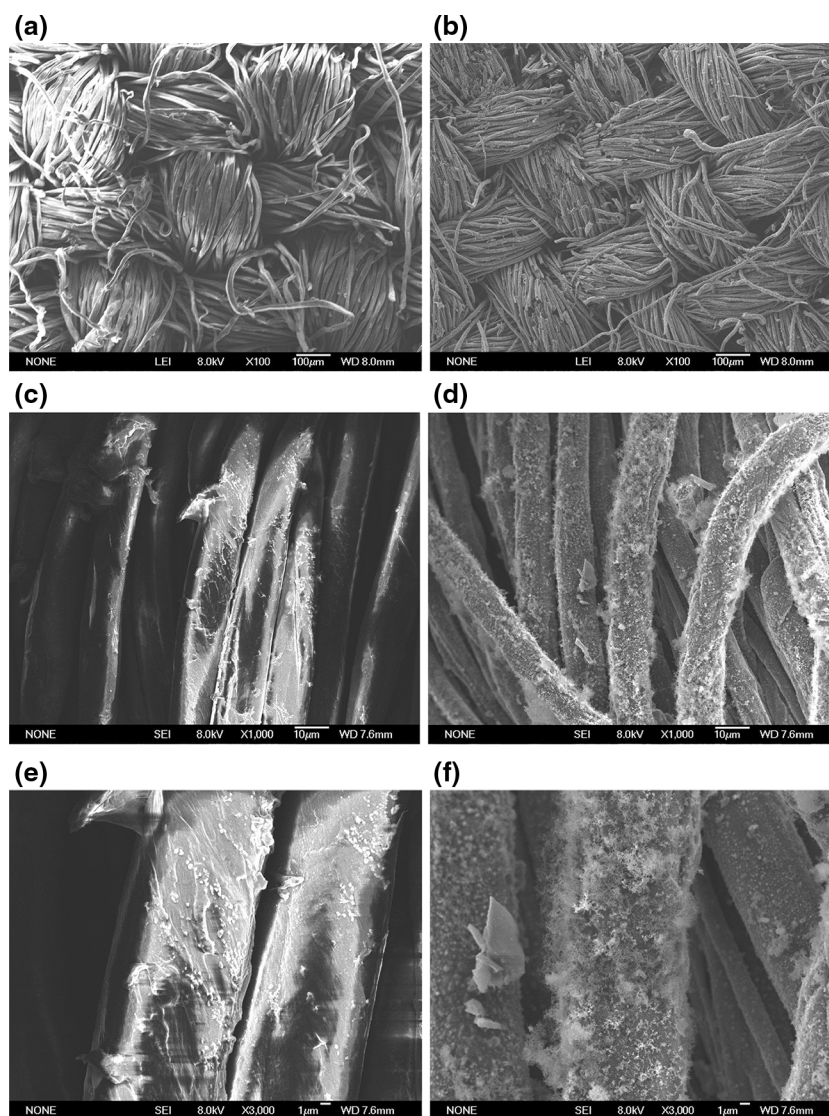
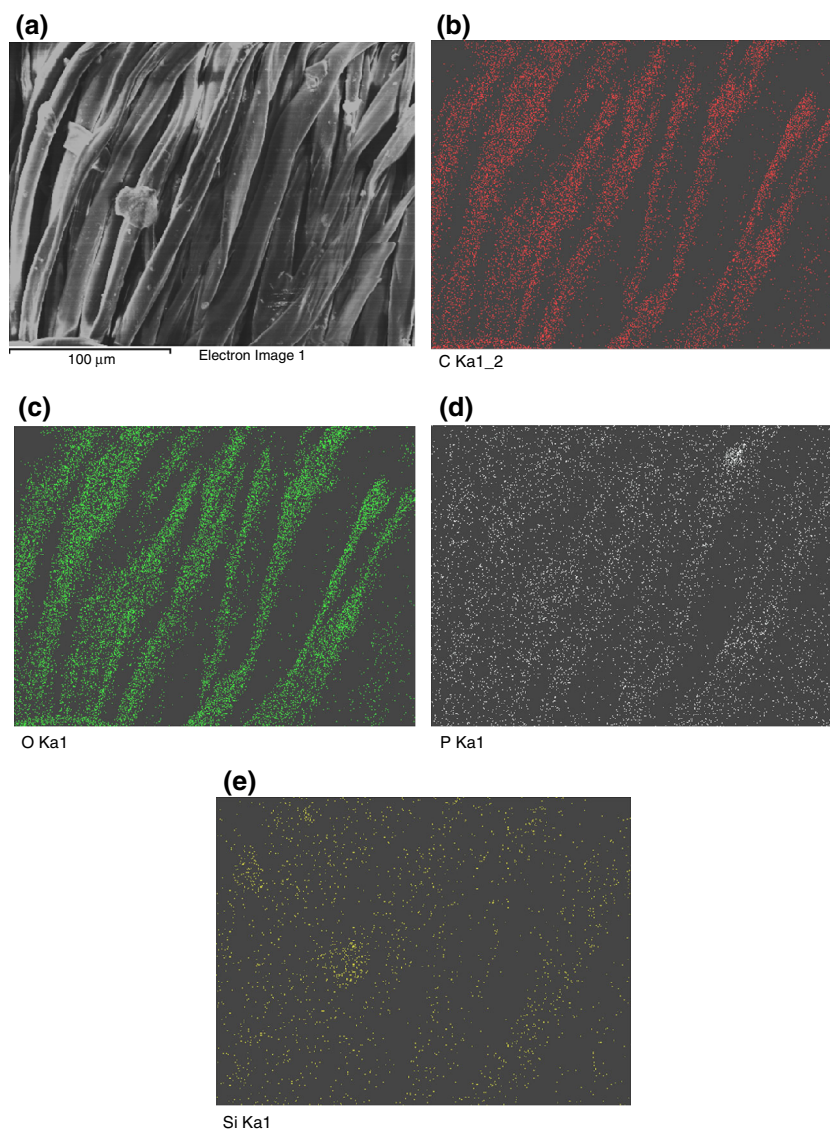


Fig. 7 SEM photographs of treated cotton fabric with (IB-co-N-MDPA)PDMS before and after burning: **a** treated cotton fabric $\times 100$; **b** residues of treated cotton fabric $\times 100$; **c** treated cotton fabric

$\times 1000$; **d** residues of treated cotton fabric $\times 1000$; **e** treated cotton fabric $\times 3000$; **f** residues of treated cotton fabric $\times 3000$

Fig. 8 EDS mapping of treated cotton fabric with (IB-*co-N*-MDPA)PDMS before combustion: **a** SEM photograph of treated cotton fabric before combustion; **b** distribution map of C element; **c** distribution map of O element; **d** distribution map of P element; **e** distribution map of Si element



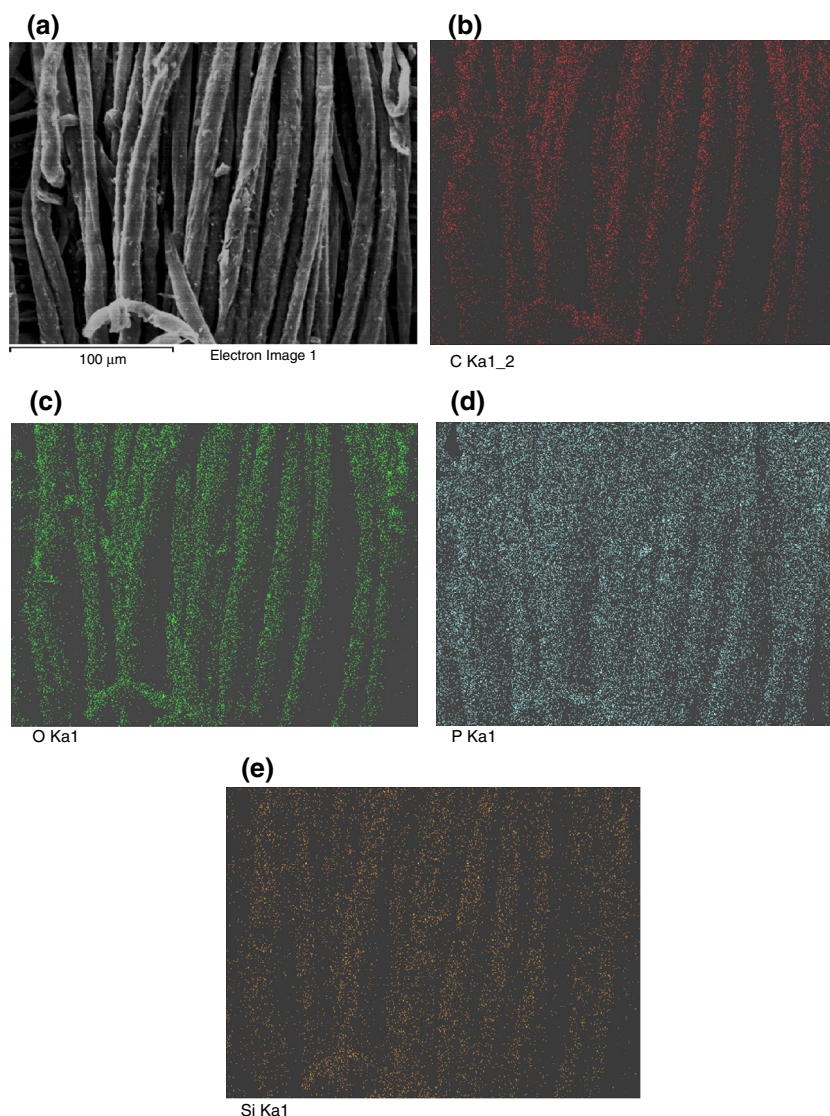
burning (Fig. 7a, c, e), the structure of treated cotton fabric after burning is still maintained as shown in Fig. 7b, and the char fiber is covered with a continuous and compact swollen charred layer as shown in Fig. 7d, f. These directly prove that (IB-*co-N*-MDPA)PDMS promotes the char formation of cotton fabric and also demonstrates the formation silica matrix on the surface of fiber during burning. To further elucidate the flame retardancy effect of (IB-*co-N*-MDPA)PDMS on cotton fabric, the elemental composition of treated cotton fabric before and after burning was investigated by EDS.

Elemental analysis

Elemental analysis (EDS) coupled to energy spectrum has assessed the elemental composition of treated cotton fabric before and after combustion as shown in Figs. 8–11, and

the data are collected in Table 5. According to the results, it can be pointed that C, N, O, Si, and P elements are main constituents of treated cotton fabric. Figures 8 and 9 show the EDS mapping of treated cotton fabric before and after combustion, respectively. It noted that the distributions of Si and P elements are homogeneous and regular in both condition, while more amount of these two elements accumulated on the fibers after combustion as confirmed by the energy spectra as shown in Figs. 10 and 11. From Table 5, we can know that the mass percentage concentrations of Si element on fibers increased from 0.67 to 1.42 % and the atomic percentage concentrations of Si element on fibers increased from 0.34 to 0.73 %, while the mass percentage concentrations of P element increased from 3.01 to 11.87 % and the atomic percentage concentrations of P element on fibers increased from 1.39 to 5.52 %. The increment of P element agrees with that

Fig. 9 EDS mapping of treated cotton fabric with (IB-*co-N*-MDPA)PDMS after combustion: **a** SEM photograph of treated cotton fabric after combustion; **b** distribution map of C element; **c** distribution map of O element; **d** distribution map of P element; **e** distribution map of Si element



(IB-*co-N*-MDPA)PDMS can decompose to phosphoric and polyphosphoric accelerating the charring of cellulose as illustrated in TG and morphology analysis. Furthermore, the remarkable amount of Si element still present on fibers after combustion establish that (IB-*co-N*-MDPA)PDMS can produce silica char conferring flame-retardant behavior to cotton fabric as demonstrated in SEM analysis.

Chemical structure of the residues after burning

To further examine the chemical structure of the residual char of cotton fabrics after burning in air, FTIR analysis was conducted and the results are shown in Fig. 12. It is noteworthy that the residue of treated cotton fabric obtained many characteristic absorbing peaks. In spectrum of residue of treated cotton fabric, the peak at 1660 cm^{-1} is ascribed to C=O stretching vibration; the two tiny peaks at

1385 cm^{-1} [29] are due to the splitting of a P=O single peak which indicates the formation of new compounds that containing P=O, and the peaks at 901 cm^{-1} [30] are due to the stretching vibration of and P–O–P, and these peaks evidence the formation of phosphoric and polyphosphoric acid as mentioned in G analysis; the peak at 1110 cm^{-1} is attributed to the Si–O–Si stretching vibration that evidenced the presence of silica charred layer. The FTIR analysis results demonstrate that (IB-*co-N*-MDPA)PDMS has positive effects on char formation of cellulose during burning which is in good agreement with results from TG and SEM analysis.

Washing durability

The flame retardancy of treated cotton fabric with (IB-*co-N*-MDPA)PDMS after washing is shown in Table 6. The

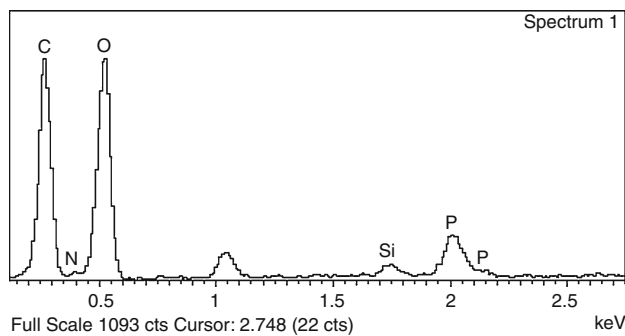


Fig. 10 Energy spectrum of treated cotton fabric with (IB-co-N-MDPA)PDMS before combustion

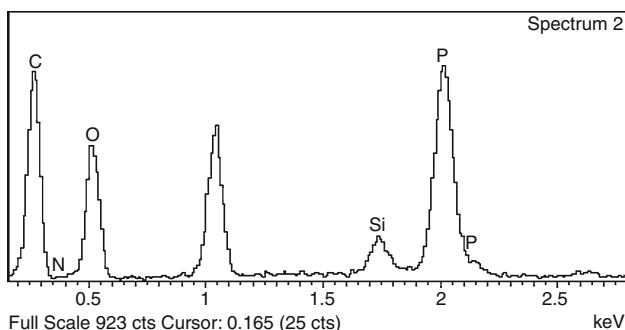


Fig. 11 Energy spectrum of treated cotton fabric with (IB-co-N-MDPA)PDMS after combustion

Table 5 Elemental composition of the fabrics obtained by EDS analysis

Elements	Mass/%		Atomic/%	
	Before	After	Before	After
C K	41.47	52.42	49.20	62.85
N K	1.84	0.34	1.87	0.34
O K	53.00	33.95	47.20	30.56
Si K	0.67	1.42	0.34	0.73
P K	3.01	11.87	1.39	5.52
Totals	100.00			

results showed that the treated cotton fabric obtained good wash ability with a LOI value of 26.2 % after 20 times washing. The reason was that (IB-co-N-MDPA)PDMS can combine to cotton fabric with covalent bond due to the activity group.

Conclusions

A novel flame-retardant agent, nitrogen- and phosphorus-containing polysiloxane (IB-co-N-MDPA)PDMS was successfully prepared. The combustion properties of the cotton

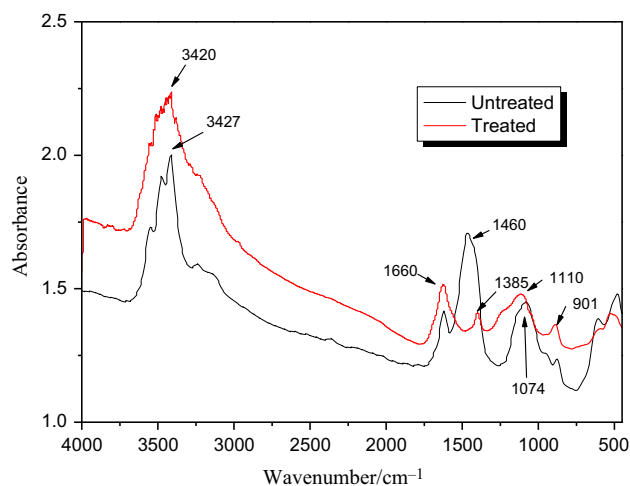


Fig. 12 FTIR spectra of residues of the treated cotton fabric after burning in air

Table 6 Flame retardancy of treated cotton fabric after washing

Washing times	0	5	10	15	20
LOI/%	28.5	28.2	27.7	26.8	26.2

fabrics treated with (IB-co-N-MDPA)PDMS were evaluated by cone calorimeter. The results demonstrated that the treated cotton fabric with (IB-co-N-MDPA)PDMS generated less combustion heat and obtained better flame retardancy which can be evidenced by the increase in TTI and FPI value and the decrease in HRR, THR, EHC, mass loss, and CO/CO₂ ratio. (IB-co-N-MDPA)PDMS improved the thermal and thermo-oxidative stability of cotton fabric and favored the char formation as evidenced by the chemical structures which was characterized by FTIR and EDS analyses. The morphology of the residues indicated that the treated cotton fabric structure was still maintained. From the above results, it can be concluded that (IB-co-N-MDPA)PDMS can confer cotton fabrics excellent flame retardancy and accelerate the char formation of cotton fabrics in combustion.

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