

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

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Abstract A novel flame-retardant agent, guanidyl- and phosphorus-containing polysiloxane (GPPDMS), was synthesized. The combustion properties of the cotton fabrics treated with GPPDMS were evaluated by cone calorimeter. The results showed that the TTI value of the treated fabric increased and the value of HRR, THR, EHC, and Mass loss decreased. It demonstrated that the treated cotton fabric with GPPDMS generated less combustion heat and obtained better flame retardancy which can be confirmed by the increase of FPI value and the decrease of CO/CO₂ ratio. It also revealed that the cotton fabric treated with 18.6 % (add-on) of GPPDMS had highest reduction in heat of combustion. The chemical structures and morphologies of the residues, and the thermal decomposition behavior of cotton fabrics were investigated by FT-IR, scanning electron microscopy, and thermogravimetric analysis, respectively. The results showed that GPPDMS played a protective role on the degradation of cotton fabrics, hindered the formation of volatile species and favored the formation of char. Furthermore, EDS analysis results showed that remarkable amount of Si and P elements were still present on the surface of fibers after combustion; it indicated that the concurrent presence of Si and P in flame retardant effectively enhances the flame retardancy of cotton fabric.

Keywords Flame retardant · Cotton fabric · Cone calorimeter

Introduction

Fire safety has been attracting more attention due to the severe damages, injuries, and deaths caused by fire [1, 2]. The major reason for the fire may be due to the combustible materials surrounding us, such as wood, paper, plastics, and cotton fabric. Among these materials, the flame retardancy of cotton fabric has been a hot topic due to its close relation with our daily life. Low thermal stability, easy ignition, and rapid combustion of cotton fabrics represent their weaknesses and limitations. Many studies have been reported about the flame retardancy of cotton fabric [2, 3].

Although many new techniques have been developed in these years such as the sol-gel technique [4, 5] and the layer-by-layer (LbL) assembly [6, 7], the application of flame retardants is also a major approach to impart flame retardancy to cotton fabric. Many types of flame retardants as one-component agents or as mixtures have been employed in cotton fabric including halogen-containing flame retardants, phosphorus-containing flame retardants, nitrogen-containing flame retardants, and silicon-based flame retardants. The most effective flame retardancy can be achieved by the employment of phosphorus-containing flame retardants and halogen-containing flame retardants.

Halogen-containing compounds are gradually eliminated due to toxic gases they generate when combusting. At the same time, silicone-based flame retardants have been attracting more attention as one of the most promising and environmental friendly flame retardants due to their very good thermal stability [8, 9]. Furthermore, the synergistic effect of different flame retardant-elements has been a focus in researches [10, 11]. Researchers have found that

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$$\text{add-on\%} = \frac{W_f - W_b}{W_b} \times 100 \%, \tag{1}$$

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

Characterization

The structure of GPPDMS was verified by ^1H NMR spectrum (JEOL LA500, Japan). FT-IR analysis was carried out on a Nicolet 5700 FT-IR apparatus (Thermo Nicolet Corporation, US) using the KBr pellet technique.

The combustion of cotton fabrics was investigated using FTT0007 cone calorimeter (Fire Testing Technology Ltd.) under a heat flux of 30 kW m^{-2} according to ISO 5660. The parameters measured were time to ignition (TTI, s), total heat release (THR, kW m^{-2}), heat release rate (HRR, kW m^{-2}) and 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.

Thermogravimetric analysis (TG) was performed using TGA851 thermal analyzer (Mettler-Toledo International Inc.) at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ with a continuous air flow rate of 20 mL min^{-1} from 23 to $600 \text{ }^\circ\text{C}$.

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 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.).

Results and discussion

Combustion behaviors

The combustion behavior of untreated sample and treated sample had been investigated by cone calorimeter. The collected data are summarized in Table 1 and plotted in Figs. 1–4. From Table 1, we can know that the time to ignition (TTI) of the treated samples have increased significantly comparing to the untreated sample [9 s (add-on% = 4.7), 16 s (add-on% = 18.6) vs. 2 s]. When

samples were ignited, the combustion proceeded: the heat release rate (HRR) increases to a maximum (namely, PHRR) and then decreases down to the flame out (FO). The treatment with GPPDMS reduces the PHRR values of cotton fabrics remarkably and a lower PHRR value is achieved when higher amount of GPPDMS was employed as shown in Fig. 1 [96.31 kW m^{-2} (add-on% = 4.7), 71.80 kW m^{-2} (add-on% = 18.6) vs. 144.23 kW m^{-2}]. It is also noteworthy that GPPDMS enhances the flame retardancy of cotton fabrics by decreasing combustion period

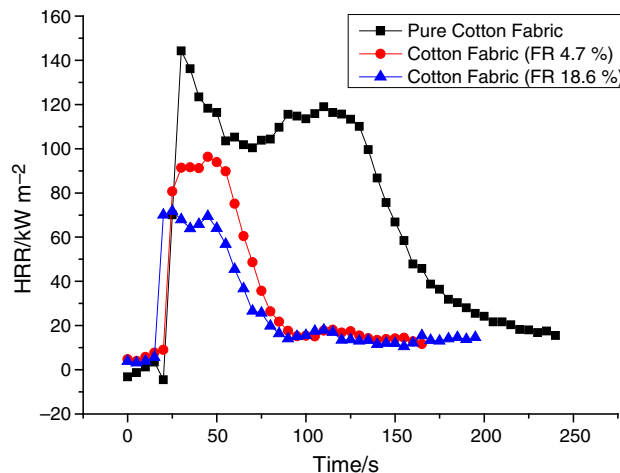


Fig. 1 HRR curves of samples

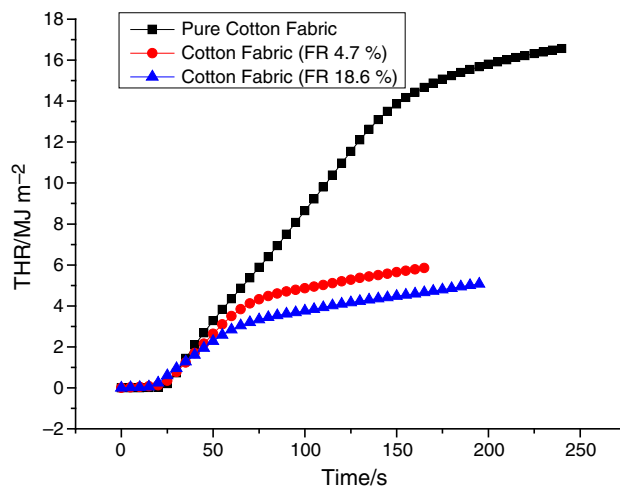


Fig. 2 THR curves of samples

Table 1 Combustion data by cone calorimeter

Sample	TTI/s	PHRR/ kW m^{-2}	FPI/ $\text{s m}^2 \text{ kW}^{-1}$	Average EHC/ MJ kg^{-1}	CO/ kg kg^{-1}	$\text{CO}_2/\text{kg kg}^{-1}$	CO_2/CO
Cotton fabric	2	144.23	0.01	12.57	0.10	2.33	23.30
Cotton fabric (FR 4.7 %)	9.6	96.31	0.10	7.97	0.06	1.32	22.01
Cotton fabric (FR 18.6 %)	16.9	71.80	0.24	7.06	0.10	1.64	16.40

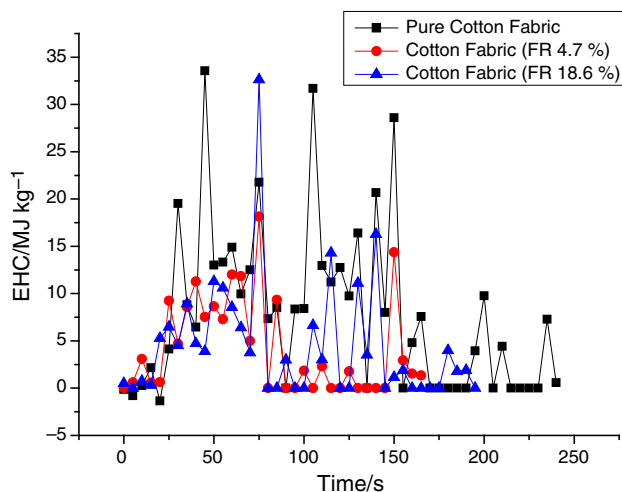


Fig. 3 EHC curves of samples

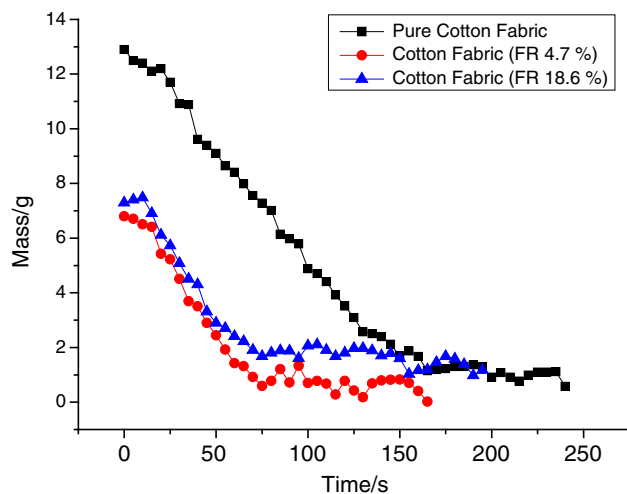


Fig. 4 Mass curves of samples

as confirmed by the FO values and hindering the formation of volatile species as evidenced by the strong decrease of total heat release (THR) values (Fig. 2), EHC values, Mass values, and the increase of FPI values (Table 1). EHC is expected in a fire where incomplete combustion takes place, and it is a parameter corresponded to the heat released from the volatile portion during combustion. From Table 1 and Fig. 3, we can know that the EHC value of cotton fabric has decreased significantly [7.97 MJ kg^{-1} (add-on% = 4.7), 7.06 MJ kg^{-1} (add-on% = 18.6) vs. 12.57 MJ kg^{-1}], since the employment of GPPDMS. Mass loss is another parameter reflecting the incomplete combustion of cotton fabrics as shown in Fig. 4: the mass loss of the treated cotton fabric is lower than the untreated ones [6.78 g (add-on% = 4.7), 5.82 g (add-on% = 18.6) vs. 11.53 g]. FPI was calculated as the ratio between TTI and PHRR. The higher FPI indicates the better flame retardancy

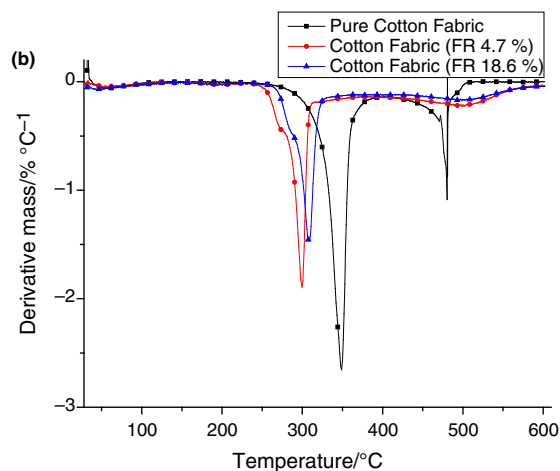
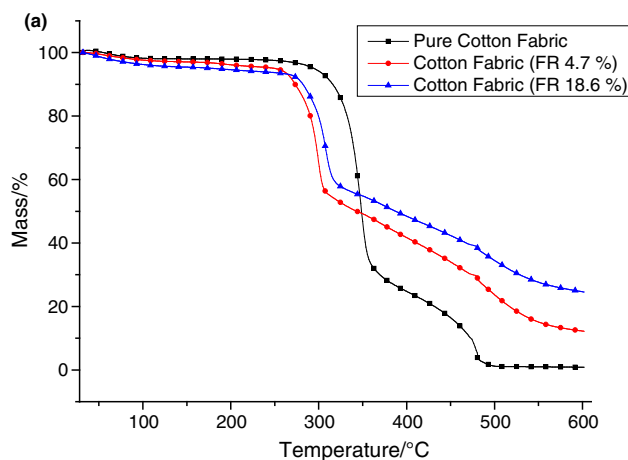


Fig. 5 a TG curves of treated and untreated cotton fabrics in air. b DTG curves of treated and untreated cotton fabrics in air

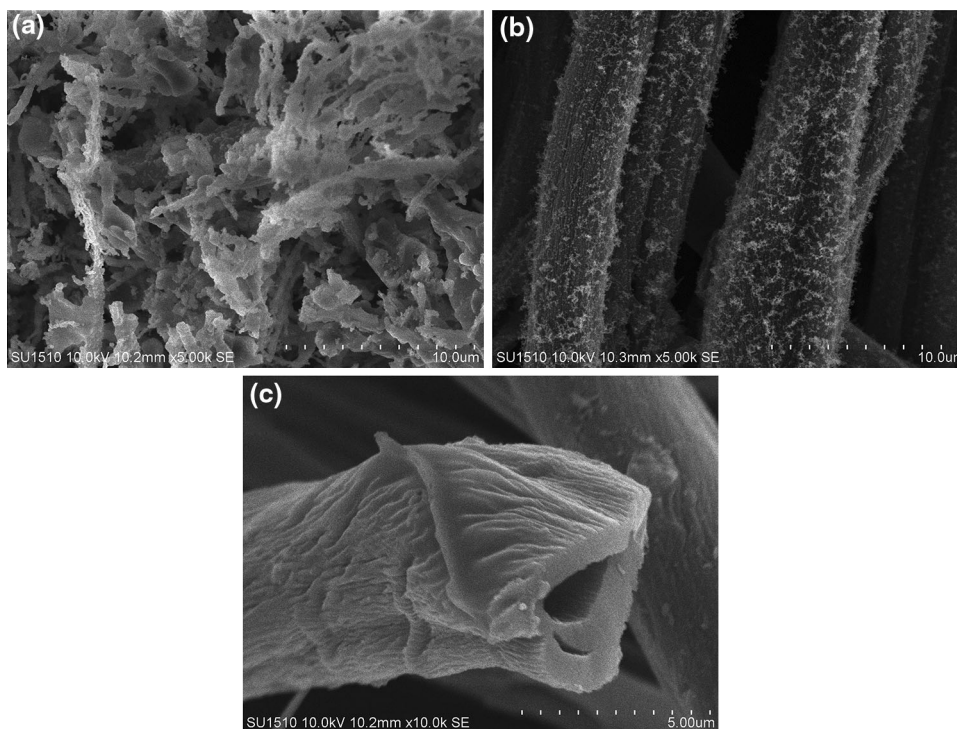
[13]. From Table 1, we can know that the FPI of treated cotton fabric is higher than the untreated ones [$0.10 \text{ s m}^2 \text{ kW}^{-1}$ (add-on% = 4.7), $0.24 \text{ s m}^2 \text{ kW}^{-1}$ (add-on% = 18.6) vs. $0.01 \text{ s m}^2 \text{ kW}^{-1}$]. It is also can be concluded that the higher the add-on of GPPDMS, the better is the flame retardancy of treated cotton fabric.

CO and CO_2 are the main components of fire gases, and the analysis of the two species can provide useful information on the mechanism of decomposition of cotton fabrics [14]. Low CO_2/CO ratios mean low conversion of CO to CO_2 and suggested inefficiency of combustion. Pure cotton fabrics produced CO and CO_2 due to two-step reaction: CO including other gases was produced in first step pyrolysis reaction, and CO_2 was released due to the oxidation of CO when enough oxygen was available in the second step. When cotton fabrics were treated with GPPDMS, the CO production changed a little, whereas the CO_2 production was decreased leading to remarkable decrease of CO_2/CO ratio [22.01 (add-on% = 4.7), 16.40 (add-on % = 18.6) vs. 23.30]. This suggested the enhancement of flame retardancy of cotton fabrics.

Table 2 Data of TG and DTG curves of the cotton fabrics

Add-on%	Initial decomposing temperature/°C	Residue/%			Maximum mass loss temperature/°C	
		400 °C	450 °C	500 °C	Stage	
					1	2
0	305.6	24.8	16.4	1.2	348.4	480.3
4.7	264.2	41.8	34.0	23.7	299.7	531.7
18.6	272.9	48.5	42.3	34.5	308.2	524.3

Fig. 6 SEM photographs of microstructures of the cotton fabrics: **a** The residue of the untreated fabric. **b** The residue of the treated fabric with GPPDMS of 18.6 %. **c** The cross-section of a fiber from the residue of the treated fabric with GPPDMS of 18.6 %



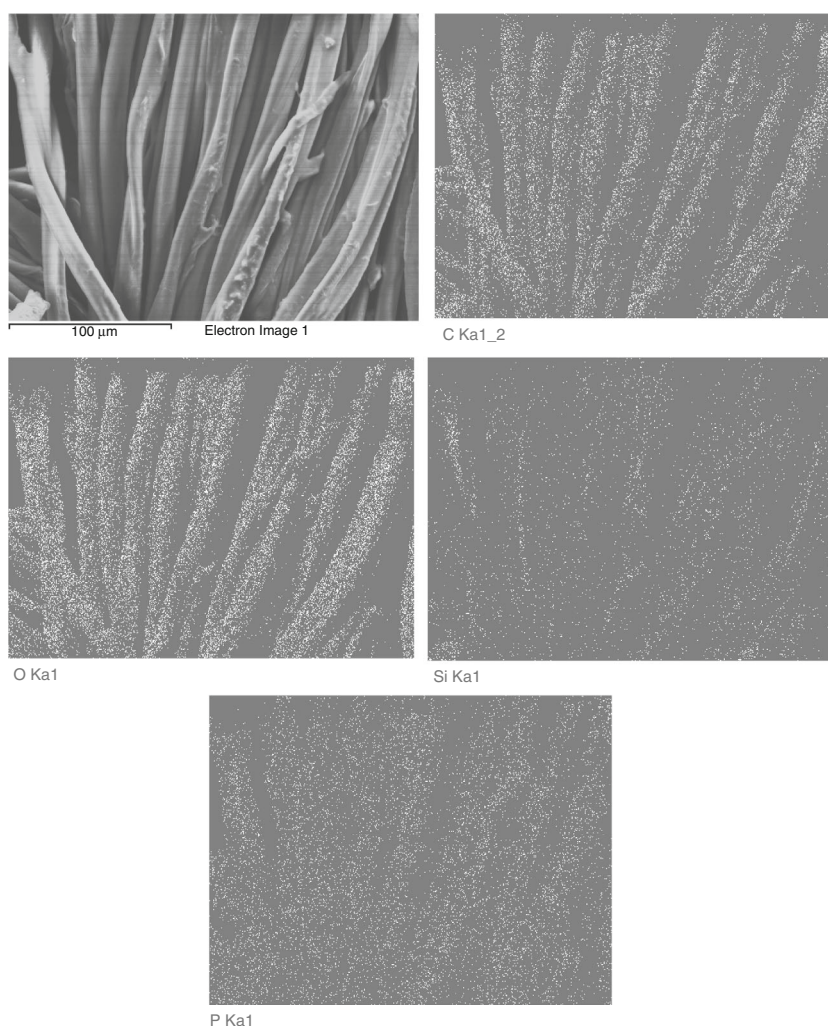
Thermal behaviors

The thermal and thermo-oxidative stability of untreated and treated cotton fabric was investigated by TG. TG curves of the fabrics under air atmosphere are shown in Fig. 5a. Data from TG and DTG curves of the cotton fabrics are presented in Table 2. It can be seen that, the initial decomposing temperatures of treated cotton fabrics with GPPDMS are 264.2 °C (add-on% = 4.7) and 272.9 °C (add-on% = 18.6), respectively, which are lower than that of the untreated cotton fabric, and the residue of the treated cotton fabrics at 500 °C are higher than that of the untreated cotton fabric. As shown in Fig. 5a and Table 2, the residues increase with the increase of GPPDMS add-on. Compared to the other fabrics, the treated cotton fabric with GPPDMS of 18.6 % has the highest residual char. DTG curves of the fabrics under air atmosphere are shown in Fig. 5b. The untreated cotton fabric has two evident mass loss stages, while the treated

cotton fabrics have a major and a minor mass loss stage. This phenomenon could be attributed to the different thermal degradation processes of the cotton fabrics.

The untreated cotton fabric favors formation of flammable volatiles and loses much mass during degradation. As shown in many literature, phosphorus-based flame retardants can evidently lower the decomposition temperature of cotton fabric by accelerating dehydration and producing more char [15, 16]. We also know that silica is an efficient flame retardant for cotton fabric because silica coating on cotton favors the formation of char [3, 4]. The cotton fabric treated with GPPDMS degrades at lower temperature due to the synergistic effect arise from P, N, and Si elements contained in GPPDMS. During combustion, the lower initial decomposing temperature of the treated cotton fabrics is due to the esterification of phosphoryl groups from GPPDMS with hydroxyl groups from cellulose, which finally induces the release of water in a relative low temperature range, and the earlier decomposition of GPPDMS on cotton fabric to form

Fig. 7 EDS mapping of treated cotton fabric with GPPDMS of 18.6 % before combustion



phosphoric and polyphosphoric acid at lower temperature which promotes dehydration of cellulose and reduces the release of volatile species with more char yield at higher temperature. GPPDMS also forms a physical barrier silica-protecting cotton fabric from heat and oxygen transfer and favoring the char formation.

The TG results indicate that GPPDMS treated on cotton fabric lowers the decomposition temperature of cotton fabric and enhances the formation of char after pyrolysis.

Char structure

After combustion, it was realized that the residue of treated cotton fabric was different from the residue of the untreated cotton fabric. The residue of treated cotton fabric showed a more compact structure. SEM analysis of the residue was carried out to further characterize the surface morphology as shown in Fig. 6. It can be seen that the structure of the untreated fabric has been destroyed seriously after combustion and the surface of the residue is discontinuous

(Fig. 6a). Compared to the residue of untreated cotton fabric, the surface of the residue of treated cotton fabric is uniformly continuous with an irregular coating (Fig. 6b) due to the formation of SiO_2 matrix in the burning and the formation of polyphosphoric acid and other derivatives of GPPDMS during the thermal decomposition process. The cross-section of the charred fibers of treated cotton fabric as shown in Fig. 6c also demonstrates the existence of separate surface coating, and the bubbles on the separate surface coating may indicate that GPPDMS acts as a kind of intumescent flame retardant. The formed coating may act as a physical barrier inhibiting the transmission of heat, energy, and O_2 .

Elemental composition

Elemental analysis was performed as shown in Figs. 7–10, and the data were collected in Table 3. The elemental mapping shows that the distribution of Si and P elements on fibers before and after combustion is homogeneous and

Fig. 8 EDS mapping of treated cotton fabric with GPPDMS of 18.6 % after combustion

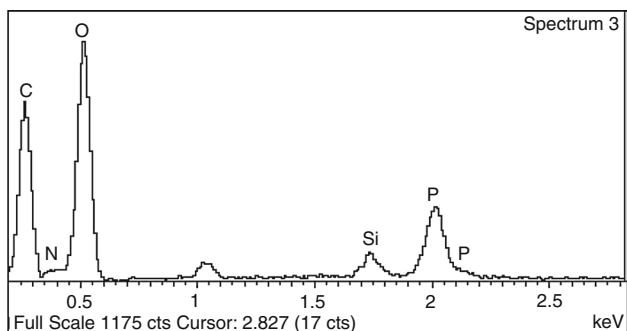
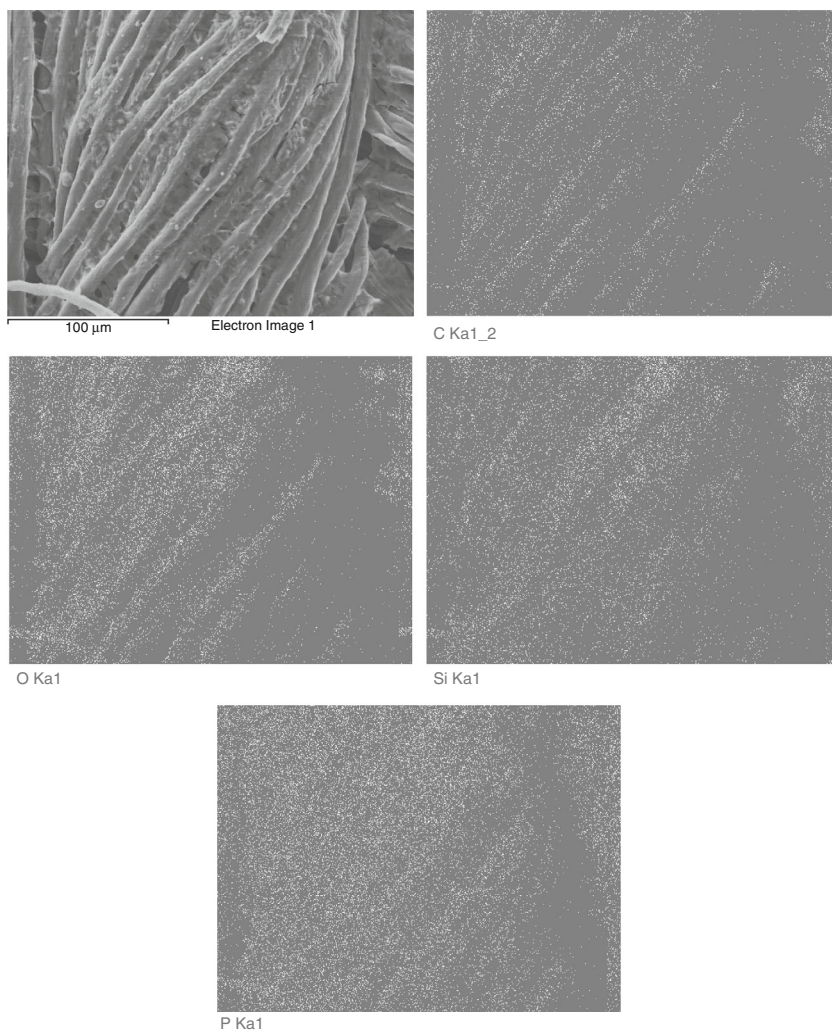


Fig. 9 EDS image of treated cotton fabric with GPPDMS of 18.6 % before combustion

regular. Furthermore, the fibers after combustion show a wider distribution of Si and P elements than fibers before combustion. From Figs. 9 and 10, it is noteworthy that

remarkable amount of Si and P elements is still present on the surface of fibers after combustion. From Table 3, we can know that the mass percentage concentrations of Si element on fibers increased from 1.21 to 2.77 % and the atomic percentage concentrations of Si element on fibers increased from 0.63 to 1.42 %, while the mass percentage concentrations of P element increased from 4.65 to 9.80 % and the atomic percentage concentrations of P element on fibers increased from 2.18 to 4.55 %. The increment of Si and P elements on fibers after combustion evidenced that Si and P elements are the main constituents of flame retardant-agent and demonstrate that SiO₂ matrix, polyphosphoric acid, and other derivatives of GPPDMS are formed during the thermal decomposition process. The results are coherent with the SEM analysis of the char that a separate surface coating formed on the surface of fibers after combustion. To further discuss the retardant mechanism of

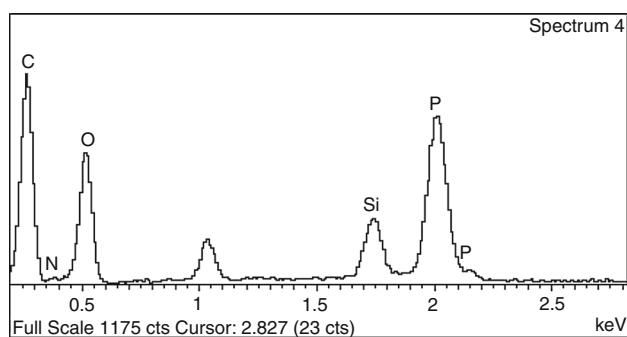


Fig. 10 EDS image of treated cotton fabric with GPPDMS of 18.6 % after combustion

Table 3 Elemental composition of the fabrics obtained by EDS analysis

Elements	Mass/%		Atomic/%	
	Before	After	Before	After
C K	36.46	50.60	44.12	60.55
N K	5.14	3.12	5.33	3.20
O K	52.54	33.71	47.73	30.28
Si K	1.21	2.77	0.63	1.42
P K	4.65	9.80	2.18	4.55
Totals	100.00			

GPPDMS, the residue of treated cotton fabric after combustion was characterized by FT-IR.

FT-IR analysis of the residues after combustion

The chemical structure of the residue of untreated and treated cotton fabric after burning in air are investigated by FT-IR analysis as shown in Fig. 11. Compared to the residue of untreated cotton fabric [spectrum (a)], treated cotton fabric shows some special characteristic peaks [spectrum (b)]. In spectrum (b), the peak at $2,330\text{ cm}^{-1}$ is attributed to the stretching vibration of $\text{C}\equiv\text{N}$ which is produced by the pyrolysis of guanidine groups; the peak at $1,060\text{ cm}^{-1}$ can be ascribed to the $\text{Si}-\text{O}-\text{Si}$ stretching vibration and the peak at 816 cm^{-1} is due to the $\text{Si}-\text{O}-\text{Si}$ bending vibration [17] which confirms the formation of SiO_2 matrix in the residue; the peak at $1,180\text{ cm}^{-1}$ is assigned to stretching vibration of $\text{P}=\text{O}$ [18] which indicates the presence of phosphoric and polyphosphoric acid. These results share same ideas with SEM analysis and elemental analysis that the flame retardancy of treated fabric with GPPDMS is improved due to the formation of phosphoric and polyphosphoric acid which promoting the

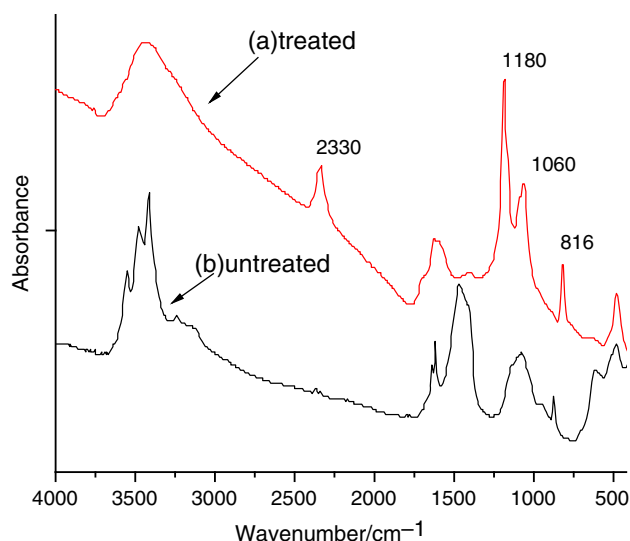


Fig. 11 FT-IR spectra of residues of the treated cotton fabric after burning in air

carbonization of fabric and SiO_2 matrix which acts as a physical barrier during burning.

Conclusions

A novel flame-retardant agent, guanidyl- and phosphorus-containing polysiloxane (GPPDMS), was synthesized, and combustion behavior of the treated cotton fabric with GPPDMS was studied. Presence of GPPDMS can increase the value of TTI and FPI and lower both the value of HRR, THR, EHC, and CO/CO_2 ratio comparing that without GPPDMS. It demonstrated that the treated cotton fabric with GPPDMS generated less combustion heat and the more addition of GPPDMS, the less combustion heat was. The TG test results indicate that GPPDMS treated on cotton fabric lowers the decomposition temperature and enhances the formation of char after pyrolysis. The cotton fabric treated with 18.6 % (add-on) of GPPDMS at $500\text{ }^\circ\text{C}$ has a char yield of 34.5 %, which is 33.3 % higher than that of the untreated cotton fabric (1.2 %). The chemical structures of the residues were investigated by FT-IR, and the results demonstrated the formation of SiO_2 matrix, polyphosphoric acid, and other derivatives of GPPDMS during the thermal decomposition process as evidenced by SEM pictures and EDS analysis results. From the above results, it can be concluded that GPPDMS improved the thermal stability of cotton fabrics effectively by hindering the formation of volatile species and favoring the formation of char.

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