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ORIGINAL RESEARCH

An eco-friendly and durable multifunctional cotton fabric incorporating ZnO and a branched polymer

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Abstract In this study, we investigated a two-step method of preparing cotton fabrics with flame retardancy and UV-blocking properties. This method involved the in situ deposition of ZnO nanoparticles (NPs) and the synthesis of a phosphorus ammonium salt. The application of ZnO NPs on cotton fabrics was achieved by an in situ ammonia-smoking method with zinc acetate and ammonia. A hyperbranched polyphosphate ammonium salt (FHPOPN) was synthesized for application to the cotton fabrics after the ammonia-smoked finish was applied. This research mainly focused on the fire-resistance and UV-blocking performance of cotton fabrics. The treated cotton fabrics were observed by scanning electron microscopy (SEM). The Fourier transform infrared (FTIR) spectroscopy results showed that ZnO NPs were successfully deposited in the fabric and that FHPOPN was bound to the fabric by covalent bonds. The flame retardancy and UV-protection properties of the treated cotton fabrics were studied. The effect of the zinc acetate concentration on the fire resistance and UV-blocking performance of the fabrics was investigated. The cotton fabrics treated with 70 g/L zinc acetate and 160 g/L FHPOPN obtained excellent flame retardancy with a char length of 57 mm and an limited oxygen index (LOI) value of 36.4%. The peak heat release rate and the total heat release of the ZnO/FHPOPN-treated samples were 26 kW/m^2 and 4.4 MJ/m^2, respectively, which were slightly lower than those of the FHPOPN-treated samples and much lower than those of the control cotton fabric sample. Furthermore, the thermogravimetric analyses of ZnO/FHPOPN-treated cotton fabric showed a char yield of 33.3% at 800 °C, whereas FHPOPN-treated cotton fabrics had a 29.7% char yield. The ZnO/FHPOPN-treated cotton fabric exhibited effective UV-protection properties with a UPF value of 224.80. These results demonstrated that the ZnO/FHPOPN-treated fabric had excellent flame retardancy, washability and UV-protection performance and revealed the importance of ZnO NPs in enhancing the flame retardancy and UV-blocking of performance cotton fabrics.

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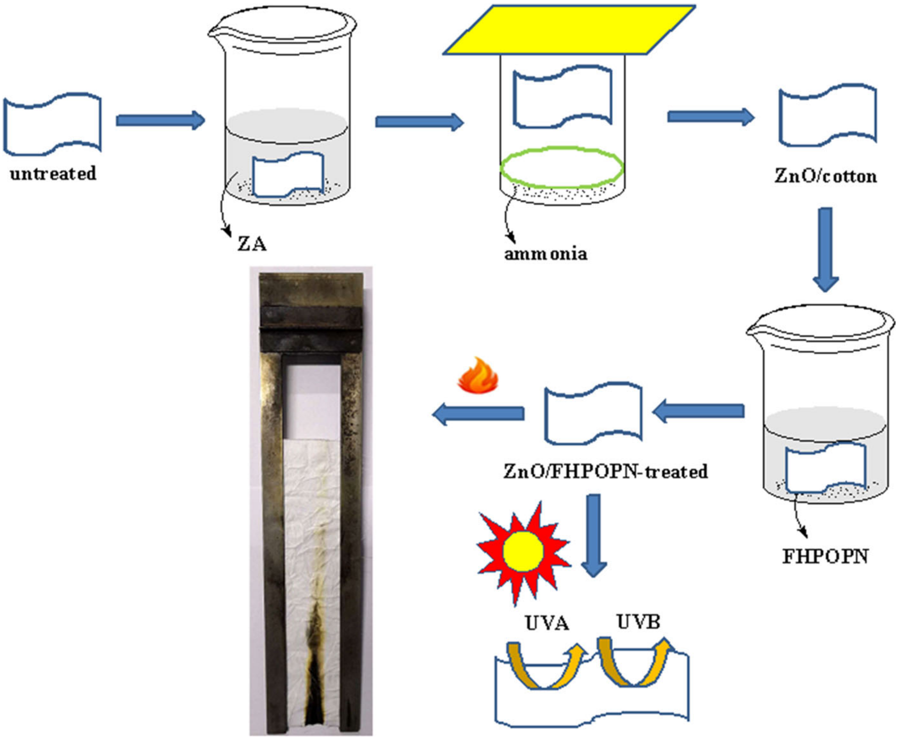
Graphical abstract



Keywords Cotton fabric · In situ · ZnO · Flame retardant · UV protection

Introduction

Cotton, one of the most important and abundant biopolymer natural fibers, has many household and industrial applications because of its characteristics in terms of biodegradation, regeneration, biocompatibility, ecofriendliness and comfort (Lam et al. 2011). However, cotton is highly flammable. Every year, fire accidents caused by cotton fabric lead to substantial losses of life and property worldwide. Therefore, researchers have paid much attention to methods of reducing the flammability of cotton fabric with flame retardant modifications (Wu and Yang 2007).

Organophosphorus-based flame retardants (FRs), including Pyrovatex CP and Proban, have been very important commercial flame retardants that endow cotton with durable flame retardancy. These compounds can form crosslinked structures on the fibers or react with the fibers (Cheng and Yang 2009; Gaan and Sun 2007; Lecoeur et al. 2001; Yang and Wu 2003; Wu and Yang 2008), which can influence the pyrolysis of cellulose to accelerate the formation of char (Gaan and Sun 2009). However, Pyrovatex CP and Proban release carcinogenic formaldehyde during treatment and use of products.

Textile materials with only a single function are considered insufficient because their use is in demand for high-performance areas (Attia et al. 2017; Doganli et al. 2016). Multifunctional textile products can provide desired functional performance (Holme 2010; Chen et al. 2015). Researchers have focused on fabricating multifunctional fabrics with many properties such as flame retardancy, UV-protection, antibacterial properties, and self-cleaning abilities (Pan et al. 2015; Li et al. 2018). In addition, fire-retardant textile products are greatly appreciated due to the high demand (Kosuge et al. 2005). Attempts have been made to meet the desired functional performance using metal oxide nanoparticles to introduce high added value to textiles.

Cupric oxide (CuO), zinc oxide (ZnO), and magnesium oxide (MgO) have been used in functional textiles (Perelshtein et al. 2009; Xu and Cai 2008; Kong and Qian 2014). Researchers found that nano ZnO applied to cotton fabrics could enhance the functional performance such as better air permeability, strength and ultraviolet (UV)-blocking properties (Yadav et al. 2006). ZnO as a catalyst could enhance the flame retardancy of materials (Weil 2004). Furthermore, nano ZnO applied to cotton yarns could withstand knitting operations (Roshan et al. 2010). ZnO nanorods grown on cotton provided excellent protection against UV radiation (Xu and Cai 2010). There have been a large number of studies on nano ZnO-treated cotton fabrics. Nano-ZnO can be coated on cotton fabric by many methods, such as pad-dry-cure (Gao et al. 2020), sol–gel (Abd El-Hady et al. 2013) and in situ deposition methods (Shokoufeh Khosravian et al. 2015). However, these methods have problems such as low durability or the generation of environmental pollution due to the production of wastewater.

The goal of this study was to develop an in situ ammonia-smoking method to fabricate multifunctional cotton fabric-based ZnO and FHPOPN for flame retardant and UV-protective finishes. The advantages of the in situ ammonia-smoking method are that it is simple, produces no wastewater, is environmentally friendly, is inexpensive and can produce ZnO inside cotton fibers, which greatly improves the washability of ZnO/cotton fabric. In addition, ZnO and FHPOPN can play a synergistic flame retardant role. The flame retardancy properties and burning behavior of the treated fabrics were studied. Furthermore, the UV-blocking performance of the developed ZnO/FHPOPN-treated cotton was investigated. These obtained results revealed that finished cotton has UV-blocking properties in addition to the flame retardant properties.

Experimental

Materials

Bleached cotton (120 g/m^2, 133 × 72, 40 s) was purchased from a market (Shanghai, China). Dicyandiamide, phosphorous acid and urea were obtained from Sinopharm (Shanghai, China). First-generation hyperbranched polyester (FHP) was purchased from Wuhan Hyperbranched Polymer Science & Technology Co., Ltd. (Wuhan, China). Zinc acetate dehydrate (ZA) and ammonia were purchased from Sinopharm (Shanghai, China).

In situ ammonia-smoking method to fabricate ZnO/cotton fabric

The fabrication of ZnO/cotton fabric was carried out using a previously described method (Ling and Guo 2019). ZA was dissolved in distilled water to obtain concentrations of 40 g/L, 55 g/L, and 70 g/L, respectively, and then pieces of cotton fabric were dipped into the solutions for 5 min. After removing the excess the solution, the samples were put into a lidded beaker with ammonia. The ammonia-smoked samples were removed after a certain time, dried and cured, then washed and dried again.

Preparation of ZnO/FHPOPN cotton fabric

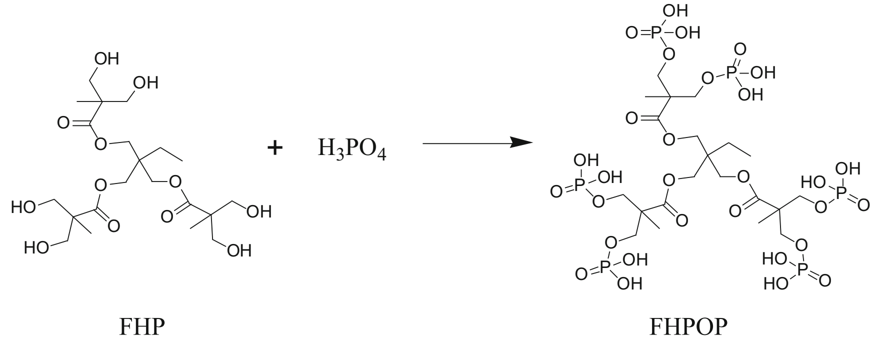
FHP was dissolved in H_3PO_4 in a flask (500 mL). The mixture was held at 120 °C for 4 h, yielding a viscous liquid FHPOP. Urea was added and incubated at 110 °C for 1 h to obtain FHPOPN by ethanol precipitation. The ^{31}P NMR spectra of FHPOPN showed three signals at -3.59 (P_1, P_2, P_3, P_4), −14.25 (P_5) and -53.63 (P_6) ppm.

FHPOPN was dissolved in distilled water to obtain varying concentrations of solution. Then, a 5 wt% dicyandiamide catalyst was added to the solutions to promote the FHPOPN reaction with cellulose. The ZnO/cotton sample was dipped into the mixture at 70 °C with a 1:20 bath ratio. The sample was padded to obtain a 100 wt% wet pickup and baked at 170 °C for 5 min in an automatic continuous baking machine. The treated sample was washed and dried at 80 °C. The weight gain (WG) was calculated using Eq. (1):

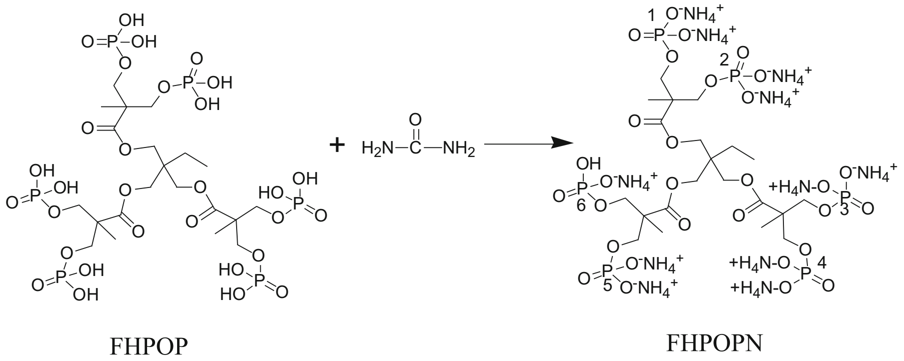
$$WG = (W_1 - W_0)/W_0 \times 100\% \tag{1}$$

where W_0 and W_1 represent the weight of cotton fabric before and after modification, respectively. FHPOPN can bind with cellulose through P-O-C covalent bonds (Gao et al. 2015). The preparation of the FHPOPN-treated sample is shown in Scheme 1.

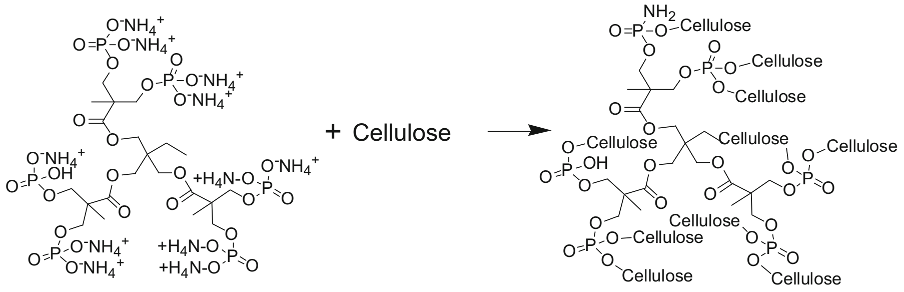
Scheme 1 **a–c** The preparation of FHPOPN-treated cotton fabric



(a) The synthesis of FHPOP



(b) The synthesis of FHPOPN



(c) The reaction between FHPOPN and cellulose

Characterization

The Fourier transform infrared (FTIR) spectra of the untreated sample, FHPOPN-treated sample, and ZnO/FHPOPN-treated sample were recorded in the range of 4000 to 400 cm^{-1} by a NicoletIn10 MX/Nicolet6700 spectrophotometer (USA).

NMR spectroscopy of FHPOPN was conducted on an AVANCE400 spectrometer (Switzerland).

The surface morphology of the untreated and treated samples was observed by a Quanta250 scanning electron microscope (Japan).

Thermogravimetric (TG) analyses were evaluated using a Pyris 1 thermogravimetric analyzer (Netherlands). The samples were tested from 30 to 800 °C at a heating rate of 20 °C/min under a nitrogen atmosphere.

Cone calorimetry was performed to investigate the combustion behavior of samples according to the ASTM E 1354 standard. The irradiation heat flux was

35 KW/m^2 in the horizontal configuration. The following parameters were recorded: time to ignition (TTI, s); heat release rate (HRR, kW/m^2); total heat release (THR, kW/m^2); and CO_2/CO were recorded.

Vertical flammability tests were performed to observe the flame retardancy of the samples, and were conducted on a YG815B fabric vertical flammability tester (China) with reference to the ASTMD6413-99 standard.

The flammability of all samples was determined by the limiting oxygen index (LOI) of the ASTM D2863-2000 standard. The LOI values of the samples were obtained using an M606B digital display oxygen index apparatus (China).

The durability of the finished samples was evaluated using a washing fastness tester (England) according to the AATCC 61–2006 standard. One washing cycle was considered equivalent to five home machine launderings.

The ultraviolet protection factor (UPF) was measured by a UV2000F-type fabric SPF analyzer to evaluate the UV-protection properties of the samples according to AATCC method 183–2010.

The tensile strength of the samples was determined by a YG026MB multifunction electronic fabric strength tester (China) according to the ASTM 5035-2006 standard.

The stiffness of the samples was tested using an LLY-01-type computer-controlled stiffness tester (China) with reference to the ASTM D 1388-96 (2002) standard.

Results and discussion

FTIR analysis of samples

The FTIR spectra of the untreated, FHPOPN-treated and ZnO/FHPOPN-treated samples are shown in Fig. 1. For untreated and treated samples, the signal peaks at 3338 cm^{-1} and 2900 cm^{-1} were assigned to –OH and -CH absorption vibrations, respectively (Li et al. 2015), and the peak at 1111 cm^{-1} corresponded to the C–O–C absorption vibration. For the FHPOPN-treated and ZnO/FHPOPN-treated samples, the peak at 1697 cm^{-1} was assigned to the N–H bond stretching vibration and the characteristic peak located at 1737 cm^{-1} was assigned to the stretching vibration C=O due to oxidation of the hydroxyl groups (Gao et al. 2015). For the treated sample, the new band at 771 cm^{-1} was assigned to the P-N peak, and the absorption band at 1244 cm^{-1} was attributed to the P = O stretching vibration (Gospodinova et al. 2002). In addition, the vibration peak of P–O–C at 1591 and 984 cm^{-1} confirmed that the FHPOPN FRs had been grafted onto cellulose by P–O–C bonds via the flame retardant finishing process (Wang et al. 2017, 2018; Alvarado et al. 2016). Compared with the FHPOPN-treated sample, a weak peak at 491 cm^{-1} appeared in the spectrum of the ZnO/FHPOPN-treated sample confirming the presence of ZnO. The FTIR spectra coincide with Scheme 1c, which may be the reason for the excellent durability of FR-treated samples.

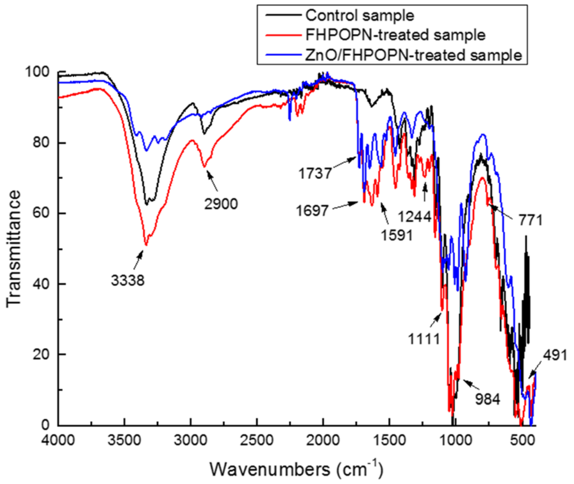


Fig. 1 FTIR spectra of the untreated sample, FHPOPN-treated sample and ZnO/FHPOPN-treated sample

Morphologies of samples.

SEM was employed to assess the surface morphologies of the samples. Figure 2a shows that the cotton fibers appeared to be flat and curly. Figure 2b shows that the ZA treatment caused almost no damage to the fibers. The FHPOPN-treated sample became slightly a little swollen compared with the untreated sample (Fig. 2c), which may be caused by FHPOPN entering the cotton fiber to expand the cellulose. In Fig. 2d, it can be seen that the carbon frames of the burnt FHPOPN-treated samples were integrated because of the polyphosphate acid formed by the FHPOPN, which can promote char formation. Some bubbles can be seen on the surface of the fibers, which may be caused by nitrogen during combustion. Compared

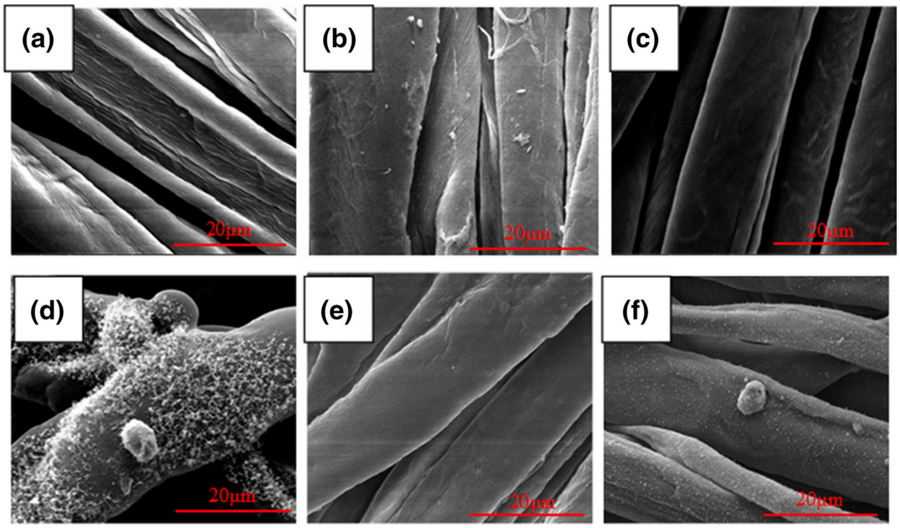


Fig. 2 SEM images of untreated sample (**a**), ZnO/cotton sample (**b**), FHPOPN-treated sample (**c**), FHPOPN-treated sample after burning (**d**), ZnO/FHPOPN-treated sample (**e**) and ZnO/FHPOPN-treated sample after burning (**f**). Scale bars are 20.0 μm in (**a**, **b**, **c**, **d**, **e**, **f**)

with the FHPOPN-treated sample, the surface of ZnO/FHPOPN-treated cotton fibers became rough as shown in Fig. 2e, showing that some FHPOPN FRs coated the fiber surfaces due to the existence of ZnO in the fibers. The residual char of the burnt ZnO/FHPOPN-treated samples also remained intact (Fig. 2f), which demonstrated that nano ZnO and FHPOPN could play a synergistic role in forming a physical barrier on the surface of samples to prevent the transfer of combustible gas and heat.

Thermal properties of samples

The thermal and thermo-oxidative stabilities of untreated and treated samples were investigated by TG analysis under a nitrogen atmosphere. Figure 3 shows the TGA (a) and DTG (b) curves of the samples. The TG data of the samples can be seen in Table 1. The thermal degradation of cotton under nitrogen involves depolymerization to generate volatile levoglucosan and dehydration to promote thermally stable char (Malucelli et al. 2014; Dong et al. 2018).

Figure 3a shows the thermal degradation of the samples. There was a slight weight loss of the samples due to the evaporation of adsorbed water at the initial temperature. For the untreated sample, the weight quickly declined from 305 to 398 °C with a 75% weight loss. The FHPOPN-treated sample decomposed earlier than the untreated sample because the FHPOPN-treated sample can release phosphorus acid to accelerate dehydration to form a stable char, which could prevent the spread of volatile gases and heat (Zheng et al. 2017). At 800 °C, the FHPOPN-treated sample left 29.7% char residue, which was much higher than that of the untreated sample (2.5%). The results implied that the FHPOPN-treated sample had an effective physical barrier that protected the combustion products from heat and oxygen (Chang et al. 2011). The ZnO/FHPOPN-treated sample underwent a degradation process similar to that of the FHPOPN-treated sample. The char yield of the ZnO/FHPOPN-treated sample was 33.3%, which was slightly higher than that of the FHPOPN sample. The results showed that ZnO played a catalytic role in the formation of char.

The thermos-oxidative stability of untreated and treated samples is displayed in Fig. 3b. The onset degradation temperature of the untreated cotton was 305 °C and presented a maximum weight loss at 383 °C, while the maximum decomposition temperature of the FHPOPN-treated sample was only 317 °C. In the first stage (below 305 °C for the untreated cotton, 253 °C for the FHPOPN-treated sample and 260 °C for the ZnO/FHPOPN-treated sample), the change in mass was caused by water evaporation. The second stage (305–566 °C for the untreated sample, 253–363 °C for the FHPOPN-treated sample and 260–350 °C for the ZnO/FHPOPN-treated sample) involved the generation of aliphatic char and volatile products. Some aliphatic char was oxidized to aromatic char, while some yielded CO and CO_2 (Shariatinia et al. 2015; Jia et al. 2017). In the third stage (above 566 °C for the untreated sample, 363 °C for the FHPOPN-treated sample and 350 °C for the ZnO/FHPOPN-treated sample), the residue was further oxidized to CO_2 and CO (Price et al. 1997). These results demonstrated that FHPOPN can catalyze the dehydration of cotton to promote the formation of stable char, preventing the spread of fire and thus improving the flame retardancy of cotton. Furthermore, the ZnO/FHPOPN-treated sample had higher thermo-oxidative stability than the origin cotton.

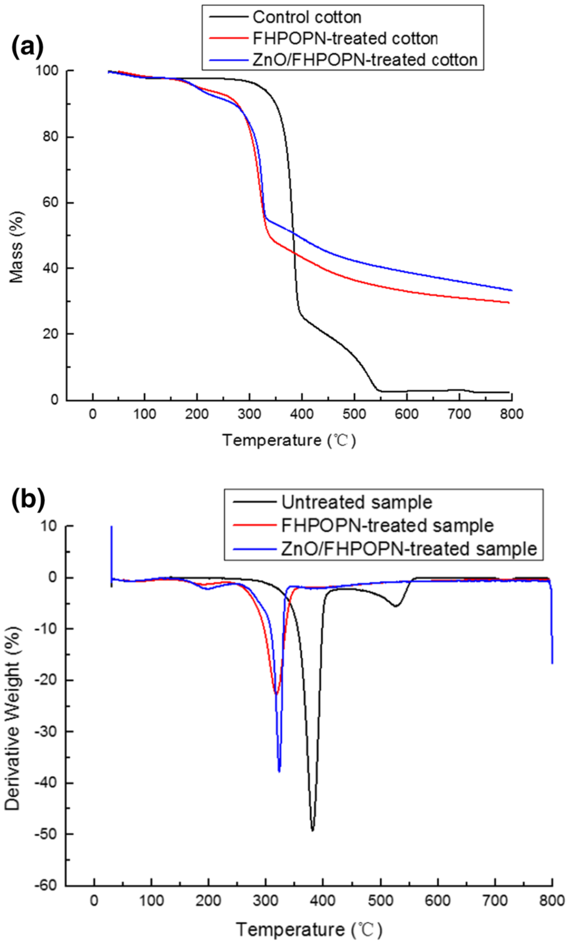


Fig. 3 Thermogravimetric analysis of the untreated sample, FHPOPN-treated sample and ZnO/FHPOPN-treated sample

Vertical flammability tests

Vertical flame tests were utilized to observe the flame retardant performance of the untreated, FHPOPN and ZnO/FHPOPN-treated samples. The results and relevant data are displayed in Table 2 and Fig. 4. As shown in Fig. 4, the untreated fabric burned intensely and quickly, and was completely destroyed after 12 s of ignition. The after-flame and after-glow times were 13 and 17 s, respectively. All FHPOPN- and ZnO/FHPOPN-treated samples did not noticeably burn and self-extinguished as soon as the ignition source was turned off. The char residue of treated samples was narrow and intact, and these results are positively correlated with flame resistances (Kandola et al. 1997). The char residual of all concentration FHPOPN-treated fabrics had no cracking, indicating that the FHPOPN-modified cotton had excellent flame retardant performance. The char lengths of ZnO/FHPOPN-treated samples with 40 g/L, 55 g/L, and 70 g/L ZA were 61, 59, and 57 mm, respectively, which showed that ZnO had little effect on vertical combustion.

LOI

LOI was used to indicate the difficulty of combustion. Table 3 lists the LOIs of samples treated with different FHPOPN concentrations. The LOIs of the samples increased from 27.4% to 38.7% with increasing of FHPOPN concentration from 80 to 200 g/L. The LOI value of the untreated sample was only 17.2%, which was far below that of the treated samples. For the 120 g/L FHPOPN-treated sample, the LOI value reached 31.6%. After 30 and 50 laundering cycles

Table 1 TG data of the samples

Samples	$T_{10\%}$ (°C)	T_{max} (°C)	Residue at 800 °C (%)
Control sample	349	383	2.5
FHPOPN-treated sample	276	318	29.7
ZnO/FHPOPN-treated sample	270	322	33.3

Table 2 Vertical flammability data of samples

Samples	FHPOPN Concentration (g/L)	ZA Concentration (g/L)	After-flame time (s)	After-glow time (s)	Char length (mm)
Untreated fabric	0	0	13	17	300
FHPOPN treated fabric	80	0	0	0	80
	120	0	0	0	73
	160	0	0	0	63
	200	0	0	0	55
ZnO/FHPOPN treated fabric	160	40	0	0	61
	160	55	0	0	59
	160	70	0	0	57

*The data of untreated samples in the manuscript are obtained from Ling and Guo (2020).

(LCs), the LOIs of the HBPOPN-treated samples remained at 27.3% and 22.9%, respectively, meaning that these samples can be considered semidurable flame retardant cotton fabrics. When the FHPOPN concentration increased to 160 g/L, the LOI value was 35.5%, which indicates a higher flame retardancy and good washability. After 30 and 50 LCs, the LOIs decreased to 30.1% and 26.1%, respectively, which could be regarded as durable flame-resistant materials. The LOIs of 200 g/L HBPOPN-treated cotton fabrics reached 38.7%, and after 50 LCs, the LOI value was still 29.0%, demonstrating the excellent flame retardancy and durability of FHPOPN-treated cotton fabrics. An FHPOPN molecule has 10 reactive groups that can react with cellulose to form P-O-C bonds. Therefore, the HBPOPN FR was difficult to remove from cotton. These results suggested that the FHPOPN FR had been successfully grafted onto cotton, which could be recognized as a durable FR for cotton fabrics. For the ZnO/FHPOPN-treated sample, the LOI value was only slightly higher than that of the FHPOPN-treated sample, which may be due to ZnO and FHPOPN playing a synergistic flame retardant role.

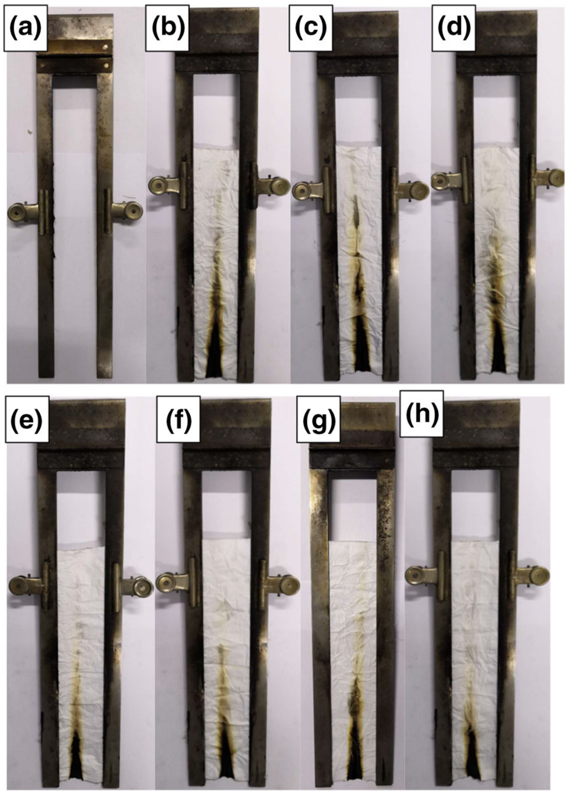


Fig. 4 The images of burnt samples **a** untreated fabric **b** 80 g/L FHPOPN **c** 120 g/L FHPOPN **d** 160 g/L FHPOPN **e** 200 g/L FHPOPN **f–g** 40, 55, 70 g/L ZA with 160 g/L FHPOPN

Cone calorimetry

Cone calorimetry was employed to investigate the combustion behavior of cotton. The relevant data, such as TTI, PHRR (peak heat release rate), FGR (fire growth rate) and CO_2/CO, are shown in Table 4. The treated samples could not be ignited, suggesting the excellent flame retardancy of the treated samples. The HRR and THR curves of the samples are shown in Fig. 5. For the FHPOPN-treated sample, a PHRR of 33 kW/m^2 showed an 81% reduction compared with that of the control sample (171 kW/m^2). The PHRR of the ZnO/FHPOPN-treated sample was 26 kW/m^2, which was slightly lower than that of the FHPOPN-

Table 3 LOIs of the untreated, FHPOPN-treated and ZnO/FHPOPN-treated cotton fabrics

Sample	Concentration (g/L)	LOI			
		0 LCs	10 LCs	30 LCs	50 LCs
Untreated fabric	0	17.2	–	–	–
FHPOPN-treated fabric	80	27.4	25.5	23.9	19.6
	120	31.6	29.3	27.3	22.9
	160	35.5	32.7	30.1	26.1
	200	38.7	34.8	32.3	29.0
ZnO/FHPOPN-treated fabric	160	36.4	32.8	30.2	26.0

Table 4 The relevant parameters of cone calorimetry

Sample	TTI(s)	PHRR(kW/m^2)	FGR[kW/(m^2 s)]	[CO$_2$]/[CO]
Untreated	17	171	3.97	56.51
FHPOPN	–	33	0.20	3.44
ZnO/FHPOPN	–	26	0.13	1.75

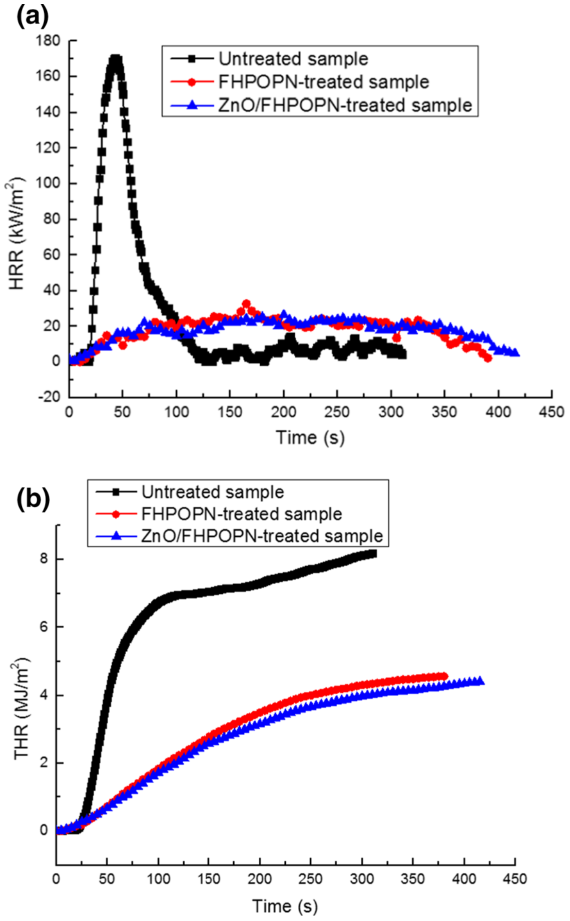


Fig. 5 HRR (**a**) and THR (**b**) curves of samples

treated sample. Figure 5b shows that the THR of the untreated sample was 8.2 MJ/m^2, and the THR of 160 g/L FHPOPN-treated sample was 4.6 MJ/m^2, which decreased 44.0% more than that of the untreated sample. When the ZA concentration of ZnO/FHPOPN-treated fabric reached 70 g/L, the THR was 4.4 MJ/m^2, which was slightly lower than FHPOPN-treated fabric. These results demonstrated that the FHPOPN FR can accelerate the dehydration and carbonization of cotton to form a dense char layer, which can limit the diffusion of heat and fuel, causing a relatively low THR (Kim et al. 2015). The FGR ([PHRR]/[T$_{PHRR}$]) represent the fire risk of materials, and the lower the FGR is, the lower the fire hazard.

[CO$_2$]/[CO] reflects combustion efficiency; the ratios for FHPOPN- and ZnO/FHPOPN-treated cotton were 3.44 and 1.75, respectively, versus 56.51 for the untreated sample. The low CO$_2$/CO value indicated prevented combustion (Dong et al. 2017). These results showed that the FHPOPN FR possessed excellent fire resistance in an actual fire environment, and ZnO NPs had a synergistic flame retardant role in the treated fabric.

UV-blocking property

Radiation at wavelengths of 320–400 nm (UVA) can cause skin damage when the skin is exposed to sunlight for a long time. Rays of light with wavelengths of 290–320 nm (UVB) cause skin burns and erythemas. Furthermore, UV radiation can cause a photochemical effect within polymer structures, which can lead to the degradation of some polymers (Bharathi Yazhini and Gurumallesh Prabu 2015). Therefore, the finish of cotton fabrics with UV protection can extend their service lifetime.

The UV-blocking properties of untreated and treated samples are shown in Table 5. The effect of ZnO NPs on the UV-blocking properties of the treated samples was also investigated. The origin cotton was measured to be 28.59 UPF, 1.64% T_{UVA} and 2.82% T_{UVB}, which indicate weak UV-protection properties. FHPOPN-treated cotton had a 36.25. The UPF value was only slightly higher than that of the original cotton. After treatment with nano ZnO, the UPF values of the cotton increased obviously, which means that the UV-protection properties increased. When the ZA concentration was 40 g/L, the UPF value of ZnO/FHPOPN-treated cotton fabric was 62.91, which indicates good UV protection. With increasing ZA concentration, the ZnO NP content in the treated samples increased, the UPF values increased, and the T_{UVA} and T_{UVB} values decreased accordingly. When the concentration of ZA was 70 g/L, the treated sample reached a higher UPF value of 224.80. UV-blocking results confirmed the excellent UV protective property of the ZnO/FHPOPN-treated sample due to the presence of ZnO NPs.

Physical properties

The breaking strength and bending rigidity were tested for a control and for treated cotton, and the results are listed in Table 6. As shown in Table 6, the tensile strength gradually decreased with increasing FHPOPN concentration. Compared with that of the control cotton sample, the breaking strength of 160 g/L FHPOPN-treated cotton was decreased by 19.2% and 21.2% in the warp and weft directions, respectively. This decrease in strength may be due to the oxidation of cellulose during the high-temperature finish. The bending rigidity of treated cotton increased with increasing FHPOPN concentration. The bending rigidity of the 160 g/L FHPOPN-treated cotton increased by 15.8% and 14.2% in the warp and weft directions, respectively, compared with that of control cotton. In addition, the breaking strength of ZnO/FHPOPN-treated cotton was decreased in the warp and weft directions compared with that of FHPOPN-treated cotton, which was ascribed to the presence of ZnO. These results suggest that the treatment only slightly influenced the application of ZnO-doped cotton in the textile industries.

Conclusions

An in situ ammonia-smoking method was developed to fabricate ZnO/cotton fabric. A novel halogen-free and formaldehyde-free FHPOPN FR was successfully synthesized and applied to ZnO/cotton fabric, as confirmed by ^{31}P NMR and FTIR. The ZnO/FHPOPN-treated cotton fabric exhibited excellent flame resistance and UV protection properties. Vertical flammability tests, LOI, TG and cone calorimetry were performed on the treated fabrics and used to investigate the flame retardancy property of treated samples. The treated cotton fabrics had no after-flame or afterglow in the vertical flammability tests. The LOI of the 160 g/L FHPOPN-treated sample was 26.1% even after 50 LCs, showing that the sample had excellent flame retardancy and washability. The FHPOPN-treated and ZnO/FHPOPN-treated cotton fabrics showed high thermal stability with 29.7% and 33.3%

Table 5 UV protective properties of samples

Sample	FHPOPN Concentration (g/L)	ZA Concentration (g/L)	T_{UVA}/%	T_{UVB}/%	UPF
Origin cotton	0	0	1.64	2.82	28.59
FHPOPN-treated cotton	160	0	1.53	2.13	36.25
ZnO/FHPOPN-treated cotton	160	40	0.89	1.17	62.91
	160	55	0.24	0.44	145.63
	160	70	0.23	0.34	224.80

Table 6 Breaking strength and bending rigidity of the samples

Samples	Breaking strength (N)		Bending rigidity (mm)	
	Warp	Weft	Warp	Weft
Control cotton	764	345	24.7	18.3
80 g/L FHPOPN	724	331	26.7	19.5
120 g/L FHPOPN	658	304	27.5	20.4
160 g/L FHPOPN	617	272	28.6	20.9
200 g/L FHPOPN	572	263	30.3	22.5
70 g/L ZA + 160 g/L FHPOPN	589	259	29.1	21.5

char yields at 800 °C, respectively. The PHRR and THR of the treated samples were dramatically decreased compared with those of the untreated sample. In total, nano ZnO played a synergistic role in increasing fire resistance. In terms of UV-protection properties, the UPF value of ZnO/FHPOPN-treated cotton fabric was 224.80, showing that the fabric has excellent UV-protection properties in addition to flame retardancy.

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