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Preparation and properties of cotton fabrics treated with a novel antimicrobial and flame retardant containing triazine and phosphorus components

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Abstract A novel antibacterial and flame-retardant agent, monochlorotriazine triethylphosphite guanidine (MCTPG) was synthesized successfully. The chemical structure of MCTPG was characterized by FTIR and ^{1}H NMR. The flame retardancy of treated cotton fabric was evaluated by limiting oxygen index (LOI), the vertical burning test and cone calorimeter, respectively. The treated cotton fabric obtained good flame retardancy with a LOI value of 31.2%, and the char length decreased to 8.5 cm. The ignition time increased, and the values of total heat release, heat release rate, mass loss decreased. The thermal stability and surface morphology of treated cotton fabric were investigated by thermogravimetric analysis and scanning electron microscope (SEM), respectively. The results showed that MCTPG played a protective role in the degradation of cotton fabrics, hindered the formation of volatile species and favored the formation of char. Furthermore, the antimicrobial activity of treated cotton fabrics was tested. And it showed that the inhibition zone of the treated cotton fabrics base to *Escherichia coli* and *Staphylococcus aureus* reached to 2.9 mm and 2.8 mm, respectively.

Keywords Cotton · Guanidine · Antibacterial and flame-retardant agent · Thermal stability · Antimicrobial activity

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Introduction

Cotton fabrics have been widely used in both military and civilian textile areas due to their excellent properties [1–6]. But the LOI value of pure cotton is only 18%. It can cause immense human and economic damage [7]. In other words, the real encumbrance of a wider application for cotton fabrics is their flammability. Therefore, it is important to explore flame-retardant agent which can improve the flame retardancy of cotton fabrics [8–10]. Some compounds which consist of flame-retardant elements such as phosphorus, silicon, boron, nitrogen and other miscellaneous elements have gained much attention as the flame retardant of polymer materials. Researchers have found these elements can obviously improve the thermal stability of cotton fabric [11]. In order to improve the flame-retardant efficiency, the attempts taking advantage of the synergetic effects of two elements with flame-retardant characteristics have been reported in the recent years [12–15].

Besides, the good hygroscopicity and breathability of cotton fabrics lead to the growth and multiplication of bacteria and other microorganisms, which can affect the appearance and wear ability of cotton fabrics [16, 17] and is harmful to human health. Therefore, there is an urgent need to develop effective antibacterial agents applied for cotton fabrics to improve antimicrobial activity of cotton fabrics.

With the development of society and economy as well as the improvement in people's living standards, fabrics with a single functional can no longer meet people's needs. In contrast, complex functional fabrics are gradually getting more attention. In recent years, various efforts have been made to develop complex functional agents. A lot of fiber composite functional additives have emerged, such as water- and oil-repellent antibacterial agents, water-

repellent flame retardants, antistatic flame-retardant and UV antibacterial agents [18, 19].

In this study, ethanolamine, cyandiamide, phosphorus trichloride and cyanuric chloride are used to synthesize monochlorotriazine triethylphosphite guanidine (MCTPG). Firstly, ethanolamine's amino reacted with cyanamide's cyano through nucleophilic addition reactions, to prepare guanidine-containing compound (GC). Secondly, GC's hydroxyl reacted with phosphorus trichloride through esterification reaction, to prepare guanidine-containing phosphate (GP). Finally, GP reacted with cyanuric chloride, to prepare the reactive flame-retardant and antibacterial composite functional compound, monochlorotriazine triethylphosphite guanidine (MCTPG). The cotton fabric treated with MCTPG obtained good antibacterial activity and flame retardancy. The treated cotton fabrics also have good durability due to the chlorine triazine structure MCTPG contains which can form a covalent bond with cotton fabrics by dechlorination reaction.

Experimental

Materials

Desized, scoured and bleached cotton fabric was purchased from Weifang Qirong Textile Co., Ltd, Weifang, China. Ethanolamine was obtained from Tianjin Guangcheng Chemical Reagent Co., Ltd, Tianjin, China. Cyandiamide was obtained from Shanghai Jingchun Biochemical Technology Co., Ltd, Shanghai, China. Phosphorus trichloride was obtained from Laiyang Economic Development Zone Fine Chemical Plant, Laiyang, China. Cyanuric chloride was obtained from Chengdu Aikeda Chemical Reagent Co., Ltd, Chengdu, China.

Tryptone and beef extract were obtained from Beijing Shuangxuan microbiological culture medium products factory. Agar powder was obtained from Shanghai Science and Technology Development Co., Ltd. Sodium chloride was obtained from Shanghai Qiangshun Chemical Co., Ltd.

Synthesis of guanidine-containing compound (GC)

In a 250-mL of glass flask equipped with a stirrer and a condenser, ethanolamine (61 g, 1 mol) and cyandiamide (42 g, 1 mol) were added. The pH value of mixture was adjusted to 3 using glacial acetic acid, and the mixture was stirred at 70 °C for 2 h. Thereafter, the mixture was gradually heated and refluxed at 70 °C for 2 h. Then, the resulting raw product was filtered and washed with ethanol. Evaporation of the solvent and other volatile species from the filtrate at room temperature gave GC (84.5 g, 82% yield) (Scheme 1).

Synthesis of guanidine-containing phosphate (GP)

A mixture of phosphorus trichloride (37.1 g, 0.27 mol) and GC (84.5 g, 0.82 mol) was putted into a 250 mL of glass flask, and then, the mixture was stirred at 5 °C for 2 h in a nitrogen atmosphere. The resulting raw product was filtered and washed with ethanol. Evaporation of the solvent and other volatile species from the filtrate at room temperature gave GP (71 g, 78% yield) (Scheme 2).

Synthesis of monochlorotriazine triethylphosphite guanidine (MCTPG)

A mixture of cyanuric trichloride (18.5 g, 0.1 mol) and GP (71 g, 0.2 mol) was putted into a 250 mL of glass flask, and then, the mixture was stirred at 90 °C for 2 h in a nitrogen atmosphere. The resulting raw product was filtered and washed with ethanol. Evaporation of the solvent and other volatile species from the filtrate at room temperature gave MCTPG (44 g, 72% yield) (Scheme 3).

Preparation of treated cotton fabrics

The cotton fabrics were dipped in finishing liquid and kept at 60 °C for 15 min. Then sodium chloride was added, and the mixture was stirred it evenly at 60 °C for 15 min. After that, the reaction temperature was increased to 90 °C; at the same time, sodium carbonate was added into the finishing liquid. The cotton fabrics were treated for 60 min in the finishing bath. At last, the cotton fabrics were washed with water and dried thoroughly (Scheme 4).

Measurements

FTIR and NMR analysis

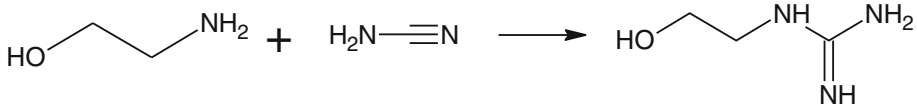
FTIR analysis was conducted by using Nicolet 5700 Fourier transform infrared spectroscopy, which can be applied to analyze the structure of the synthesized product.

The structure of MCTPG was verified by ^{1}H NMR spectrum (JEOL LA500, Japan). The sample was placed in a nuclear tube, dissolved with CD_3OH.

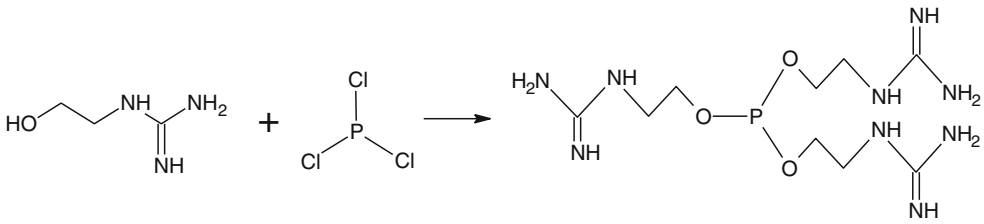
Flame-retardant test

Limiting oxygen index was referred to GB/T 5454-1997, using LFY-606B Digital limiting oxygen index analyzer. The vertical burning test was conducted according to GB/T 5455-2014, using LFY-601A instrument, Shandong, China.

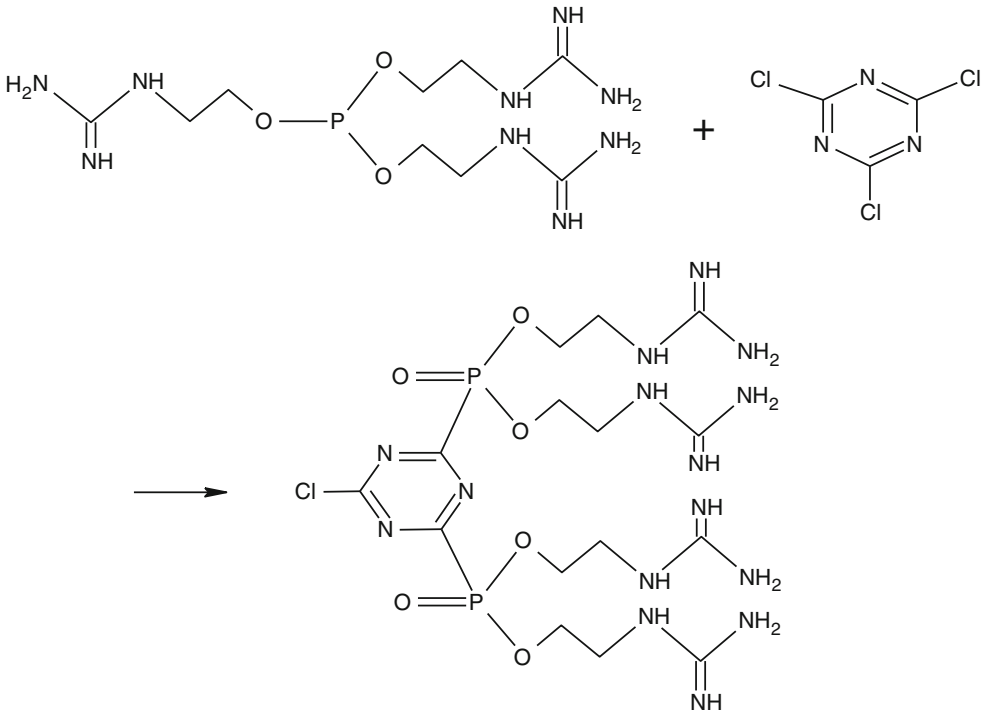
Scheme 1 Preparation of GC



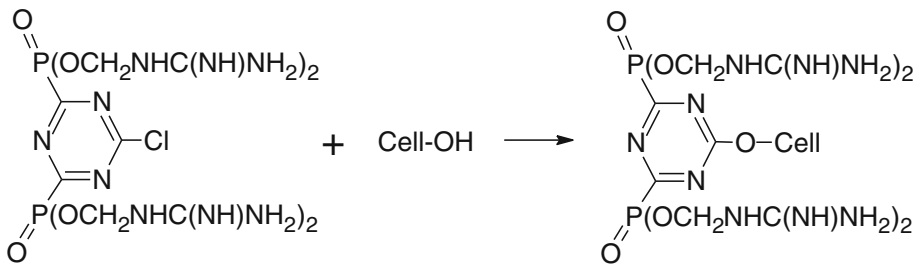
Scheme 2 Preparation of GP



Scheme 3 Preparation of MCTPG



Scheme 4 Preparation of treated cotton fabric



Combustion test

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. The parameters calculated were fire performance index (FPI, s m^2 kW^{-1}) and CO_2/CO ratio.

Thermal analysis

Thermogravimetric analysis was conducted by using HTG-1 thermal analyzer in a temperature range of 50–700 °C in static air atmosphere at a heating rate of 10 °C min^{-1}. Sample mass was in the range of 3–5 mg.

Antibacterial test

Antibacterial test was referred to GB/T 20944.3-2008. Two layers of agar were poured on glass plate, the bottom layer was a sterile medium, and the top layer was culture medium for inoculating bacteria. The treated cotton fabric was cut into a round specimen having a diameter of 25 mm. The sample was placed on two layers of medium. Each of the bacteria tested four samples (two frontside samples, two backside samples). After the glass plate was incubated in biochemical incubator for 24 h, the outermost diameter of the antibacterial zone was measured.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was conducted to investigate the surface morphology of the residue of the samples after combustion.

Breaking strength test

Breaking strength test was referred to GB/T 3923.1-2013. Ten pieces of treated samples (five warp samples, five weft samples, and the size of each sample is 200 mm × 50 mm.) were tested.

Whiteness test

Whiteness test was referred to GB/T 17644-2008. The treated samples were folded into eight layers, using the automatic colorimeter SC-80C to measure the whiteness of the samples.

Washing durability test

Washing durability test refers to GB/T 8629-2001. The finished cotton fabric was washed with simulated household washing conditions. The LOI values of cotton fabric and the inhibition zone of *Escherichia coli* and *Staphylococcus aureus* were measured after washing.

Results and discussions

FTIR and NMR analysis

The absorption peaks at 1620 and 1499 cm^{-1} are assigned to stretching vibration of C = N. The characteristic peaks at 3479 and 3378 cm^{-1} were attributed to the stretching vibration of N–H. The characteristic peaks at 1227 cm^{-1} are due to the stretching vibration of P = O [20]. These absorption peaks arising from characteristic groups prove that the target product of MCTPG is synthesized successfully (Fig. 1).

The ^{1}H NMR spectrum of MCTPG is shown in Fig. 2. The peak at δ 3.36 ppm is attributed to $\underline{CH_2}NH$ protons (2H), and δ 2.58 ppm is attributed to $\underline{CH_2}O$ protons (2H). The peak at δ 3.02 ppm is attributed to guanidyl groups (4H). The peak of guanidyl groups becomes a whole broad peak [21], because of the forming of hydrogen bonds. The peak of CD_3OH is at δ 3.31 ppm. However, it's covered by the peak of CH_2NH. These results prove that the target product is synthesized successfully.

Flame-retardant performance

LOI values of the fabric samples are presented in Table 1. It shows that the LOI values of the treated samples are much higher than those of the untreated sample. The fabric sample treated with 300 g L^{-1} of MCTPG has the highest LOI value of 31.2%, which is 13.2% higher than that of the untreated sample (18.0%). The LOI value of treated cotton fabrics increases from 24.3 to 31.2% while the concentration of MCTPG in the flame-retardant finishing bath increases from 150 g L^{-1} to 300 g L^{-1}. The upward burning behavior of the cotton fabric samples has been

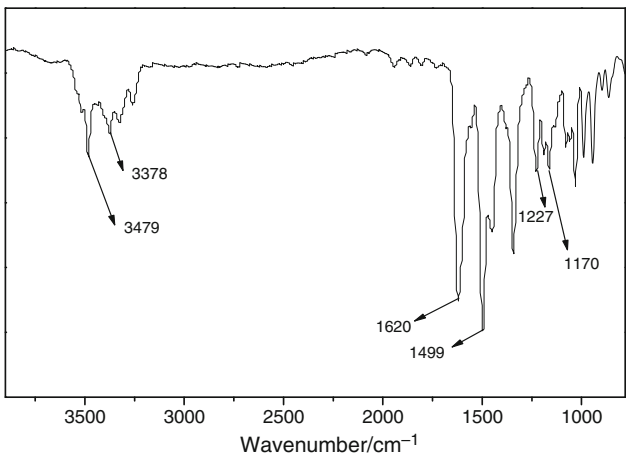


Fig. 1 FTIR spectra of MCTPG

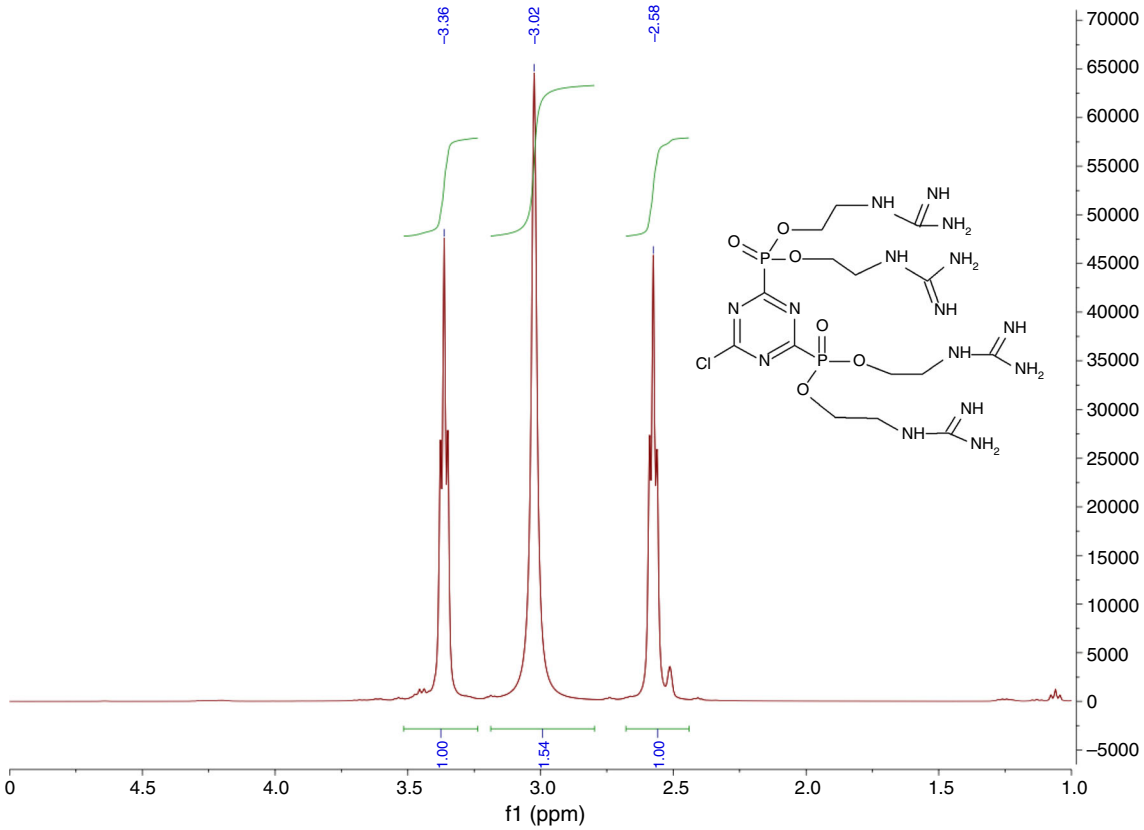


Fig. 2 ^{1}H NMR spectrum of MCTPG in CD_3OH

Table 1 Flame-retardant performance of the cotton fabrics

MCTPG/ g L^{-1}	LOI/ %	Vertical burning test		
		After-flame time/s	After-glow time/s	Char length/ cm
0	18.0	N.R[a]	N.R	T.D[b]
150	24.3	0	2.2	14
200	27.7	0	1.4	12
250	30.2	0	0	10
300	31.2	0	0	8.5

[a] N.R denotes no record due to the complete destruction of the fabrics

[b] T.D denotes the case that fabrics were completely destroyed during the test

studied by the vertical burning test, and the results are shown in Table 1. Compared to the untreated sample, the treated samples have shorter after-glow time, shorter char length and no after-flame in the vertical burning test. The char of the treated samples after the vertical burning tests is thicker and more compact than that of the untreated sample, and the spread speed of flame on the treated sample is retarded. It can be observed that the combustion of the fabric sample treated with MCTPG of 300 g L^{-1} cannot be self-sustained in air. These phenomena are attributed to the incorporation of MCTPG, which enhances the thickness and compactness of the char and finally prevents fire from spreading. These results show that the flame retardancy of cotton fabrics can be improved with the treatment of MCTPG.

Table 2 Combustion data of cone calorimeter test

Sample	TTI/ s	PHRR/ kW m^{-2}	FPI/ s m^2 kW^{-1}	Peak EHC/ MJ kg^{-1}	Average EHC/ MJ kg^{-1}	CO/ kg kg^{-1}	CO_2/ kg kg^{-1}	CO_2/ CO
Untreated cotton	2	109.98	0.018	32.57	8.7	0.07	1.82	26
Treated cotton	16	52.89	0.3	11.29	2.3	0.13	1.29	9.92

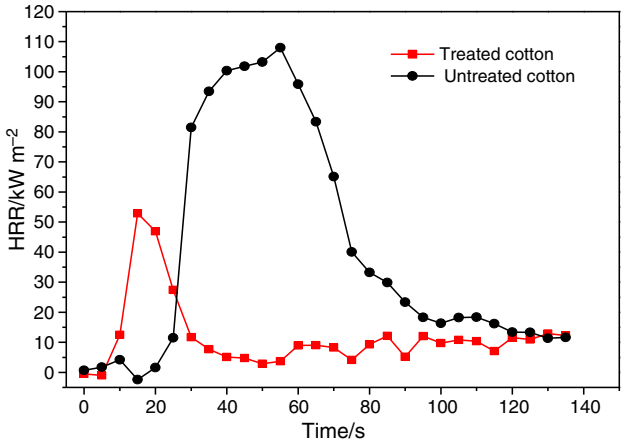


Fig. 3 HRR curves of untreated and treated cotton fabric with MCTPG

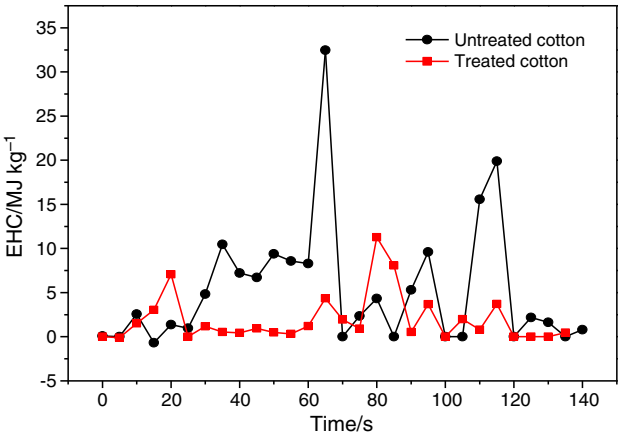


Fig. 5 EHC curves of untreated and treated cotton fabric with MCTPG

Combustion behaviors

The combustion behavior of untreated cotton and treated cotton had been investigated by cone calorimeter. The collected data are summarized in Table 2 and plotted in Figs. 3–6. From Table 2, we can know that the time to ignition (TTI) of the treated cotton (16 s) has increased significantly compared to the untreated cotton (2 s). When samples were ignited, the heat release rate (HRR) increased to a maximum (namely, PHRR) and then decreased down to the flame out (FO). The treatment with MCTPG reduces the PHRR values of cotton fabrics remarkably as shown in Fig. 3. The PHRR values of treated cotton are 52.89 kW m^{-2} while the PHRR values of untreated cotton are 109.98 kW m^{-2}. At the same time, MCTPG enhances the flame retardancy of cotton fabrics by decreasing combustion period as confirmed by the FO values and hindering the formation of volatile species as evidenced by the strong decrease in total heat release (THR) values (Fig. 4), EHC values, mass values and the increase in FPI values (Table 2). From Fig. 4, we can see THR of the untreated cotton (5.6 kJ m^{-2}) is more than THR of treated cotton (1.6 kJ m^{-2}). Effective heat of combustion (EHC) is the ratio of the mass to heat loss measured at a certain time. It reflects the degree of combustion of flammable volatile gases in the gas phase flames. From Table 1 and Fig. 5, we can know that the EHC values of treated cotton have decreased significantly. The peak ECH values and average ECH values of untreated cotton are 32.57 and 8.7 MJ kg^{-1}, respectively while the peak ECH values and average ECH values of treated cotton are 11.29 and 2.3 MJ kg^{-1}, respectively. Mass loss reflects pyrolysis of the samples at a certain temperature and thermal radiation intensity (Fig. 6). The mass loss of the treated cotton is lower than the untreated one. CO and CO_2 are the main components of fire gases. The information about mechanism of cotton fabrics' decomposition can be got by analyzing the two species [22]. Low CO_2/CO ratios mean low conversion of

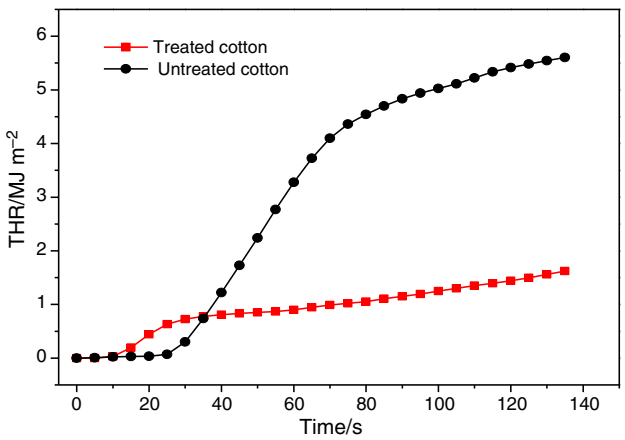


Fig. 4 THR curves of untreated and treated cotton fabric with MCTPG

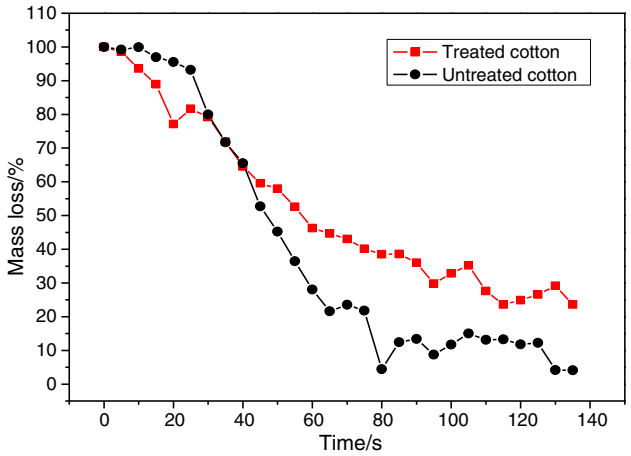


Fig. 6 Mass Loss curves of untreated and treated cotton fabric with MCTPG

CO to CO_2 and suggested inefficiency of combustion. Firstly, CO is produced in the pyrolysis of the cotton fabric. Then CO_2 was released due to the oxidation of CO when enough oxygen was available. Compared with that of untreated cotton (26), the CO_2/CO ratio of treated one is lower (9.92). All of these indicate that MCTPG enhances obviously combustion properties of cotton fabrics.

Thermogravimetric analysis

Thermal degradation properties of untreated and treated cotton fabrics have been investigated by TG analysis in air atmosphere. The results are shown in Figs. 7 and 8. The corresponding data are presented in Table 3. It can be seen that the starting decomposition temperature of the treated fabric sample with MCTPG is 197 °C, which is lower than that of the untreated sample (304 °C). As shown in many literatures, phosphorus-based flame retardants can evidently lower the decomposition temperature of cotton fabric by accelerating dehydration and producing more char [23, 24]. The cotton fabric treated with MCTPG degrades at lower temperature due to the synergistic effect arise from P, N elements contained in MCTPG. The earlier decomposition of MCTPG on cotton fabric forms 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. The main degradation temperature of untreated cotton fabric was 304–483 °C approximately. In this stage, speed of mass loss is quick and percent of mass loss is great. When the cellulose fibers degrade at a lower temperature, the molecular chain of 1,4-glycoside bond will break, and fragments of molecules will rearrange, which would lead to the generation of L-glucose. L-glucose may be formed tar-like substance by dehydration and polycondensation, and then, it decomposes into organic matter, gas and water under high temperature. What's more, flame-retardant effect of phosphorus-containing compound measures up the flame-retardant mechanism of condensed phase. It can react with hydroxyl groups of the cellulose molecules forming an ester, which can prevent the production of L-glucose and promote cellulose dehydration and facilitate cross-linking between cellulose molecules. Actually, it promotes the formation of the carbon layer, so that the final amount of char increased to 10.3%, which is higher than that of the untreated sample. Thermogravimetric analysis showed that fabrics treated with MCTPG obtained better thermal stability relative to untreated cotton.

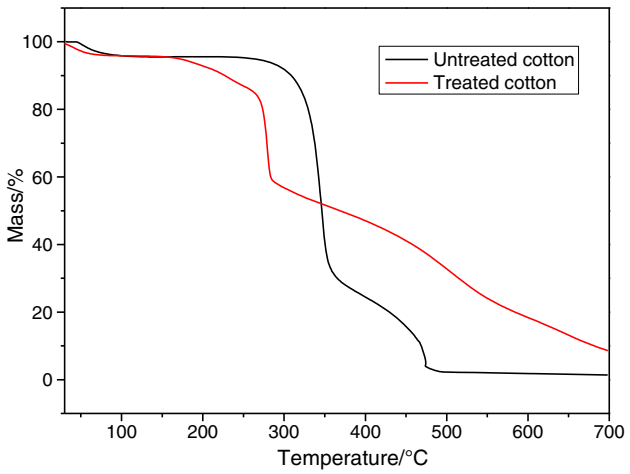


Fig. 7 TG curves of the cotton fabric samples in air

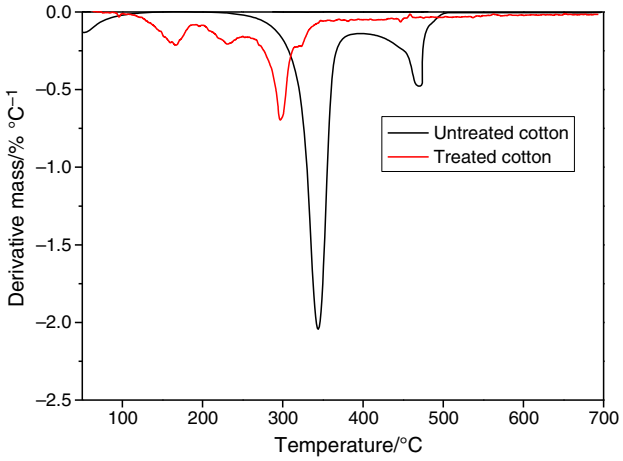


Fig. 8 DTG curves of the cotton fabric samples in air

Table 3 TG data of treated cotton fabric with MCTPG in air

Finishing agent dosage/g L^{-1}	Initial decomposed temperature/°C	Residue/%	
		600 °C	700 °C
0	304	2.1	1.9
250	197	19.8	9.6

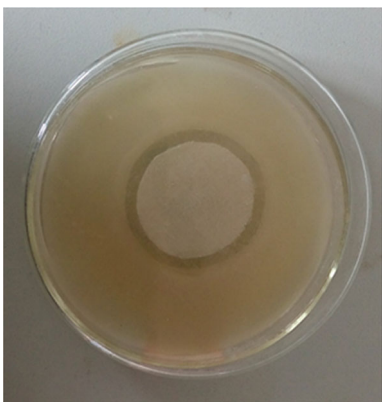


Fig. 9 Inhibition zone of *E. coli*

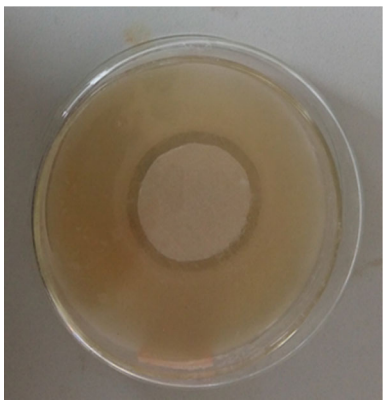


Fig. 10 Inhibition zone of *S. aureus*

Antibacterial test

As shown in Figs. 9 and 10, the inhibition zone is obvious. The inhibition zone of the treated cotton fabric base to *E. coli* and *S. aureus* reaches to 2.9 and 2.8 mm which demonstrates that treated cotton fabrics obtain a good antibacterial activity. The reason is that guanidino group of MCTPG can destroy the normal matter and energy metabolism of bacteria and kill the bacteria at last.

Surface morphology of the residues after combustion

Surface morphology of the untreated cotton fabric sample and the treated fabric sample with MCTPG was investigated by SEM (Fig. 11a, b). It showed that the untreated cotton fabric sample has a more fluffy structure compared with the treated sample. After combustion, the treated fabric sample with MCTPG still keeps its original structure completely while the untreated cotton fabric without an integral structure. The fibers morphology of the untreated pure cotton fabric sample and the treated cotton fabric sample in SEM photographs is shown in Fig. 11 c, d. The untreated pure cotton fiber was burned into ash whose structure was fluffy. In contrast, the structure of treated cotton fiber was dense which is covered by a layer. As shown in Fig. 11d, the surface of the residual char from the treated sample is uniformly continuous, which may be due to the enhancement of the char formation by flame-retardant finishing with MCTPG. Enlarged photograph (Fig. 11d) shows that the char layer on the fibers has microconvexities structure, which also indicates the compactness of the char layer. It can be concluded that MCTPG can improve the formation of the char, which acts as a physical barrier between flame and the underlying cellulose component. During the combustion, the char layer as the physical barrier inhibits the transmission of heat, energy and O_2 and retards the spreading of fire.

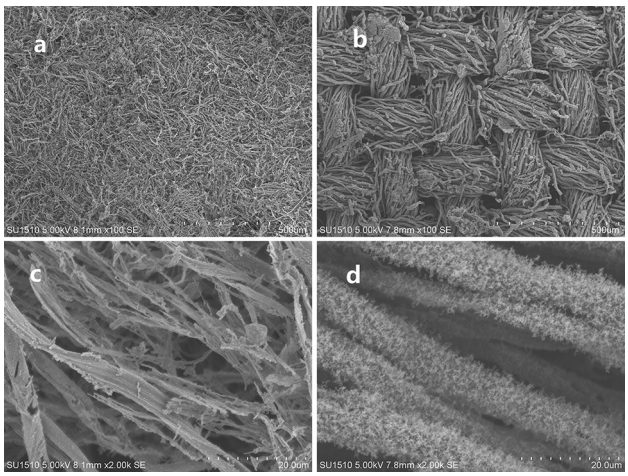


Fig. 11 SEM photographs of microstructures of the cotton fabric samples: **a** the residue of the untreated fabric sample × 100; **b** the residue of the treated fabric sample with MCTPG × 100; **c** the residue of the untreated fiber sample × 2000; **d** the residue of the treated fiber sample × 2000

Whiteness and breaking strength test

The data of the strength and whiteness of the treated cotton fabric and the untreated cotton fabric are summarized in Table 4. Compared with the pure cotton fabric, the warp breaking strength and weft breaking strength of treated fabric were decreased by 85 and 57 N, respectively. MCTPG can combine to cotton fabric with covalent bond leading to making the degree of polymer macromolecule polymerization, degree of orientation and crystallinity change. So the treated cotton fabric tensile strength decreased. In addition, the change of treated cotton fabric whiteness was not very obvious, decreased by 1.2%. So the finishing agent did not affect the whiteness of cotton fabrics.

Washing durability

From Table 5, we can see the LOI values of cotton fabric treated with MCTPG and the inhibition zone of *E. coli* and *S. aureus* were gradually reduced. After washing for 20 times, LOI of treated cotton fabric was reduced to 27.3%,

Table 4 Tests results of whiteness and breaking strength

Test content	Breaking strength/N		Whiteness
	Warp	Weft	
Untreated sample	787	388	84.12
Treated sample	732	351	83.11

Table 5 Antibacterial and flame retardant of treated cotton fabric after different times of washing

Washing times	Width of inhibition zone/mm		LOI/%
	E. coli	*S. aureus*	
0	2.9	2.8	31.2
5	2.6	2.5	30.3
10	2.5	2.4	28.8
15	2.3	2.1	27.4
20	2.0	1.9	27.3

and the inhibition zone of *E. coli* and *S. aureus* was reduced to 2.0 and 1.9 mm, respectively. Therefore, the results showed that the treated cotton fabric obtained good wash ability. The reason was that MCTPG can combine to cotton fabric with covalent bond due to MCTPG structure containing monochlorotriazine.

Conclusions

A novel antibacterial and flame-retardant agent monochlorotriazine triethylphosphite guanidine (MCTPG) was synthesized successfully. The chemical structure of MCTPG was characterized using FTIR and ^{1}H NMR. The treated cotton fabric obtained good properties. The LOI value of the treated cotton fabrics increased to 31.2%, and the char length decreased to 8.5 cm. The PHRR, HRR, THR, mass loss and CO_2/CO values of the untreated fabric were higher than those of treated fabric; on the other hand, the TTI and FPI values are higher. And the final amount of residual char is higher than untreated cotton sample. The inhibition zone of the modified cotton fibers base to *E. coli* and *S. aureus* reached to 2.9 and 2.8 mm. The surface morphology of the samples residue after combustion indicated that the treated cotton fabric had good flame retardancy. Besides, the treated cotton fabric had good washability. All these results demonstrated that the treated cotton fabric with MCTPG obtained good flame retardancy and antibacterial activity.

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