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A Novel Cyclic Polysiloxane Linked by Guanidyl Groups Used as Flame Retardant and Antimicrobial Agent on Cotton Fabrics

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Abstract: A novel flame retardant and antibacterial agent, (tetramethylcyclosiloxyl-piperazin) tetra guanidine (GNCTSi) used for cotton fabrics was successfully synthesized. The limiting oxygen index (LOI) value of cotton fabric treated with 250 g/*l* GNCTSi reached to 30.1 %. The vertical burning test results showed that the char length of the treated cotton fabric was 6.5 cm and have no after-flame and no after-glow. Compared with untreated cotton fabric, the treated cotton fabric showed better flame retardancy and higher residue rate by themogravimetric analysis (TG). The GNCTSi exists on the treated cotton fabric was observed and the residues of cotton fabric after combustion had a homogeneous surface without break by scanning electron microscopy (SEM). The treated cotton fabric showed good antibacterial activity against *E. coli* and *S. aureus* and the inhibition zone were 2.5 mm and 2.3 mm, respectively. After repeated washing, the LOI of cotton fabric is still higher than 26 %.

Keywords: Cyclic polysiloxane, Cotton fabric, Flame retardancy, Antibacterial, Wash durability

Introduction

Cotton fabrics are widely used because of their excellent properties, such as softness, breathability and water absorbance [1-7]. Meanwhile, cotton fabrics are easily modified by some functional additives to improve their inherent disadvantages, such as flammable and mildew and remain the advantages. Compounds containing phosphorus, nitrogen, silicon and boron atoms are more commonly used as flame retardants now because of they are environmentally friendly compared with the traditional flame retardants [8,9]. The flame retardants can promote the dehydration of cotton fabrics and increase the amount of char during the thermal degradation process to produce a physical barrier to cut off oxygen and heat [10]. Formaldehyde is not produced yet [11]. In addition, Metal ions [12], quaternary ammonium salts [13,14], *N*-halamines [15] and guanidine derivatives [16] are considered to be cotton fabric finishing agents with excellent antibacterial properties. Among them, *N*-halamines exhibit the best broad-supectrum antimicrobial properties, but it has poor water absorbance property and requires chlorination procedure to restore its antibacterial properties for repeated use. The quaternary ammonium salt shows weaker antibacterial ability than that of *N*-halamine, but better hydrophilic properties [17]. Fei *et al*. endowed cotton fabrics with durable antibacterial properties and good thermal stability by using a novel method called thiolmaleimide click reaction to produce the *N*-phenyl-maleimide [18]. Guanidine derivatives are biocompatible, friendly to mammalian cells and have been used as a kind of cotton fabric antibacterial agent [19]. Dong *et al*. prepared a novel guanidyl- and phosphorus-containing polysiloxane [20] and majority of additives containing triazine and phosphorus were then synthesized [21] to improve the flame retardancy and antibacterial properties.

Organosilicon compounds have attracted more and more attention to be used as additives of cotton fabrics because of their high thermal stability and low toxicity. The activities of the organic groups make it possible to introduce different functional groups to the organosilicon structure. The organosilicon groups can also worked as reinforcement agents when connect with cotton fabrics [22]. The researchers have concerned introducing the siloxanes containing the flame-retardant elements and antibacterial groups, such as polysiloxanes and silsesquioxanes to the cotton fabrics. The organosilicon structure could also improve the thermodynamic stability of cotton fabrics [23].

In this work, we synthesized a novel multiple pendent guanidyl moieties cyclic siloxane macromolecules (tetramethylcyclosiloxyl-piperazin) tetra guanidine (GNCTSi) by linking dicyandiamide to provide guanidyl with cyclotetrasiloxanolate as the substrate. The product was used as finishing agents on cotton fabrics. Its structure was confirmed by FTIR, and finished it on the cotton fabrics. The flame retardancy of cotton fabric with GNCTSi was determined by limiting oxygen index (LOI). The thermal stability and antibacterial properties of treated cotton fabric were investigated in detail by thermogravimetric (TG) and antibacterial tested. Scanning electron microscope (SEM) was used to investigate the surface morphology of cotton fabric before and after combustion. Then the washing resistance was also tested.

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Experimental

Materials

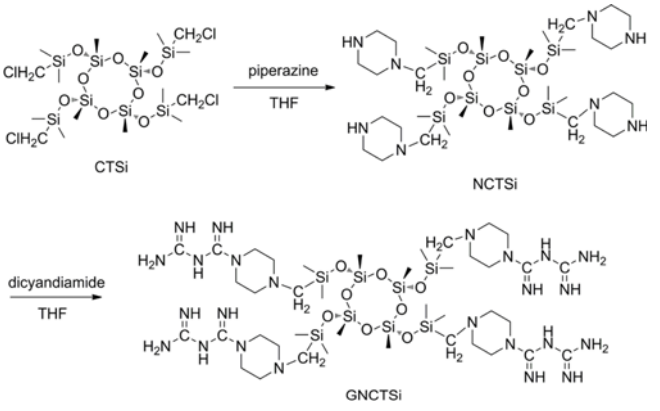
Desized, scoured and bleached 100 % plain-woven cotton fabric was obtained from Weifang for China Qi Rong Textiles Co., Ltd. *n*-Hexane, tetrahydrofuran (THF), ethanol and isopropanol were supplied by Tianjin Fu Yu Fine Chemical Co., Ltd. (China). Methyltriethoxysilane and 2-phosphonobutane-1, 2, 4-tricarboxylic acid (PBTCA) were supplied by Shanghai Macklin Biochemical Co., Ltd. (China). Chloromethyl dimethylchlorosilane was supplied by Hunan Hua Teng Pharmaceutical Co., Ltd. (China). Dicyandiamide was supplied by Tianjin Bo Di Chemical Reagent Co., Ltd. (China). Soybean-casein digest agar medium (TSA) was supplied by Qingdao Hope Bio-technology Co., Ltd. (China).

Synthesis of GNCTSi

Tetrapiperazin-tetramethylcyclosiloxyl (NCTSi) [24] (30.62 g, 0.033 mol) was dissolved in 100 m*l* THF in a three-necked round bottom flack (250 m*l*) equipped with a magnetic stirrer, a thermometer and a circumference condenser. Dicyandiamide (11.17 g, 0.133 mol) was then added with hydrochloric acid to control the mixture liquid pH value of about 5. Then the mixture liquid was stirred for 60 min at 60 °C under N_2 protection [25]. After the reaction, the solvent was removed by filtration. The volatile substances including excess THF further were removed by evaporation to give GNCTSi (40.54 g, 97 % yield) as pale yellow gelatinous solid. The synthesis step is shown in Scheme 1.

Preparation of Treated Cotton Fabrics

Preparation of GNCTSi solution: the percentage of urea was 5 % and the percentage of PBTCA was 10 %, water:isopropanol=1:1, cotton:bath=1:10. The concentrations of GNCTSi were 100 g l^{-1}, 150 g l^{-1}, 200 g l^{-1}, 250 g l^{-1}, 300 g l^{-1}. After the finishing bath was well matched, the cotton fabrics were soaked in finishing bath at room temperature for 30 min, and then through a laboratory-scale padder with two dips and two nips to wet pick up of 80 %. Then the samples were rinsed in water to remove unfixed agent. After that, the cotton fabric samples were dried in oven at 80 °C for 10 min and cured at 160 °C for 5 min.



Scheme 1. Synthetic route of GNCTSi.

The account (wt% owf) of flame retardant added on cotton fabric was calculated as follows equation (1):

$$\text{Add-on\%} = \frac{Wa - Wb}{Wb} \times 100\ \% \quad (1)$$

where, *Wb* and *Wa* represent the weights of cotton fabrics before and after flame retardant treatment, respectively.

Characterization

The structure of GNCTSi was measured by Nicloet 5700 FTIR instrument (Termo Nicolet Corporation, US) using the KBr pressed-disk technique.

Limited oxygen index (LOI) tests were measured by a digital display oxygen index apparatus LFY-606 according to GB/T 5454-1997. Vertical burning test was evaluated according to GB/T 5455-2014 by LFY-601A apparatus.

Thermogravimetric analysis (TG) was carried out on a TGA851 thermal analyzer (Mettler-Toledo International Inc.). Samples were tested under the condition of air flow rate of 20 m*l*·min^{-1} and a heating rate of 10 °C·min^{-1} from 25 °C to 800 °C.

The scanning morphologies of treated cotton fabric and the residue of the treated cotton fabric after combustion were investigated by using JSM-6010LA SEM apparatus (Japan Electron Optics Laboratory Co., Ltd.). The sputter coater was used to spray conductive gold on the surface of cotton fabric, and the microstructure of the surface was observed at 10 kV beam voltage.

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

The antimicrobial properties of the treated cotton fabrics with GNCTSi were investigated by GB/T 20944.3-2008.

Tear force test was based to GB/T 3923.1-2013. Whiteness test was based to GB/T 17644-2008.

According to GB/T 8629-2001 (National Standards of the People's Republic of China for textile, experiment with the family washing and drying procedures), the treated cotton fabric was washed five times in 2.0 g/*l* neutral detergent, five minutes each time. According to the operational processes mentioned above, the cotton fabric was washed 25 times. After cleaning and drying, the limit oxygen index was measured.

Results and Discussion

Characterization of Prepared GNCTSi

The chemical structure of GNCTSi was measured by FTIR, as shown in Figure 1. The peaks at 3366 cm^{-1} and

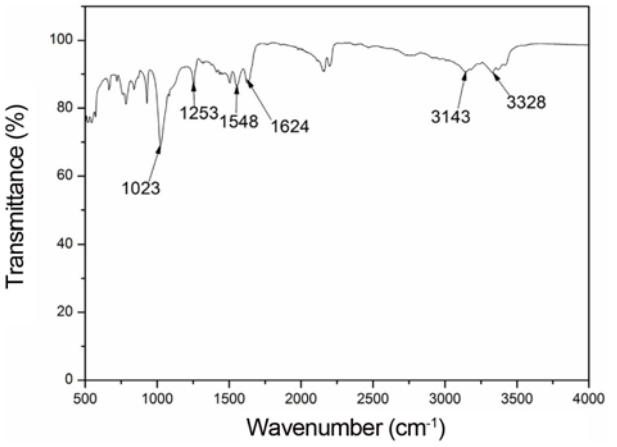


Figure 1. FTIR spectrum of GNCTSi.

1548 cm^{-1} were ascribed to the stretching vibration and scissor vibration of N-H band, respectively. Peak at 1624 cm^{-1} was ascribed to C=N band, proving the reaction of NCTSi and dicyandiamide. Occurred the absorption peak at 1253 cm^{-1} attributed to the stretching vibration of C-N band indicated the substitution reaction between chloromethyl and piperazine. The absorption peak at 1023 cm^{-1} belonged to the stretching vibration of Si-O-Si band. The chemical structure of GNCTSi was confirmed in the FTIR spectrum [26].

Elemental Analysis

Elemental analysis (EDS) and energy spectra were carried out to assess the elemental composition of treated cotton fabric with GNCTSi as shown in Figure 2. The data are summarized in Figure 3. The C, O, Si, N, P elements were observed in Figure 2. Compared with C and O elements, Si and N elements showed low density. It was mainly because

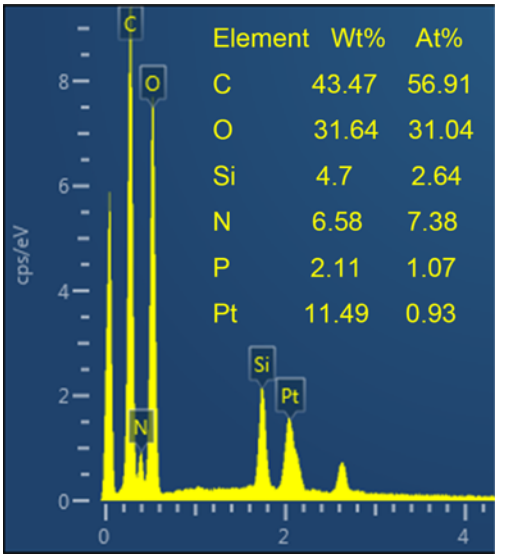


Figure 3. Elemental composition of the fabrics obtained by EDS analysis.

C and O atoms were only from the cotton fabric. Very little P atom was found in Figure 3, due to the existence of crosslinking agents PBTCA. The distributed uniformly on the surface of cotton fiber of different elements was observed [27-29], which was good agreement with SEM images in Figure 5, indicating the GNCTSi has been successfully finished on cotton fabric.

Flammability of Treated Cotton Fabric of GNCTSi

The LOI and vertical tests were carried out on the treated and untreated cotton fabrics to investigate flame retardant. The data is summarized in Table 1. The untreated cotton fabric was easily ignited in the air with LOI value as low as

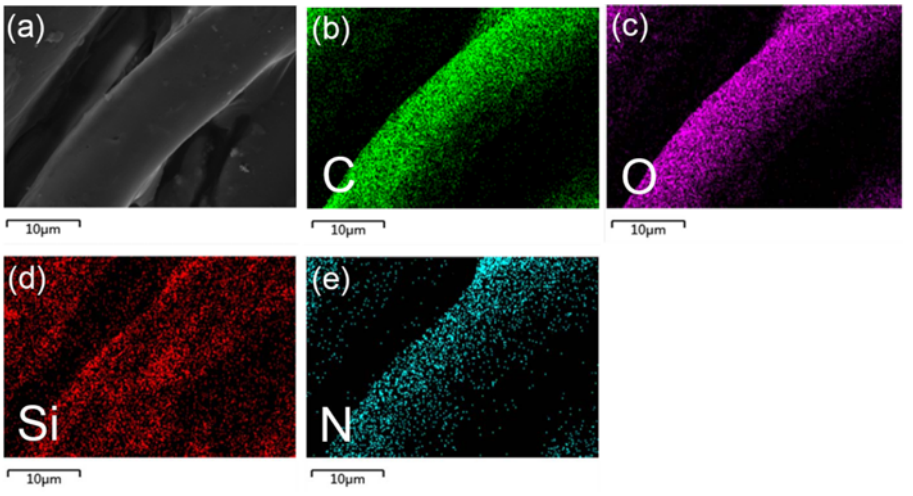


Figure 2. EDS mapping of treated cotton fabric with GNCTSi; (a) SEM photograph of treated cotton fabric, (b) distribution map of C element, (c) distribution map of O element, (d) distribution map of Si element, and (e) distribution map of N element.

Table 1. Flame retardant performance of treated and untreated cotton fabrics

GNCTSi (g l^{-1})	Add-on (%)	LOI (%)	Vertical burning test		
			After-flame time (s)	After-grow time (s)	Char length (cm)
0	0	18.0			
100	8.2	23.8	23.5	0	23.4
150	11.3	25.4	12.6	0	14.8
200	14.7	27.9	3.2	0	9.8
250	18.5	30.1	0	0	6.5
300	20.3	30.5	0	0	5.4

18 %, making it could difficult to complete the vertical combustion test. The LOI values of treated cotton fabric increased significantly from 23.8 % to 30.5 % with the concentration of GNCTSi of treated fabric increasing from 100 g l^{-1} to 300 g l^{-1} and the concentration of treated cotton fabric increasing from 8.2 % to 20.3 %. No after-grow time of treated cotton fabric, and after-flame time gradually decreased and even disappeared with the increase of concentration of treated cotton fabric and the char length was gradually reduced. It can be concluded that GNCTSi can give cotton fabrics excellent flame retardancy. In addition, it was observed that flame retardant property was not significantly improved when the flame-retardant finishing bath increased from 250 g l^{-1} to 300 g l^{-1}, so the 250 g l^{-1} of GNCTSi was elected as the concentration for other experiments.

Combustion Behaviors

The thermal behaviors measured by TG and DTG in air of treated and untreated cotton fabrics are shown in Figure 4 and the key data are summarized in Table 2. There were two evident mass loss of treated cotton fabrics with GNCTSi as shown in Figure 4. The initial degradation temperature of the first stage was 241 °C, a weight loss of 33 %. It was earlier

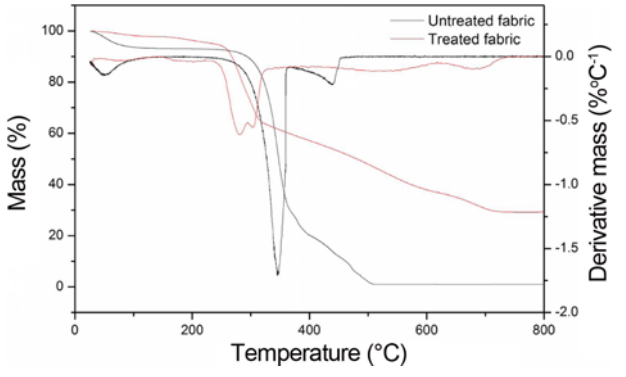


Figure 4. TG and DTG curves of untreated fabric and treated fabric with GNCTSi in air.

Table 2. Data of TG curves of cotton fabric in air

Sample	T_{onset} (°C)		T_{max} (°C)		Residue at 800 °C (%)
	1	2	1	2	
Untreated fabric	270	367	340	440	1.0
Treated fabric	241	330	281	535	29.0

than the initial degradation temperature of untreated cotton fabric, this was ascribed to the dehydration of cotton fabric and the breakage of some GNCTSi chemical bonds [30]. The second weight loss from 330 °C to 738 °C and a weight loss of 34 %, this was due to the continued cracking of cotton fibers and the carbonization of silica. At 738 °C, the cotton fabric was completely decomposition and 29 % residued, it was because the pyrolysis of cotton fabrics treated with GNCTSi and produced plenty of silica and inorganic carbon. It was significantly higher than the residual percent of untreated cotton fabric, indicating the thermal stability of cotton fabrics treated with GNCTSi had been marked improvement. The flame retardant mechanism was assumed that the treated cotton fabric gradually produces a layer of inorganic silicon-carbon structure during pyrolysis process, which acted as a barrier against oxygen and heat transfer [31]. On the other hand, there were two weightlessness stages for the untreated cotton fabric, the initial degradation temperature was 270 °C, and the temperature that burnt completely was 500 °C, with a residual rate of 1 % [32,33].

Morphology

The surface morphology images of the cotton fabric treated with GNCTSi before and after combustion were investigated by SEM as shown in Figure 5. Plenty of rougher salt particles could be seen on the treated cotton fiber surface as shown in Figure 5(a) and a clear structure could be seen after amplification as shown in Figures 5(c) and 5(e), because of the deposition of GNCTSi through padded with two dips and two nips on the surface of cotton fiber. The result of SEM of treated cotton fabric with GNCTSi was consistent with the EDS results. The residue morphology of treated fabric after the vertical combustion test was shown in Figures 5(b), 5(d) and 5(e). Compared with unburned cotton fabric, a similar integrity cotton fiber structure was observed [34,35] attributed to the stability of Si-O-Si bonds. The organosilicon also worked as a reinforcing effect to maintain the original structure of cotton fibers. The difference was that after burning, the cotton fiber surface formed a layer of intumescent silica crystalline structure and some structures with ruptured bubble were produced (Figure 5(b)), due to the production of large amounts of inert gas such as nitrogen and nitrogen oxides during the combustion process of treated cotton fabric with GNCTSi, these gases overflow the composite silsesquioxane polymer network surface of cotton fibers.

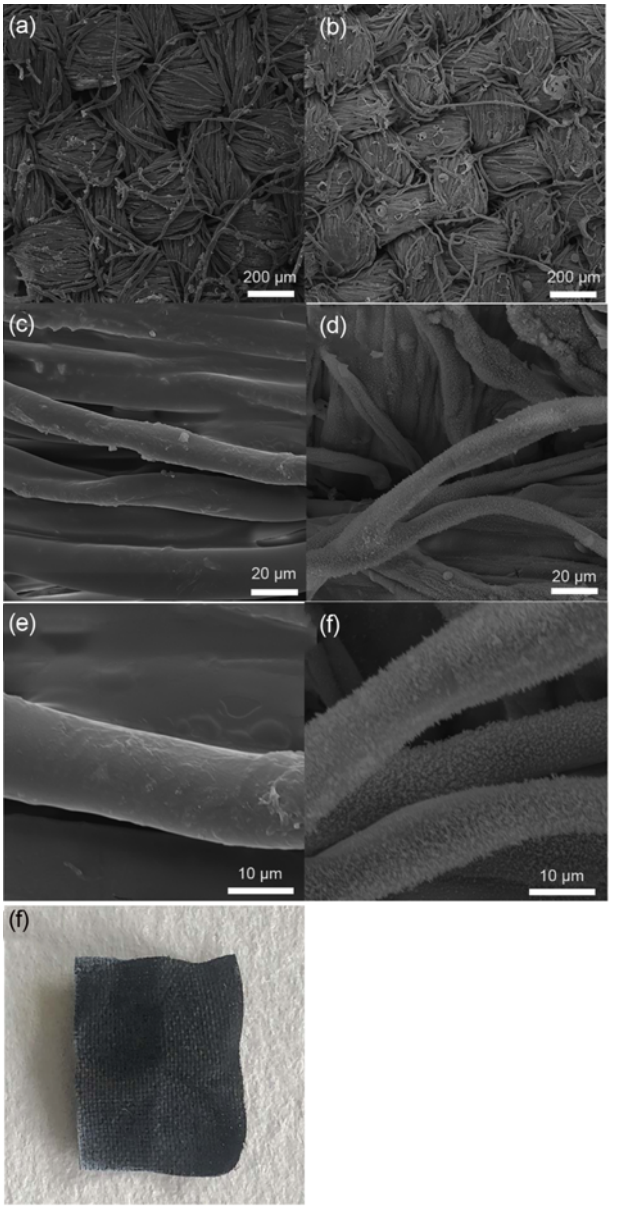


Figure 5. SEM images of cotton fabric treated with GNCTSi before and after combustion; (a, c, and e) treated fabric and (b, d, f, and g) residues of treated fabric.

FTIR Analysis of Char Layer after Combustion

Figure 6 shows the FTIR spectra of treated and untreated cotton fabric residue. The absorption peaks of the treated fabric residue were relatively simple, indicating that most of the organic groups were disappeared in the heating process. The residue of treated cotton fabric shows several characteristic absorption peaks. The peak at 1267 cm^{-1} ascribed to P=O group was from the thermal decomposition of the crosslinking agent PBTCA. The peak at 1042 cm^{-1} ascribed to Si-O-Si bond stretching vibration, and the peak at 800 cm^{-1} belonged to C-C bond proved the silicon carbon

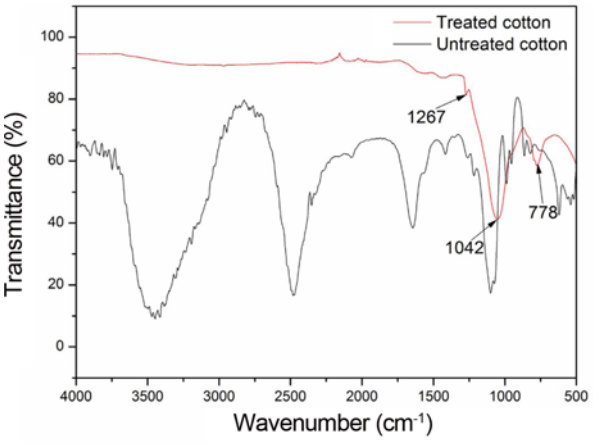


Figure 6. FTIR spectra of the untreated fabric and treated fabric char layer in air.

layer formed on the surface of the cotton fiber and worked as a reinforcing role to maintain the original shape of cotton fabric. The results of FTIR and SEM of cotton fabric residues were consistent with the thermogravimetric results.

Antibacterial Properties

The antibacterial properties of the neat and cotton fabrics treated with GNCTSi (250 g/*l*) were evaluated against Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureus*, and the inhibition zone images are shown in Figure 7. The cotton fabric treated with GNCTSi was endowed with 2.5 and 2.3 mm inhibition zone to *E. coli* and *S. aureus* that showed a good antibacterial activity. Meanwhile, no inhibition zone was observed to on neat cotton fabric. It was because that guanidine group interacts with phospholipid layer on the surface of bacterial cell membrane through electrostatic and hydrogen bonding and destroys the permeation barrier of cell membrane, thus achieving antibacterial effect [36,37].

Tensile Strength and Whiteness Testing

The tensile strength and whiteness data of neat fabric and treated fabric with GNCTSi are shown in Table 3. The SEM

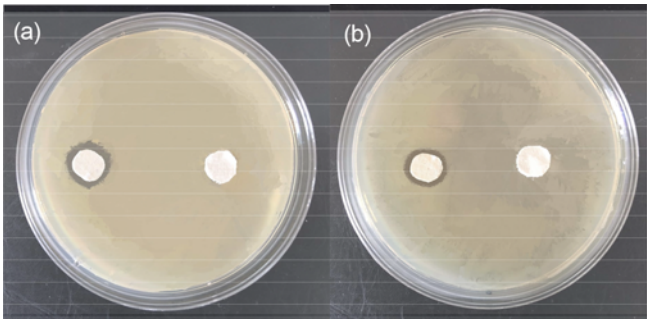


Figure 7. Inhibition zone of *E. coli* (a) and *S. aureus* (b).

Table 3. Tests results of tensile strength and whiteness

Sample	Breaking strength (N)		Whiteness (°)
	Warp	Weft	
Untreated fabric	736	615	83.17
Treated fabric	708	582	74.32

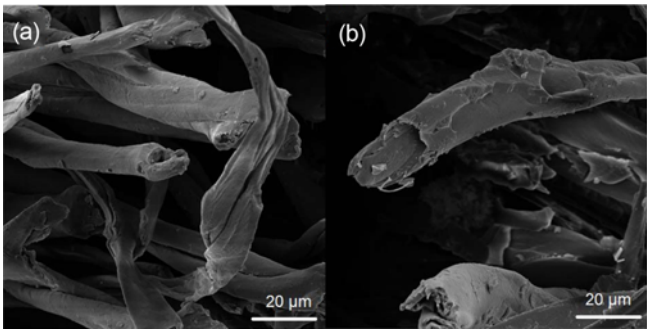


Figure 8. SEM images of (a) neat fabric and (b) treated fabric with GNCTSi by tensile strength.

images of the cotton fabric after tensile strength test are displayed in Figure 8. Compared with neat fabric, the tensile strength and whiteness were reduced to varying degrees, the warp and weft breaking strength of treated fabric reduced 26 N (3.53 %) and 33 N (5.37 %), respectively. This may be because the cotton fibers were covered with GNCTSi and the surface becomes smoother, reducing friction resistance between cotton fibers. After the neat cotton fabric was broken, there was a slight rupture on the cotton fiber surface, the fibers become disordered, and the ear-shaped cavity structure of the cotton fibers can still be observed. The surface of treated cotton fabrics with GNCTSi showed fragmented structure after being pulled off, which may be due to the shedding of GNCTSi. Whiteness reduced by 10.6 %, this indicated that the whiteness of treated cotton fiber had changed to some extent.

Washability of Treated Cotton Fabric

After repeated cleaning, the cotton fabric treated with GNCTSi still showed flame retardancy and antibacterial properties, though the properties were reduced. After 25 cycles of washing, the LOI value of cotton fabric was 26.3 % and the inhibition zone of *E. coli* and *S. aureus* were reduced to 1.8 and 1.5 mm, respectively due to the elution of GNCTSi in the cleaning process. After cleaning experiments, the cotton fabric treated with GNCTSi showed excellent washability. The results of LOI values and the inhibition zone of *E. coli* and *S. aureus* are summarized in Table 4.

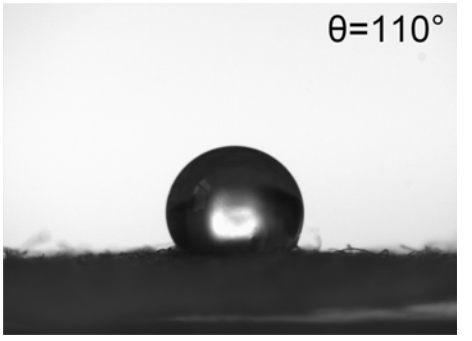


Figure 9. CA of water drop on the cotton fabrics.

Evaluation of Water Resistance Properties

The CA of treated cotton fabric sample with GNCTSi was presented in Figure 9. The CA of treated cotton fabric reached 110°. This was mainly due to the existence of a large number of hydrophobic Si-CH3 groups in GNCTSi. These groups can significantly reduce the surface tension and surface potential energy of cotton fabrics.

Conclusion

A new type of flame retardant and antibacterial agent used for cotton fabrics (tetramethylcyclosiloxyl-piperazin) tetra guanidine (GNCTSi) had been successfully synthesized. The LOI of the treated cotton fabric reached to 30.1 %. No after-flame time and no after-glow were observed and the carbon length was shorter than that of untreated cotton fabric. A silicon carbon layer was formed to cover the cotton fibers in the completely burned process and the layer could isolate air and break the heat conduction, increasing the residue rate significantly. The treated cotton fabric also showed favorable mechanical properties and durability. The above results showed that GNCTSi is an excellent flame retardant and antibacterial agent for cotton fabrics.

Acknowledgements

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Table 4. Flame retardancy and antibacterial of treated cotton fabric after washing

Washing time		0	5	10	15	20	25
LOI (%)		30.1	29.8	29.1	28.3	26.8	26.3
Width inhibition zone (mm)	*E. coli*	2.5	2.4	2..2	2.0	1.9	1.8
	S. aureus	2.3	2.1	1.9	1.8	1.6	1.5

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