

Synthesis of a New Phosphorus/Nitrogen Durable Flame Retardant for Cotton Fabrics

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Research Article

Keywords: FR, treated cotton, chemical grafting, thermal stability, durability

Posted Date: June 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-552835/v1>

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Abstract

Phosphorus/nitrogen flame retardant ammonium three phosphoric acid glycerol ester (FR) with reactive $-P-O^-NH_4^+$ groups was synthesized from glycerol, phosphoric acid and urea. At high temperature, the $-P-O^-NH_4^+$ group in FR is decomposed into $-P-O^-H^+$ group. Under the action of catalyst dicyandiamide, $-P-O^-H^+$ forms phosphonic anhydride. Phosphonic anhydride can dehydrate and condense with the hydroxyl group on the 6-position carbon atom in the glucose ring of cotton fiber, forming a firm P-O-C bond, thus fixing FR molecule firmly on cotton fiber. XRD suggested that the finishing process only slightly affected the cotton fiber structure and the surface morphology, elemental composition of char residues in cotton fabrics were tested by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). Confirmed that FR was grafted well with slight damage to the cotton structure. When the treated cotton with 25.3% weight gain (WG) in FR, the treated cotton has self extinguishing property and passed UL-94 vertical burning V-0 classification, the limiting oxygen index (LOI) was improved from 17.0–40.5%, and the LOI can still reach 30.9% after 50 laundering cycles, the cone calorimetry (CONE) analysis indicated that the peak heat release rate (PHRR) of the treated cotton was reduced from 190.3 kW/m² to 17.9 kW/m², and the total heat release (THR) was reduced from 2.8 MJ/m² to 1.8 MJ/m². The thermogravimetric (TG) and Differential scanning calorimeter (DSC) showed that the addition of FR inhibited the initial thermal degradation temperature of the treated cotton under heating conditions, and TG showed that the initial thermal degradation temperature of treated cotton in nitrogen and air was 225.9 °C and 221.8 °C, respectively, which was lower than that of untreated cotton. The mechanical properties are in the usable range, which showed that treated cotton have excellent flame retardancy, durability and good flexibility.

Highlights

- An eco-friendly phosphorus/nitrogen-based flame retardant (FR) was developed to cotton fabrics.
- FR can react with cotton fabric to form P-O-C covalent bonds.
- The PHRR and the THR of the treated cotton were reduced 90.6% and 35.7%.
- Cotton treated with FR exhibited high flame retardancy and excellent durability.
- The flame-retardant mechanism of the FR was revealed in detail.

1. Introduction

Due to its good hygroscopicity, biodegradability and natural skin friendly characteristics, cotton fabric is widely used in industrial fire clothing, military protective clothing, home decoration, building industry (such as building decoration materials, wallboard materials, fences, etc.) and automotive industry (such as doors, door dashboard, etc.) (Shahidi et al. 2013; Emam et al. 2019). However, cotton fabric is very easy to be ignited, LOI value is about 17.0% (Liu et al. 2018b). The flame spreads quickly. It can be treated by flame retardant finishing (Pethsangave et al. 2017) and blending with other flame retardant fibers

(Mohamed et al. 2014). Common flame retardant elements include phosphorus, halogen, nitrogen, silicon, magnesium, aluminum, boron, sulfur, etc. Halogen flame retardant has good fire prevention effect. However, chlorine and bromine atoms will release halogen free radicals or hydrogen halide, which will produce corrosive and toxic smoke in the degradation or burning process, which has been banned in many countries (Abou-Okeil et al. 2013).

At present, N-hydroxymethyl phosphoryl Propionamide (CP) is the main commercial phosphorus/nitrogen flame retardant widely used in cotton fabric flame retardant (Fang et al. 2016). It has the synergistic effect of solid phase barrier, gas phase dilution and endothermic cooling (Liu et al. 2018a), high efficiency and low toxicity. The treated cotton shows excellent flame retardancy. However, the finished fabric is affected by the hydrolysis of N-hydroxy methyl group and the crosslinking agent of polyhydroxy methyl melamine, which contains a lot of free formaldehyde and seriously endangers people's health. Therefore, it is a very important challenge to find the active groups of new flame retardants (Manfredi et al. 2018). Phosphorus containing compounds are considered to be the most promising durability flame retardants for cotton (Alongi et al. 2013). At high temperature, phosphorus containing compounds can be decomposed into phosphoric acid/polyphosphoric acid and other acidic fluid substances. These acidic intermediates can react with the matrix materials, catalyze the dehydration reaction of materials and promote the carbonization of materials. At the same time, these phosphoric acid compounds can still maintain the liquid state and strong acidity at 864 °C, forming a protective film on the surface of the fiber, preventing oxygen and heat from penetrating into the deep fiber, thus blocking the burning of the material (Rosace et al. 2017). This is also the reason why the flame retardancy of phosphorus containing compounds is better than that of acidic flame retardant compounds (such as sulfates, borax, nitrates, etc.) (Molaba et al. 2016). In addition, Urea including nitrogen during combustion can release NH_3 , N_2 and other non combustible gases, dilute the air. At the same time, it has excellent carbonization ability and thermal stability (Sharma et al. 2017). Therefore, phosphorus/nitrogen flame retardant are selected to synthesize target flame retardants for flame retardant finishing of cotton fabric (Mohammad et al. 2015).

In recent years, some durability, halogen free and environmentally friendly flame retardants and technologies have been reported. Various surface treatments such as LBL self-assembly (Carosio et al. 2018; Fang et al. 2019), sol-gel technology (Alongi et al. 2012; Bentis et al. 2019), nano coating and chemical grafting (Liu et al. 2017) have been used to prepare functional textiles with antibacterial (Tudu et al. 2020), flame retardant (Rosace et al. 2018), water repellent (Vince et al. 2006), UV resistant (Abidi et al. 2009; Yuan et al. 2012) or self-cleaning property (Ahmed et al. 2019). Annalisa (Annalisa et al. 2016) used layer by layer self-assembly method to finish 30 layers of DNA chitosan double-layer structure on cotton fabric, and then cured by UV, which gave the cotton fabric good self extinguishing property, reduced the initial pyrolysis temperature and maximum pyrolysis rate temperature of cotton fabric, and increased the amount of coke. The main problem to be solved by this method is to maintain the friction and washing durability of the treated fabric. Sol-gel technology is considered to be a multipurpose synthesis method based on hydrolysis and condensation two step reaction. However, under acidic pH conditions, the mechanical properties of cotton fabric often drop sharply (Kundu et al. 2018; Nabipour et

al. 2020). Zhang (Zhang et al. 2017) proposed a simple and economical method to prepare cotton fabric with hydrophobic and flame retardant properties through sol-gel reaction and self-assembly technology. However, due to the lack of low surface energy and micro nano structure, the WCA of the fabric is about 120 °C, which can not meet the requirements of hydrophobicity. Nano materials are environmentally friendly, non-toxic and other characteristics, and have also been used in flame retardants. However, the main disadvantage is poor washing durability, which leads to unstable flame retardancy (Malucelli et al. 2014; Lin et al. 2019). So far, environmentally friendly and washable flame retardant coatings are a great challenge for the scientific and industrial circles. Some studies show that (Wang et al. 2016) chemical grafting is considered to be an effective method to prepare durability flame retardant.

In this study, FR was successfully grafted onto cotton fabric by chemical grafting with simple heating, soaking and rolling processes, and it has certain chemical stability. The treated cotton with durable, flame retardant, smoke suppression and environmental protection is realized. The raw materials used in this method are safe and easy to obtain, and the process flow is simple. TG was used to analyze the thermal stability and oxidation resistance of cotton fabrics before and after finishing. XRD and FT-IR were used to characterize the crystal structure and chemical structure of cotton fabrics before and after finishing. SEM-EDS was used to analyze the surface morphology and element composition of carbon residue of cotton fabrics before and after finishing. LOI, vertical burning and CONE were used to test the combustion properties of cotton fabrics before and after finishing. Finally, the flexibility and mechanical properties of cotton fabrics before and after finishing were evaluated.

2 Experimental

2.1 Materials

Plain woven cotton fabric (area density 122 g/m², 570 × 340) was obtained from market in Jilin, China. Glycerol was purchased from Tianjin North Tianyi Chemical Reagent Plant, China. Dicyandiamide was obtained from Aladdin Reagent (Shanghai) Co., Ltd. (Shanghai, China). Phosphoric acid, urea and ethanol were supplied by the Tianjin Damao Chemical Reagent Plant (Tianjin, China). All the chemicals were of reagent grade and used without further purification.

2.2 Synthesis of FR

Put 0.1 mol glycerol into a 250 ml beaker, add 0.3 mol phosphoric acid into the beaker, stir and raise the temperature to 110 °C, and react for 25 h. At this time, the reaction system changes from colorless transparent mixture to brown viscous liquid. Then, reduce the reaction temperature to 80 °C, slowly add 0.3 mol urea into the beaker, stir and raise the temperature to 110 °C to continue the reaction, and stop the reaction when the pH value of the mixture reaches 6. The white solid flame retardant FR was obtained after the crude product was extracted with anhydrous ethanol to remove impurities and dried. The yield was 70.0%. The structure of FR was analyzed by ¹³CNMR, ¹HNMR and ³¹PNMR. The results were as follows:

^{13}C NMR (D_2O , 600 MHz) δ (ppm): 77.52 (s, CH) and 84.93 (s, 3CH_2). ^1H NMR (D_2O , 600 MHz) δ (ppm): 3.42 (s, CH), 3.70 (s, 2CH_2) and 4.60 (s, D_2O). ^{31}P NMR (D_2O , 600 MHz) δ (ppm): 10.59 (s, 3P). The test results are consistent with the structure of FR.

2.3 FR finishing of cotton fabric

Finishing prescription: soak cotton fabric in FR solution with a specific concentration, and add a certain amount of dicyandiamide as catalyst in the solution. Finishing process: Dipping (soaking at 60 °C for 20 min, twice dipping and twice rolling, so that the liquid carrying rate reaches about 80%) → pre-drying (80 °C, 10 min) → baking (160 °C, 2 min) → water washing → drying. Scheme 2 describes the chemical grafting reaction between cotton fabric and FR. Scheme 3 describes the FR finishing process of cotton fabric. At 160 °C, some $-\text{P}-\text{O}-\text{NH}_4^+$ groups may also form phosphoramidate group $\text{O}=\text{P}-\text{NH}_2$.

WG was calculated in accordance with Eq. (1):

$$\text{WG}(\%) = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

In which: W_1 is the mass of untreated cotton, g; W_2 is the mass of treated cotton, g.

2.4 Characterization

^1H , ^{13}C and ^{31}P (600 MHz) nuclear magnetic resonance (NMR) spectra of FR spectra were obtained using a Bruker 600 M spectrometer.

FT-IR(Fourier transform infrared) test: The synthesized FR and cotton fabric were dried to remove moisture, then characterized by Fourier transform infrared spectrometer, and their structures were analyzed. The spectral scanning range is $4000 \sim 500 \text{ cm}^{-1}$, and the resolution is 2.0 cm^{-1} . Tensor II Fourier transform infrared spectrometer, BRUKER Company, Germany.

TG test: In nitrogen and air atmosphere, carry out thermogravimetric test at 30 °C-600 °C at a heating rate of 10 °C/min. TG Q50 thermogravimetric analyzer, Waters Company, USA.

SEM-EDS test: After spraying gold on the surface for 1 min, the surface morphology and elemental composition of char residues of fabric were observed at different magnifications under the working voltage of 20 kV. TESCANVEGA3 scanning electron microscope, Czech Tesken Company.

XRD test: the crystal region of fabric was tested by XRD, with light tube voltage of 35 kV, tube current of 30 mA, scanning step width of 0.02° and scanning speed of $0.1 (^\circ)/\text{s}$, and the products were characterized by XRD. SHL-2 XRD temperature controller, manufactured by Dandong Fangyuan Instrument Co., Ltd.

UL-94 vertical burning test: The size of cotton samples was 300 x 90 mm², test according to GB/T 5455 – 2014 *Determination of damage length in vertical direction, smoldering and afterburning time of textile burning performance*. YGB815 Vertical and Horizontal Burning Tester, Wenzhou Fangyuan Instrument Co., Ltd.

Washing test: According to AATCC 61-2013 *Color fastness to washing: accelerated method*, the washing fastness of flame retardant finished fabrics was measured by using a washing fastness tester. The concentration of detergent is 3.7 g/L, the washing temperature is 40 °C, and the washing time is 45 min. When washing, put 10 steel balls, which is equivalent to 5 times of household washing. SW-12A washing fastness tester, Wuxi Textile Instrument Factory.

LOI test: The size of cotton samples was 150 x 58 mm², test according to GB/T 5454 – 1997 *Oxygen Index Method for Textile Burning Performance Test*. ZR-01 oxygen index tester, Qingdao Shanfang Instrument Works.

CONE test: The sample is 100 × 100 × 4 mm³ with a heat flux of 35 kW/m² for 20 min. JCZ-2 Cone Calorimeter, Nanjing Jiangning Analytical Instrument Factory.

DSC test: Record the heat capacity of the sample at a heating rate of 10 °C/min in the temperature range from room temperature to 400 °C under nitrogen atmosphere. DSC131 EVO differential scanning calorimeter, Beijing Setaram Instrument Company.

Flexibility test: *according to the ASTM D 1388-96 (2002) standar*. using a LLY-01- type computer-controlled flexibility tester (Jilin electromechanical equipment Co. Ltd. Jilin, China)

Whiteness and yellowness test: Referring to GB/T 8424. 2-2001 *Instrumental Evaluation Method for Relative Whiteness of Textiles Color Fastness Test*, the whiteness of cotton fabrics before and after flame retardant finishing is measured on a digital display automatic whiteness meter, and the average value of each sample is taken after multiple measurements. WBS – 1 whiteness meter, Shanghai Xinrui Instrument Co., Ltd.

Mechanical property test: According to GB/T 3923.1–2013 *tensile properties of textiles and fabrics part 1: determination of breaking strength and elongation at break (strip method)*, the breaking strength of cotton fabrics before and after finishing is tested on a material testing machine. HD026N multifunctional electronic fabric strength tester, Nantong Hongda Experimental Instrument Co., Ltd.

3 Results And Discussion

3.1 FT-IR analysis of FR

The infrared spectrum of FR is presented in Fig. 1. 1460 cm⁻¹ was the bending vibration characteristic peak of C-H in -CH₂, 1160 cm⁻¹ was the stretching vibration characteristic peak of P = O (Liu et al. 2019),

1060 cm^{-1} was the stretching vibration characteristic peak of P-O-C (Wang et al. 2020), 960 cm^{-1} was the stretching vibration characteristic peak of -P-O-H⁺ (Jia et al. 2017a). That is because the -P-O-NH₄⁺ group in FR was thermally decomposed into -P-O-H⁺. In conclusion, the infrared spectrum of the synthesized product was consistent with the characteristic group of the target product, which indicates that FR has been successfully synthesized.

3.2 LOI and durability analysis of untreated cotton and treated cotton

The WG value of the cotton treated with different FR concentrations change are presented in Fig. 2(a). The WG value of the cotton treated with 100g/L, 200g/L, 300g/L and 400g/L FR before washing are 8.5%, 19.1%, 25.3% and 33.7%, respectively. After 50 LCs, their WG value are 3.7%, 8.3%, 10.3% and 12.1%, respectively. The cotton fabric treated with 400g/L FR solution achieves a large WG of 33.7%. If the concentration of FR is too high, the WG% of treated cotton will also increase, which will affect the physical properties such as handle and original comfort.

The LOI value represents the minimum oxygen concentration required to maintain the flame state when the sample is burned in oxygen and nitrogen atmosphere (Dutkiewicz et al. 2018). As shown in Fig. 2(b), the LOI values of treated cotton with 8.5%, 19.1%, 25.3%, 33.7% WG FR solution reached 26.1%, 31.7%, 40.5% and 42.0% respectively, which were higher than 17.0% of the untreated cotton. After 50 LCs, the LOI values of 25.3% and 33.7% WG FR were 30.9% and 33.9% respectively, which were higher than the LOI values of international flame retardant standard (26%-28%) (Li et al. 2015). Therefore, the cotton fabric with 25.3% WG FR or more can be regarded as durability treated cotton. At the same time, the LOI value of the treated cotton decreases with the increase of laundering cycles. That is why the unreacted FR and the covalent bond P-O-C in some FR are washed away in the washing process. FR has the active group of -P-O-NH₄⁺, which can combine with cellulose through P-O-C covalent bond. In addition, FR can react with -OH on cellulose to form P-O-C bond at the same time. Only when the P-O-C covalent bond between FR and cellulose is completely hydrolyzed can FR be removed from the treated cotton. However, due to the polymerization of flame retardant molecules to a certain extent, it is difficult to hydrolyze all P-O-C covalent bonds. Therefore, the cotton fabric treated with flame retardant has excellent durability.

3.2 Thermal and thermo-oxidative analysis of FR, untreated cotton and treated cotton

Thermal and thermo-oxidative processes of FR, untreated cotton and treated cotton have been investigated by TGA. $T_{5\%}$ and $T_{10\%}$ were temperature at 5%, 10% mass loss, T_{max} was the maximum thermal degradation rate temperature. R_{max} was the maximum thermal degradation rate.

The TG and DTG curves and data of FR, untreated cotton and treated cotton in N₂ atmosphere are presented in Fig. 3(a) and 3(b) and Table 1., For FR, $T_{5\%}$ was 101.6 °C, which was caused by water

evaporation and oligomer decomposition. $T_{10\%}$ was 126.8 °C, and weight loss was 33.1%. The rapid weight loss in this stage was due to the fact that the phosphoric acid released from FR molecular fracture can promote the dehydration and carbonization of FR. T_{max} of FR was 161.9 °C, and the R_{max} was 0.6%/°C. The pyrophosphoric acid produced by dehydration of phosphoric acid promotes the carbonization of FR, and then C-C, P = O, -O- break a lot, releasing volatile substances such as NH_3 , H_2O and other small molecular products. The residual carbon rate was 21.0% at 600 °C. These results indicated that FR has good thermal stability. For untreated cotton and treated cotton, in the initial stage, the fabric has a little weight loss, which was due to the loss of bound water due to the heating of the fabric. The main weight loss of the fabric was between 250 °C-350 °C, and the mass loss rate increases rapidly in this stage. This was mainly due to the depolymerization of cellulose macromolecules to produce L-glucose, which was further decomposed to form pyrolysis products and coke (Hussain et al. 2019). When the temperature continues to rise, the cellulose burning residue will continue to dehydrate and release water and carbon dioxide, and the mass loss rate will be significantly reduced, and the char residues content will be higher and higher (Pan et al. 2018). $T_{5\%}$ and $T_{10\%}$ of untreated cotton are 257.5 °C and 280.7 °C respectively, while treated cotton is 184.4 °C and 225.9 °C respectively. That is because FR catalyzes the decomposition of cellulose (Shafizadeh et al. 1982). The T_{max} of untreated cotton was 331.6 °C, and the R_{max} was 1.4%/°C, while the T_{max} and R_{max} of treated cotton were 263.6 °C and 1.1%/°C, respectively. That is why the treated cotton decomposes to form phosphoric acid when heated, and then polymerizes to form polyphosphoric acid, which inhibits the production of L-glucose and further improves the thermal stability. FR dehydrate the cellulose and promote the formation of char residues. The char residues were covered on the surface of the fiber to isolate heat and inhibit the further decomposition of the fiber. The char residues rate of treated cotton at 600 °C was 28.6%, while that of untreated cotton was only 18.9%, which indicates that improve the thermal stability of cotton fabric.

The thermo-oxidative processes of FR, untreated cotton and treated cotton curves and data are presented in Fig. 3(c) and 3(d) and Table.1. For FR, $T_{5\%}$ was 92.2 °C, $T_{10\%}$ was 136.1 °C, which indicated that FR began to decompose at lower temperatures in air atmosphere. T_{max} of FR was 179.1 °C, and the R_{max} was 0.6%/°C. In the range of 200–500 °C, the weight loss of FR was slow. The residual carbon rate was 35.9% at 600 °C. For untreated cotton and treated cotton, Below 100 °C, it belongs to the dehydration stage of water molecules in cellulose. The second degradation occurs when the temperature rises to about 200 °C. When the temperature is kept at 262.6 °C, the weight loss rate reaches the maximum, and the weight loss is 30.6%. The weight loss rate of the untreated cotton was the highest at 372 °C, The weight loss was 72%. In addition, the residue of treated cotton is 12.6% at 600 °C in air atmosphere, while the residue of untreated cotton is 1.0%. Compared with the untreated cotton, the initial decomposition temperature of treated cotton decreased and the residual content increased significantly in both nitrogen and air atmospheres. The above test results show that FR can promote the thermal decomposition of cotton fabric, form a carbon slag protective layer to protect the deep fiber and reduce the decomposition rate of cellulose matrix. It also shows that FR presents a typical condensed phase flame retardant mechanism.

Table 1

TG and DTG data of FR, untreated cotton and treated cotton under N₂ atmosphere and air and air atmosphere

Sample	T _{5%} (°C)	T _{10%} (°C)	T _{max} (°C)	R _{max} (%/°C)	Residue at 600°C (%)
Untreated cotton in N ₂	257.5	280.7	331.6	1.4	18.9
Treated cotton in N ₂	184.4	225.9	263.6	1.1	28.6
Untreated cotton in air	153.1	259.8	301.4	1.1	1.0
Treated cotton in air	178.4	221.8	262.6	1.4	12.6
FR in N ₂	101.6	126.8	161.9	0.6	21.0
FR in air	92.2	136.1	179.1	0.6	35.9

3.3 XRD patterns of Untreated cotton and treated cotton

The crystal structures of untreated cotton and treated cotton were determined by XRD analysis. As shown in Fig. 4, the diffraction peaks of treated cotton were at 14.62, 16.44, 22.18 and 34.36, corresponding to (110), (110), (200) and (004) grid planes respectively. The diffraction peaks of untreated cotton were at 14.80, 16.60, 22.56 and 34.28, corresponding to (110), (110), (200) and (004) grid planes respectively (Kwak et al. 2015; Zheng et al. 2016). The peak position and shape of untreated cotton and treated cotton were very similar, which means that the plane spacing between crystal planes does not change, and the finishing process has little effect on the structure of treated cotton. The results show that the crystal structure of cellulose was slightly expanded or layered by the dehydration reaction of FR and cotton fabric cellulose (Lee et al. 2018), and the diffraction peak intensity of treated cotton was slightly lower than that of untreated cotton. This may be due to the penetration of dicyandiamide and FR into the amorphous region of the fiber during the process of cotton fabric soaking in flame retardant finishing solution, and these small molecules were grafted in the subsequent high temperature grafting reaction. In this region, the content of cellulose in the treated cotton decreases, which affects the spatial chemical structure of the fiber. That is to say, the proportion of crystalline region of treated cotton grafted with FR decreases, which leads to the decrease of diffraction peak intensity.

3.4 FT-IR patterns of untreated cotton and treated cotton

The FT-IR of untreated cotton and treated cotton are presented in Fig. 5, The absorption peaks at 3471 cm⁻¹ and 3488 cm⁻¹ were caused by the stretching vibration of O-H in untreated cotton and treated cotton respectively (Zhang et al. 2018), the treated cotton has a new strong absorption peak at 1200 cm⁻¹, which was caused by the stretching vibration of P = O (Bosco et al. 2017), and a weak P-O-H stretching vibration absorption peak at 850 cm⁻¹ (Mao et al. 2015). In addition, The P-O-C stretching vibration has an enhanced absorption peak at 1050 cm⁻¹. Indicates that the flame retardant molecules have been successfully introduced into the cotton fiber (Choi et al. 2018). The absorption peak at 1625 cm⁻¹ was

caused by the stretching vibration of C = O (Nguyen et al. 2014), That is why the glycosidic bond of cellulose was oxidized to C = O under high temperature and acid environment.

3.5 Surface morphology and elemental composition of char residues from untreated cotton and treated cotton

In order to better study the flame retardant effect of cotton fabric, the morphology of carbon residue in cotton fabric more valuable than that of raw cotton. SEM and EDS were used to study the surface morphology and element composition of fabric char residues. The SEM of untreated cotton char residues with different magnification are shown in Fig. 6(a) and (b), the fiber structure was obviously damaged, and the SEM of treated cotton char residues with different magnification are shown in Fig. 6(c) and (d), the fiber structure can still remain intact, indicating that FR can effectively protect the structure of the fabric after burning, and there are obvious particles on the surface of the treated cotton after burning, indicating that FR is successfully attached to the treated cotton. As shown in Fig. 6(e) and (f), EDS shows that phosphorus is evenly distributed on the surface of the char residues of the treated cotton, and the carbon content was increased compared with that before combustion, which indicates that FR can improve the flame retardant performance of cotton fabric by promoting carbon formation.

3.6 Vertical burning analysis of untreated cotton and treated cotton

The vertical burning method is used to evaluate the burning performance of cotton fabric. Figure 7 shows the electronic photos of untreated cotton and treated cotton after vertical burning. As shown in Table 2, the treated cotton with 8.5%, 19.0%, 25.3% and 33.7% WG FR solution have carbon length equal to reach 50 mm, 42 mm, 38 mm and 33 mm. The untreated cotton was ignited immediately in the vertical burning test, the flame spread rapidly and finally completely burned out, the after-flame time(t_1) and after-glow time(t_2) were 7.0s and 11.2s respectively, while the flame diffusion speed of treated cotton decreased, the t_1 and t_2 were 0, and the treated cotton went out immediately after leaving the flame. The results show that the treated cotton has good flame retardancy. When the fire source was removed, with the increase of FR concentration, the length of carbon decreases, and the t_1 and t_2 are both 0. The carbon length increased after 50 LCs. When the treated cotton with 25.3% WG, the treated cotton has self extinguishing property, and passed UL-94 V-0 classification of vertical burning test. The mechanism of flame retardant is that phosphorus element can strengthen the system, which can be transformed into phosphorus/base acid in the condensed phase, thus accelerating the carbonization of cotton fabric. The carbonization layer can protect the treated cotton fabric from heat transfer and the release of combustible volatiles. Active factors such as $PO\cdot$ can also be released in the gas phase to terminate the free radical reaction. At the same time, small molecules such as CO_2 , H_2O and NH_3 can be produced during the burning and decomposition of treated cotton. The reduction of the contact between the treated cotton and O_2 and other combustibles indicates that the treated cotton has good flame retardant properties and plays a flame retardant effect in both condensed phase and gas phase.

SEM of char residues of untreated cotton and treated cotton under different magnification is shown in Fig. 8. Figure 8(a), (b) show the char residue of untreated cotton indicated that the fiber structure was obviously destroyed, Fig. 8(c), (d) show the char residues of treated cotton after burning was continuous and uniform, and the structure was relatively complete. That is why FR containing phosphorus decomposes into phosphoric acid during heating, and phosphoric acid forms polyphosphoric acid at high temperature, which plays the role of dehydration, thus inhibiting the formation of L-glucose and further dehydrating and carbonizing cellulose. The continuous carbon layer formed insulates the contact between internal fiber and oxygen, slows down the rate of thermal decomposition reaction (Naebe et al. 2016), and makes the structure of residual carbon relatively complete. The surface was rough with particles, which indicates that FR was successfully attached to the treated cotton.

Table 2
Vertical burning data of untreated cotton and treated cotton.

WG (%)	LCs	t ₁ (s)	t ₂ (s)	Char length(mm)	Self-extinguishing property
Untreated cotton	-	7.0	11.2	0	No
8.5	0	0	0	50	No
	50	0	0	95	
19.0	0	0	0	42	No
	50	0	0	82	
25.3	0	0	0	38	Yes
	50	0	0	61	
33.7	0	0	0	33	Yes
	50	0	0	56	

3.8 CONE analysis of untreated cotton and treated cotton

The ignitability and combustion behavior of untreated cotton and the treated cotton with 25.3% WG are further studied by CONE. The curves of heat release rate (HRR), THR and CO₂ release are shown in Fig. 9(a), (b) and (c). SEM of char residues of untreated cotton and treated cotton after CONE are shown in Fig. 9(e) and (f). It can be seen that the PHRR and THR of treated cotton were 17.9 kW/m² and 2.8 MJ/m² respectively, which are significantly lower than 190.3 kW/m² and 1.8 MJ/m² of untreated cotton. That is why FR promotes the dehydration and carbonization of cellulose macromolecules, reduces the generation of combustible gas, and the carbon layer was wrapped on the fiber surface to isolate heat and oxygen (Basak et al. 2018; Jiao et al. 2010). The peak value of CO₂ emission of treated cotton was 15.8%, which was higher than that of untreated cotton by 7.8%, indicating that the burning efficiency of treated cotton was lower (Nazare et al. 2008).

It can be seen from Fig. 9(d) and (e) that the fiber structure of the untreated cotton has been destroyed after CONE, while the structure of the treated cotton was complete. The results show that FR not only improves the thermal stability of treated cotton, but also protects the internal structure of the fiber. And there are fine particles on the surface of the fiber, which is because the excessive FR molecules can not graft with the active groups in the cellulose molecules, but adhere to the surface of the fiber in the form of coating at high temperature. The relevant data of CONE are shown in Table 3. Time to ignite (TTI) and time to PHRR (T_{PHRR}) of treated cotton were 28.7s and 30.3s, respectively, which were higher than those of untreated cotton (13.0s and 20.6s), which means that treated cotton is not easy to be ignited in the same environment, and people have a greater chance to escape from fire. The fire growth rate (FGR, $FGR = PHRR/T_{PHRR}$) of treated cotton is 0.6 kW/(m²·s), while that of untreated cotton is 9.2 kW/(m²·s), which indicates that the slower the burning growth rate of treated cotton, the lower the fire risk (Wang et al. 2015). The average mass loss rate (av-MLR) decreased from 1.23 g/s to 0.55 g/s, indicating that the treated cotton released less heat in the burning process. FR can promote the formation of carbon layer of cellulose to isolate heat and make the burning difficult to spread. The char residues rate of treated cotton was 29.4%, and that of untreated cotton was 5.6%. It also shows that FR promotes the dehydration of cellulose into carbon and improves the flame retardancy of treated cotton. In addition, the total smoke rate (TSR) was significantly increased, because some flame-retardant gases containing NH₃, H₂O and CO₂ were released at high temperature, which diluted the O₂ concentration on the surface of the treated cotton, making the treated cotton burning insufficiently.

Table 3
CONE data of untreated cotton and treated cotton.

Sample	TTI (s)	T_{PHRR} (s)	TSR (m ² /m ²)	av-MLR (g/s)	FGR (kW/m ² s)	Residue (%)
Untreated cotton	13.0 ± 0.5	20.6 ± 0.4	5.0 ± 0.2	1.23 ± 0.1	9.2 ± 0.5	5.6 ± 1
Treated cotton	28.7 ± 0.6	30.3 ± 0.6	33.1 ± 1	0.55 ± 0.1	0.6 ± 0.01	29.4 ± 1

3.9 DSC analysis of untreated cotton and treated cotton

The thermal stability of the fabric was further studied by DSC. As shown in Fig. 10(a), the total heat released by the treated cotton was 43.7 mW, which was lower than 36.3 mW of the untreated cotton. Figure 10(b) shows the thermal degradation rate of the untreated cotton and treated cotton. As shown in Table 4, The T_{max} and R_{max} of untreated cotton were 300.0 °C and 0.6%/°C respectively, and the T_{max} and R_{max} of treated cotton were 276.9 °C and 0.8%/°C respectively. These effects may be attributed to the lower pyrolysis temperature of FR, the formation of polyphosphoric acid or pyrophosphoric acid compounds in the decomposition process, which promotes the dehydration and carbonization of cotton fiber, and makes the treated cotton have a lower maximum exothermic rate temperature. At 400 °C, the char residues of treated cotton was 32.8%, which is higher than that of untreated cotton by 7.7%. Compared with the untreated cotton, the treated cotton has better thermal stability.

Table 4
DSC data of untreated cotton and treated cotton

Sample	Heat flow(mW)	T _{max} (°C)	R _{max} (%/°C)	Residue at 400°C (%)
Untreated cotton	43.7	300.0	0.6	7.7
Treated cotton	36.3	276.9	0.8	32.8

3.10 Flexibility,whiteness and yellowness index analysis of untreated cotton and treated cotton

The flexibility, whiteness and yellowness index of untreated cotton and treated cotton are shown in Fig. 11 and Table 5. With the increase of the WG in FR, the ring height of the untreated cotton was 10.0 mm, and thus it has good flexibility. The ring height of treated cotton flexibility increased slowly, which indicates that FR has a negative effect on the flexibility of cotton fabric. The whiteness decreased slowly and the yellowness increased slightly, which may be due to the decomposition of $-P-OH^+$ by FR in the process of high temperature baking. Although there was a catalyst to catalyze the grafting reaction, the $-P-OH^+$ group obtained in the future will make the cellulose in a strong acidic environment, destroy part of the fibronectin, and make the treated cotton whiteness decreased and yellowness increased. When the treated cotton with 25.3% WG, the treated cotton have good flexibility and whiteness. But when the treated cotton reaches 33.7% WG, the ring height of treated cotton flexibility increased obviously and the whiteness of treated cotton decreased obviously.

Table 5
Flexibility, whiteness and yellowness data of untreated cotton and treated cotton

WG(%)	Whiteness index (%)	Yellowness index (%)
Untreated cotton	90.1	7.5
8.5	83.2	16.6
19.1	81.7	17.1
25.3	79.4	18.2
33.7	70.2	19.1

3.11 Mechanical properties analysis of untreated cotton and treated cotton

Vapor transmissibility Fig. 12 (a), water absorbability Fig. 12 (b), tensile strength Fig. 12 (c) and elongation at break Fig. 12 (d) are important indices to measure the comfort of the cotton fabric.

Therefore, the properties of the treated cotton were tested. There is no significant difference in vapor transmissibility and water absorbability between treated cotton and untreated cotton, which indicates that flame retardant finishing does not affect the warp and weft density of cotton fabric. The tensile strength and elongation at break of fabric can reflect the external resistance of fabric. When the treated cotton with 25.3% WG, the tensile strength of treated cotton in warp and weft direction decreased by 18.3% and 28.4% respectively, the decrease of tensile strength was due to the high temperature treatment of the cotton fabric during the grafting reaction, which causes some damage to the strength of the cotton fiber. In addition, during the chemical grafting reaction, when the cotton fiber was in the high temperature acidic environment, part of the glycosidic bond of cellulose was oxidized into C = O group, and the number of damaged nodes in the fiber increases, which leads to the decrease of tensile strength and fracture of the treated cotton. The change of elongation at break was small, which was due to a FR molecule with multiple reactive groups can bond with multiple cellulose macromolecules. This strong and close cross-linking reaction reduces the deformation ability of the fabric under the action of external force. Therefore, it has little effect on the elongation at break of cotton fabric. But when the treated cotton reaches 33.7% WG, the tensile strength of the cotton fabric decrease obviously, So the best treated cotton was with 25.3% WG.

4 Conclusion

In this study, reactive phosphorus/nitrogen FR with $-P-O-NH_4^+$ group was synthesized by two-step method. FR has the advantages of halogen-free, formaldehyde free, environmental protection and high efficiency. XRD results show that FR has little effect on the crystal structure of cotton fabric. FT-IR results indicated that the P-O-C covalent bond formed gave cotton fabric good flame retardancy and durability. SEM-EDS showed that FR not only successfully finished cotton fabric, but also effectively protected the structure of cotton fiber in the combustion zone. When the cotton fabric treated with 25.3% WG, The LOI of the treated cotton was improved to 39.5%, without after-time or after-glow. TG and DSC analysis showed that FR changed the decomposition path of cotton fabric at high temperature, TG showed that the char residues rate of treated cotton was improved from 18.9–28.6% at 600 °C. CONE results indicated that PHRR and THR decreased by 90.6% and 35.7% respectively. The mechanical property of the treated cotton slightly decreased but retained more than 70%. It is considered that FR can be used as an efficient, flame retardance and durability for cotton fabric, and it has flame retardant effect in condensed phase and gas phase at the same time.

Declarations

Acknowledgements

This work was supported by the 2013 Science and Technology Fund Project (20130206070 GX) of Jilin Provincial Department of Science and Technology.

Funding: This work was supported by the 2013 Science and Technology Fund Project (20130206070 GX) of Jilin Provincial Department of Science and Technology.

Conflicts of interest/Competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Availability of data and material: Data and material have authenticity, every experimental data in the manuscript is tested by the author, which is reliable.

Authors' contributions: Jinfeng Li: responsible for the synthesis of flame retardant, post-processing of treated cotton, data testing, sorting, and writing the first draft of the article.

Wei Jiang: being the manager of the whole project, participating in the synthesis and selection of flame retardants, planning the concept, design and analysis, participating in market research, drug selection, article guidance, data processing and proposing novel methods for this manuscript.

Maolin Liu: Market Research on flame retardants and cotton fabrics, and participated in the experimental process of synthesis and sample preparation.

This manuscript does not contain any studies with animals performed by any of the authors, and there is no ethical issue. In line with ethical standards, no conflict of interest.

Ethics approval: We submit a manuscript entitled "Synthesis of a new phosphorus/nitrogen durable flame retardant for cotton fabrics". This manuscript does not contain any studies with animals performed by any of the authors, and there is no ethical issue. In line with ethical standards, no conflict of interest.

Consent to participate: We declare that this manuscript entitled "Synthesis of a new phosphorus/nitrogen durable flame retardant for cotton fabrics" has not been published before; that it is not under consideration for publication anywhere else; that its publication has been approved by all co-authors, The publisher will not be held legally responsible should there be any claims for compensation.

Consent for publication: We declare that this manuscript entitled "Synthesis of a new phosphorus/nitrogen durable flame retardant for cotton fabrics" is original and has never been published before, and we do not consider publishing it elsewhere at present. We confirm that all the authors have read and approved this manuscript, and we further confirm that the order of authors listed in the manuscript has been approved by all of us. We agree that this manuscript will be published in cellulose, we know that the corresponding author is the only contact in the editing process, and she is responsible for communicating progress with another author, submitting revisions and finally approving proofs.

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Figures

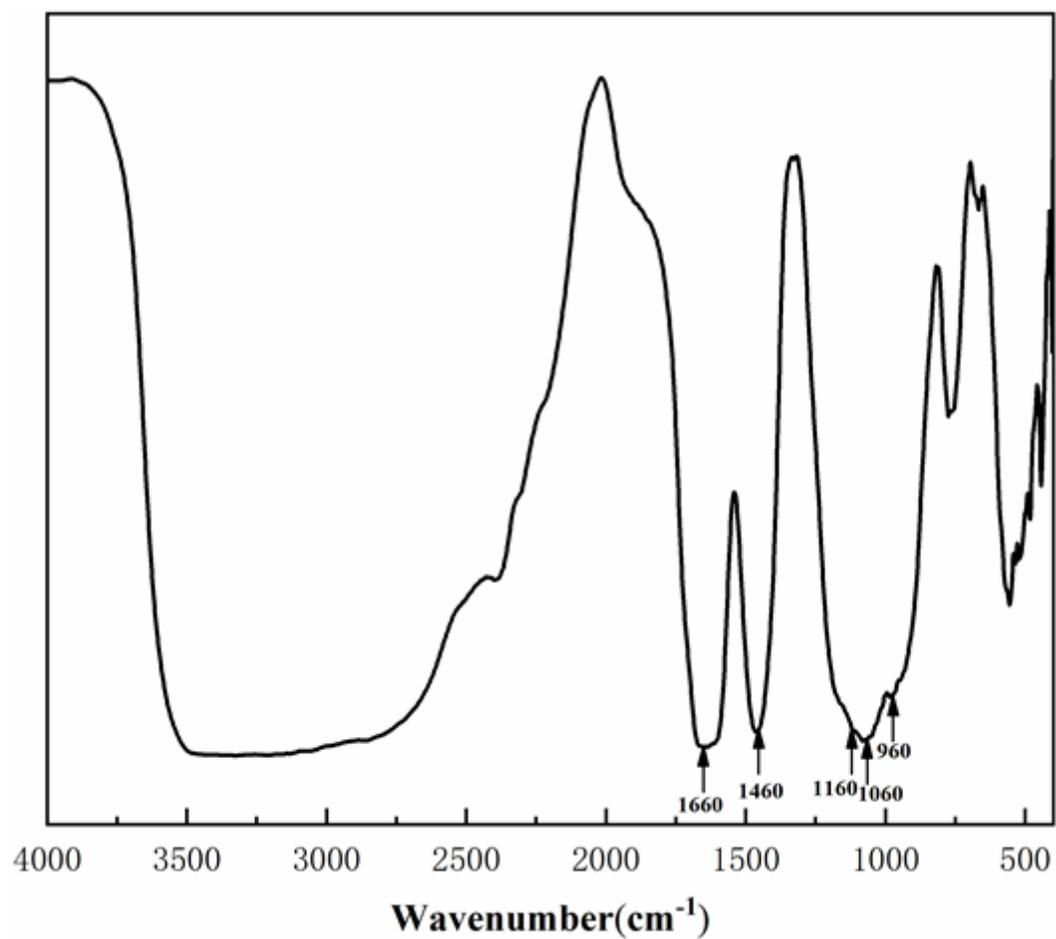


Figure 1

FT-IR spectra of FR

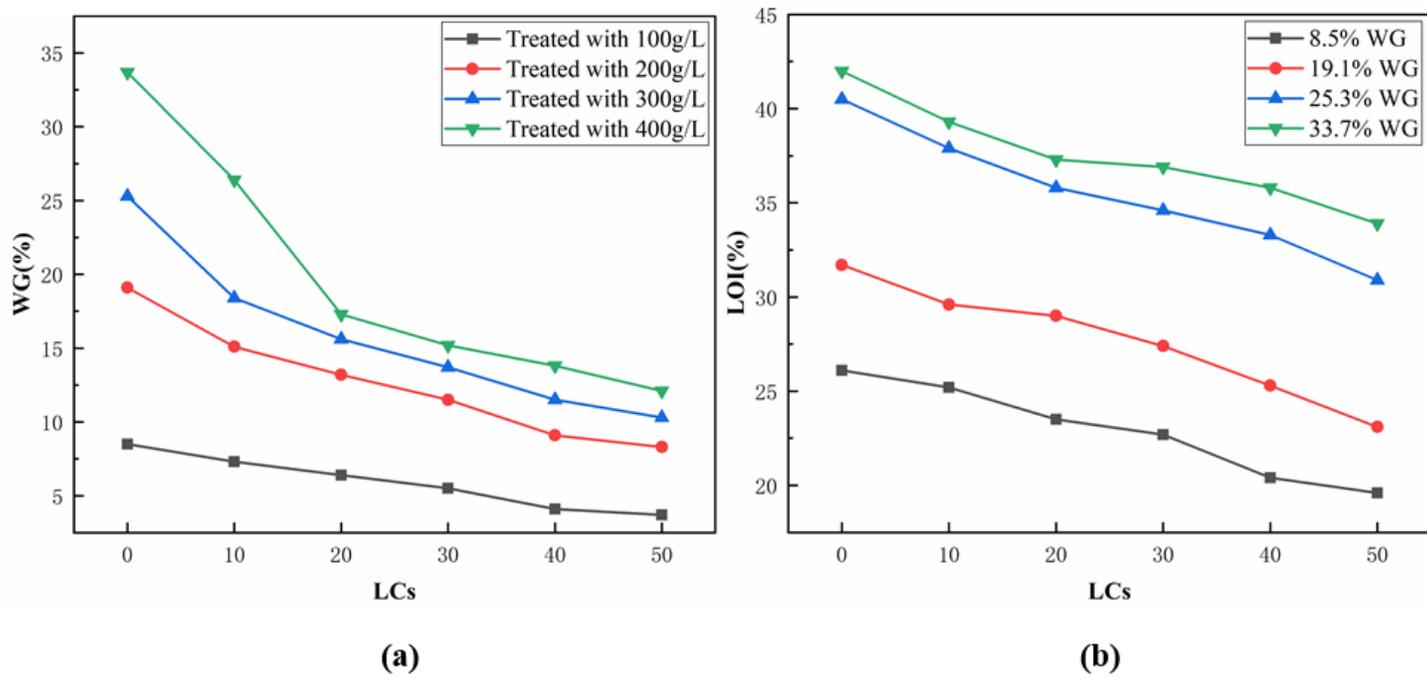
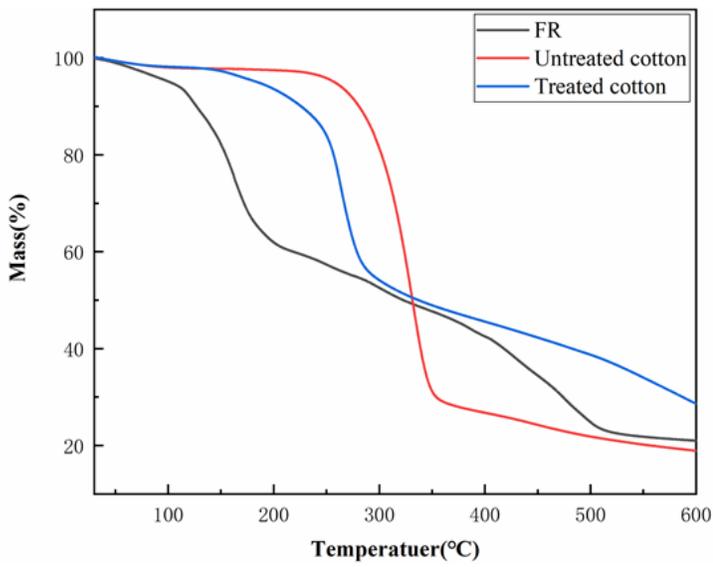
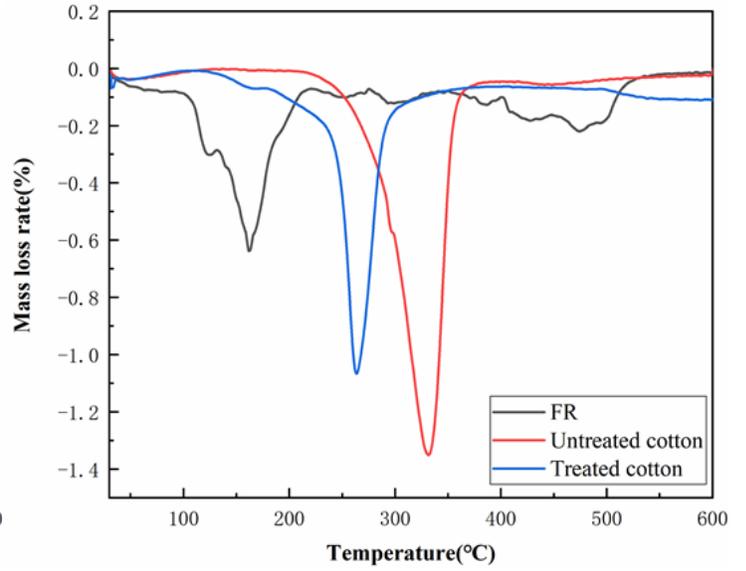


Figure 2

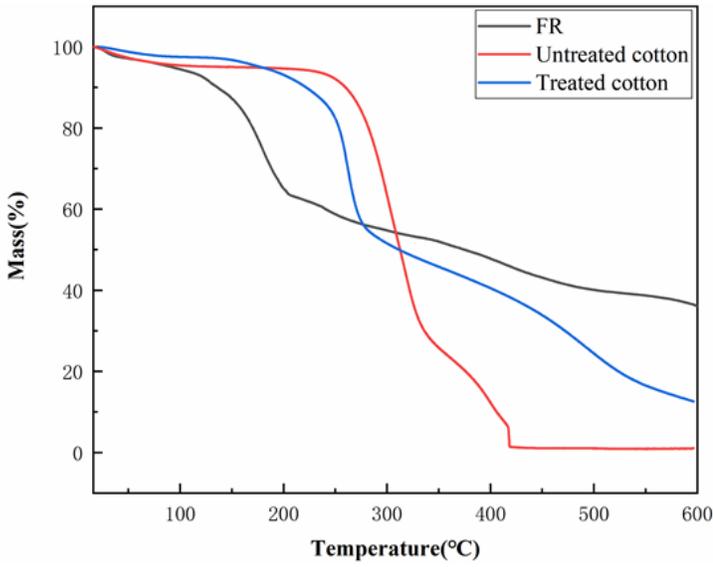
Change in WG% as a function of LCs(a) and LOI curves of treated cotton(b)



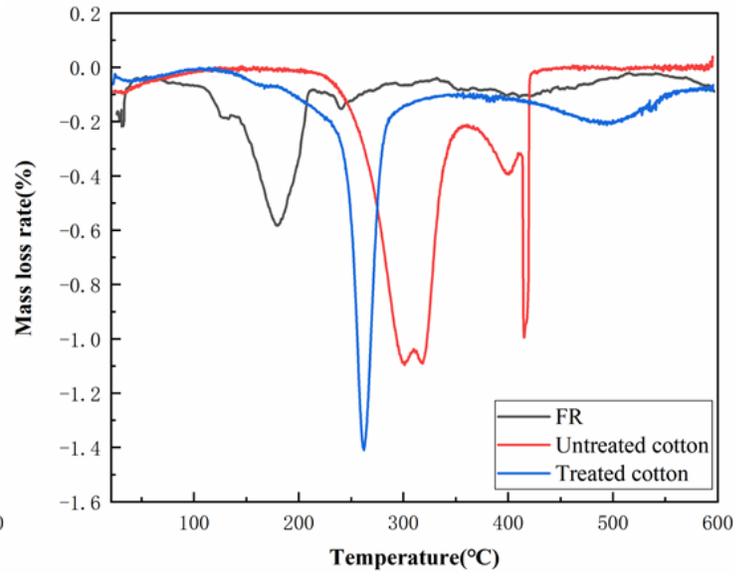
(a)



(b)



(c)



(d)

Figure 3

TG(a) and DTG(b) curves of the FR, untreated cotton and treated cotton under N2 atmosphere, and TG(c) and DTG(d) curves of the FR, untreated cotton and treated cotton under air atmosphere

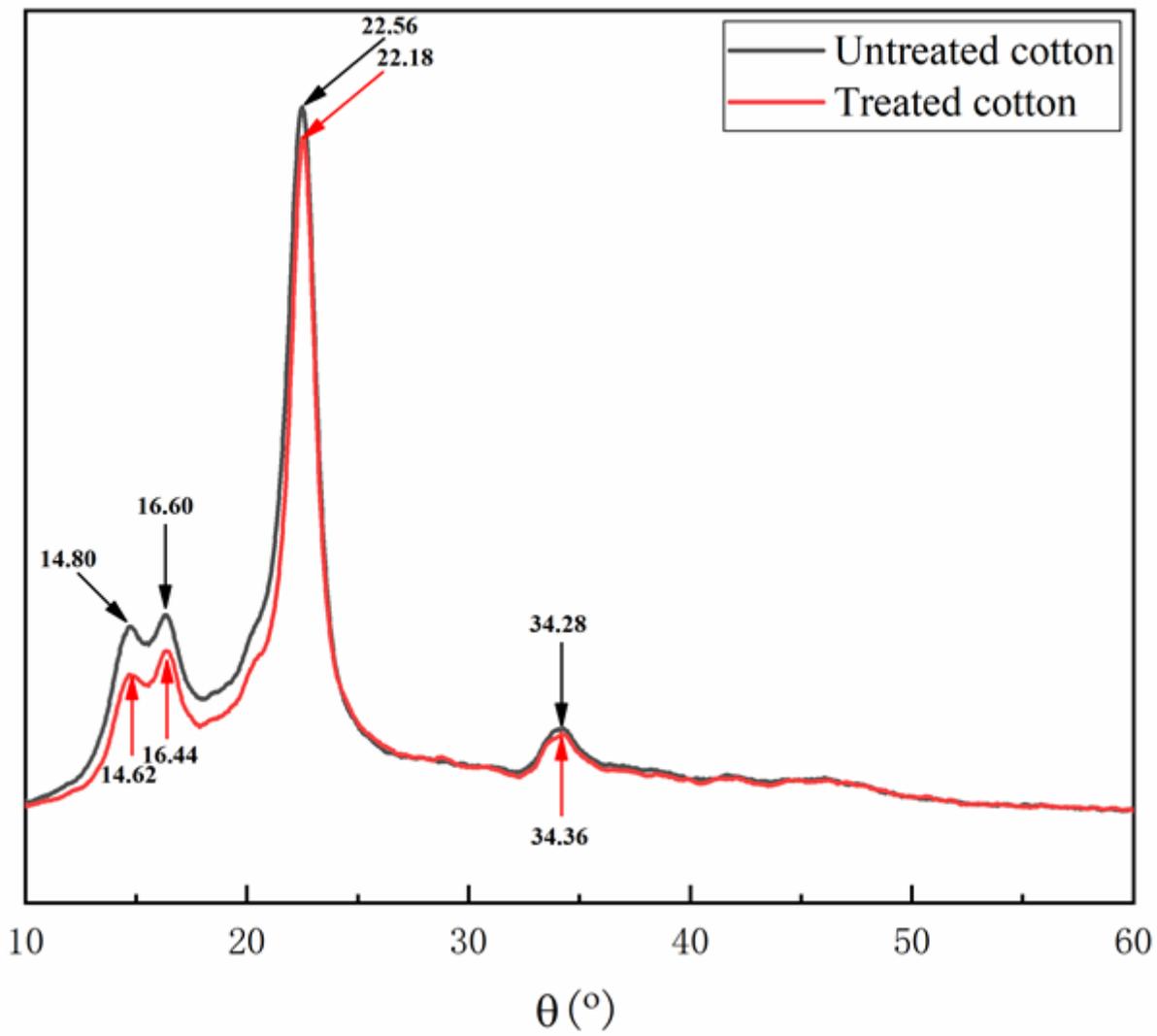


Figure 4

XRD spectra of untreated cotton and treated cotton

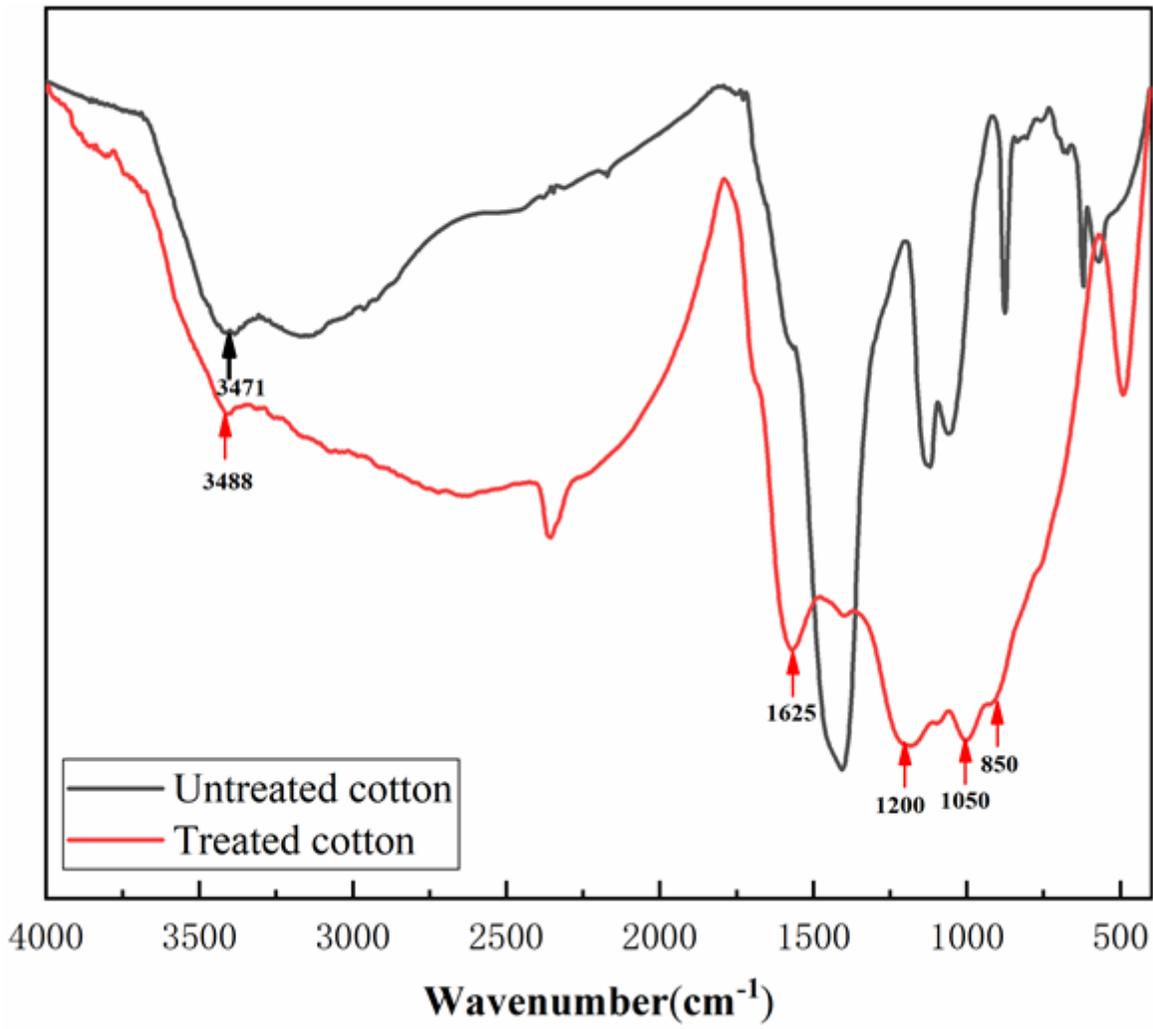
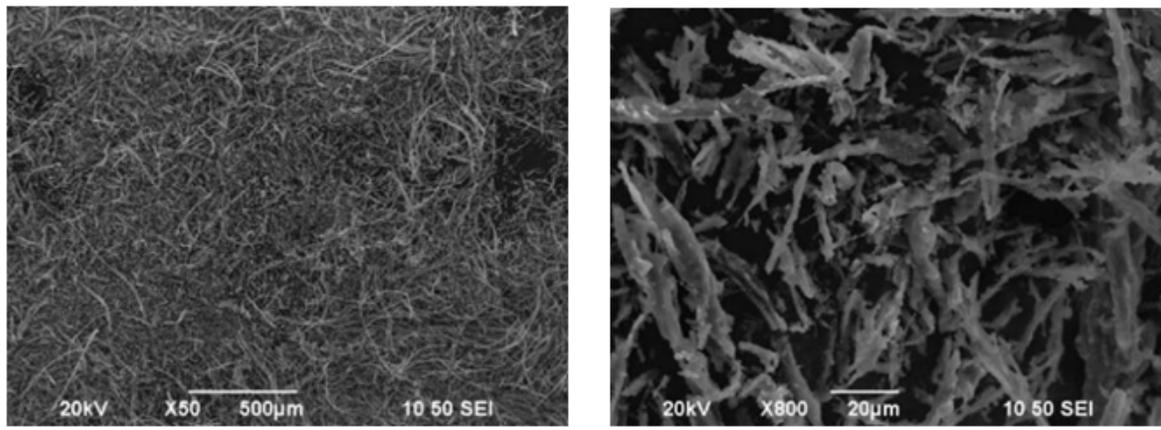


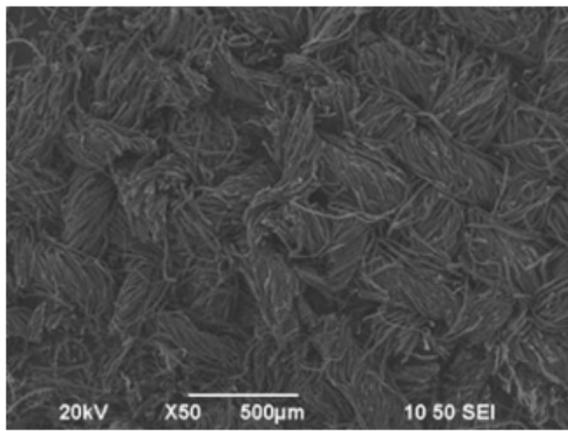
Figure 5

FT-IR spectra of untreated cotton and treated cotton

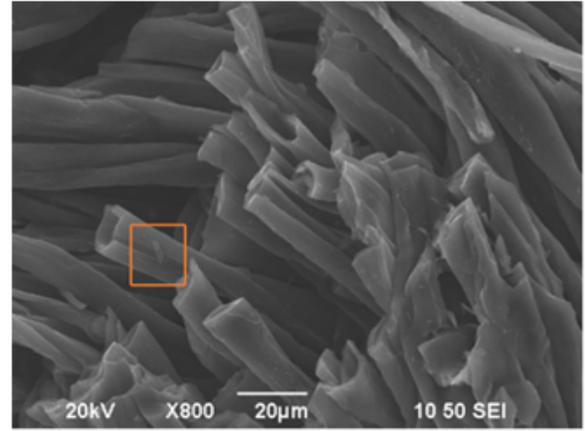


(a)

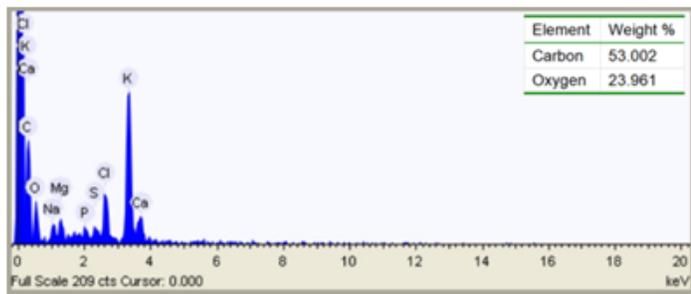
(b)



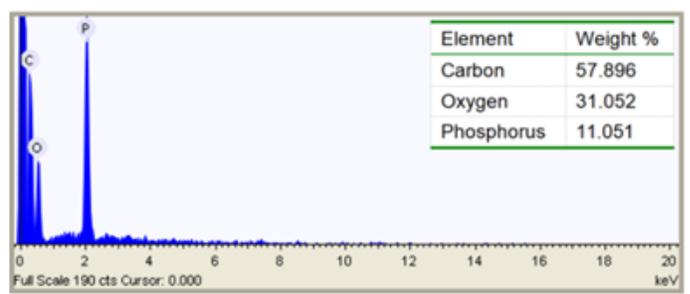
(c)



(d)



(e)



(f)

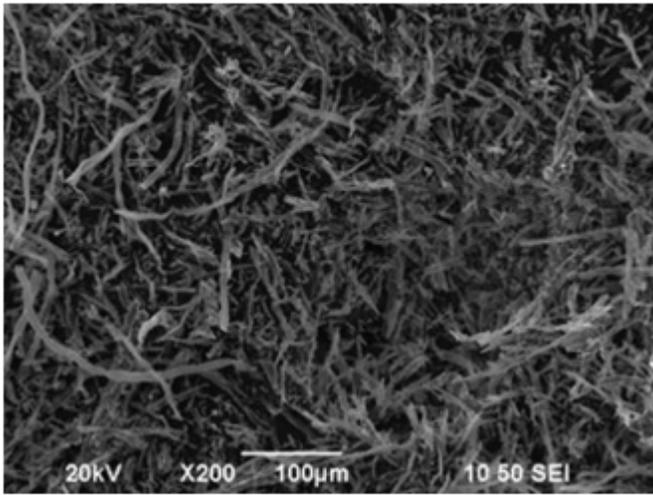
Figure 6

SEM images of the burnt cotton fabrics before treatment (a, b), burnt cotton fabrics after treatment (c, d) and EDS of burnt cotton fabrics before treatment (e) and burnt cotton fabrics after treatment (f)

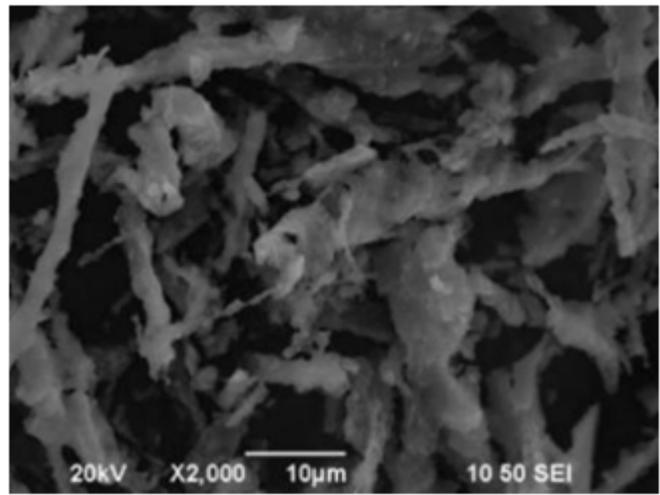


Figure 7

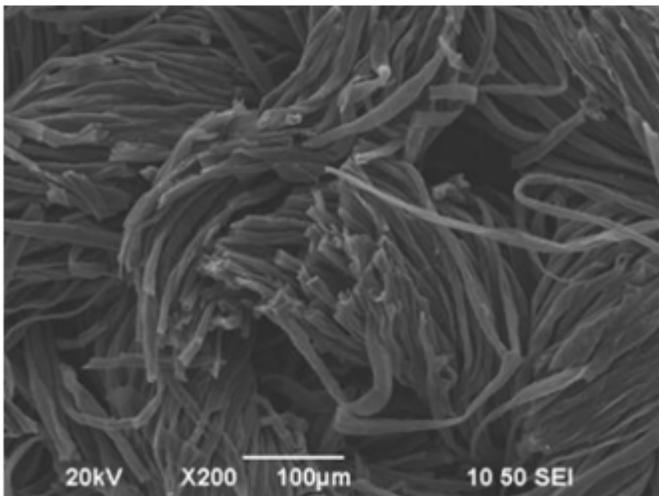
Vertical burning results of the untreated cotton (a) and the treated cotton with 8.5%, 19.1%, 25.3%,33.7% WG FR solutions(b,d,f,h) and the treated cotton with 8.5%, 19.1%, 25.3%,33.7% WG FR solutions after 50 LCs(c,e,g,i)



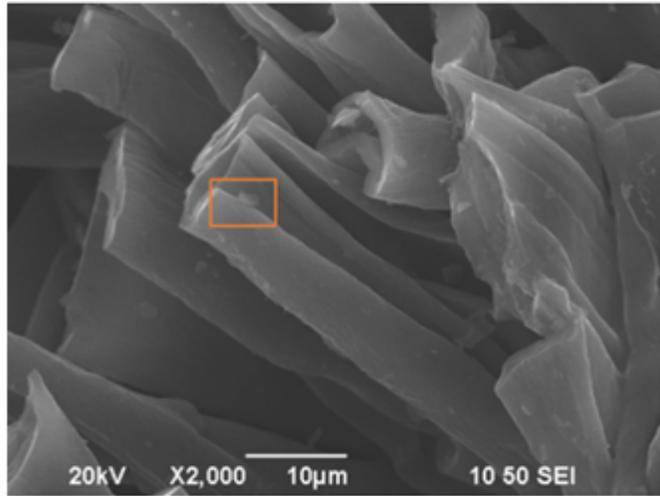
(a)



(b)



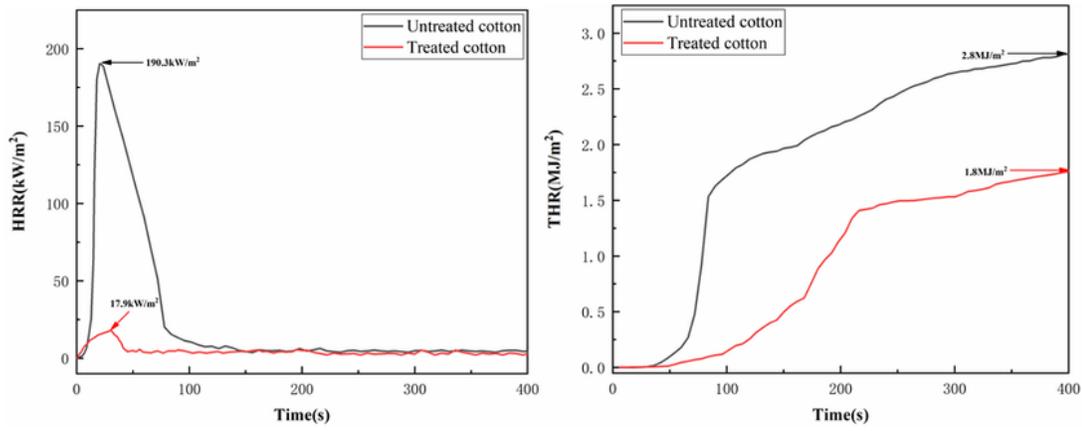
(c)



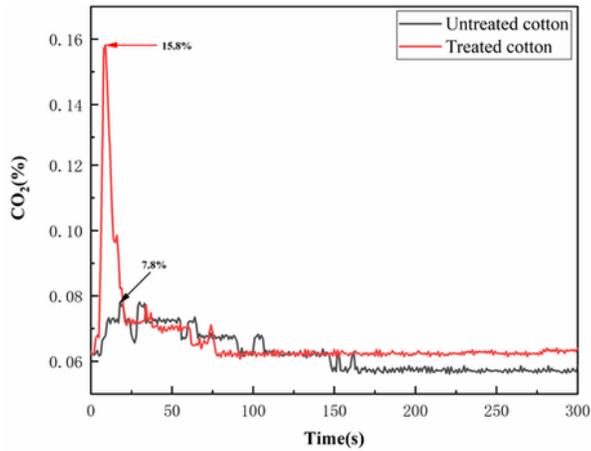
(d)

Figure 8

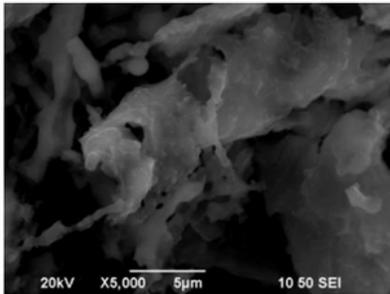
SEM images of burnt untreated cotton and treated cotton after vertical burning



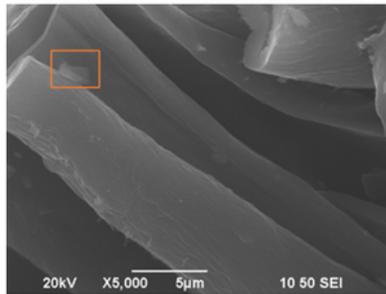
(a) (b)



(c)



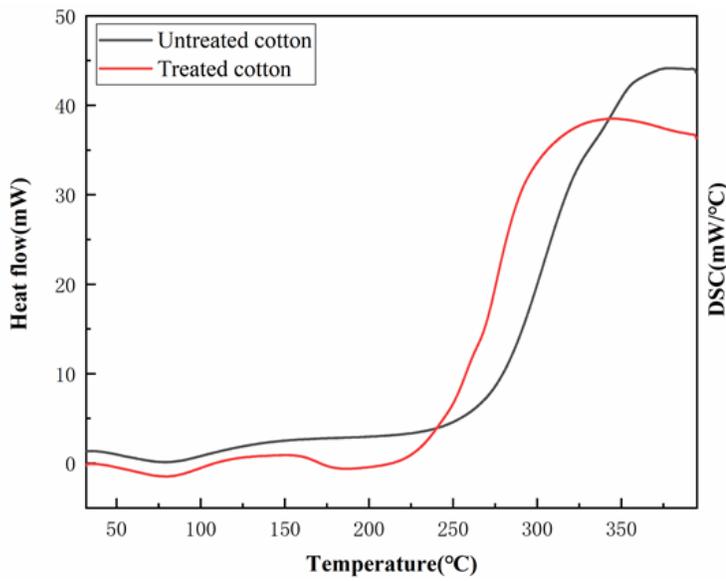
(d)



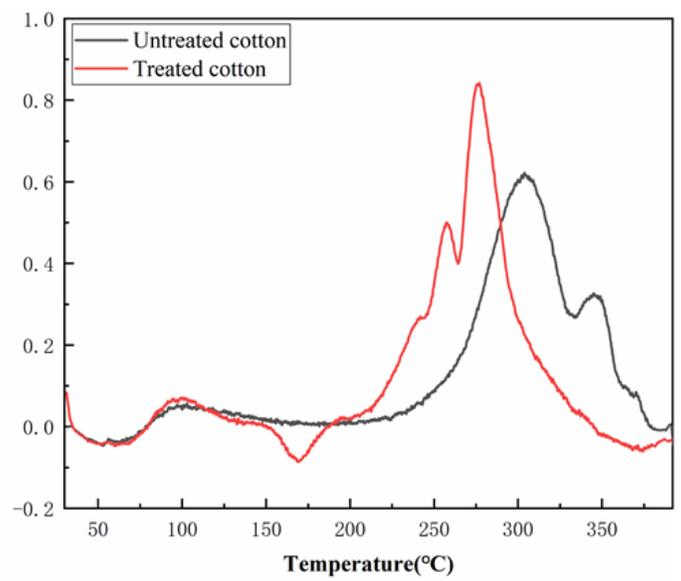
(e)

Figure 9

HRR (a), THR (b) and CO₂(c) curves of the untreated cotton and treated cotton and SEM images char residues of the untreated cotton (d) and treated cotton(e) after CONE



(a)



(b)

Figure 10

DSC curves of the untreated cotton and treated cotton

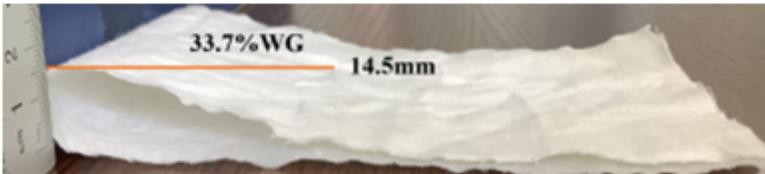
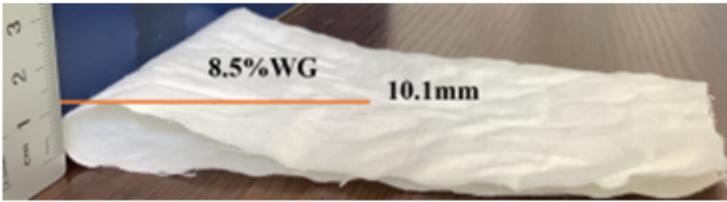
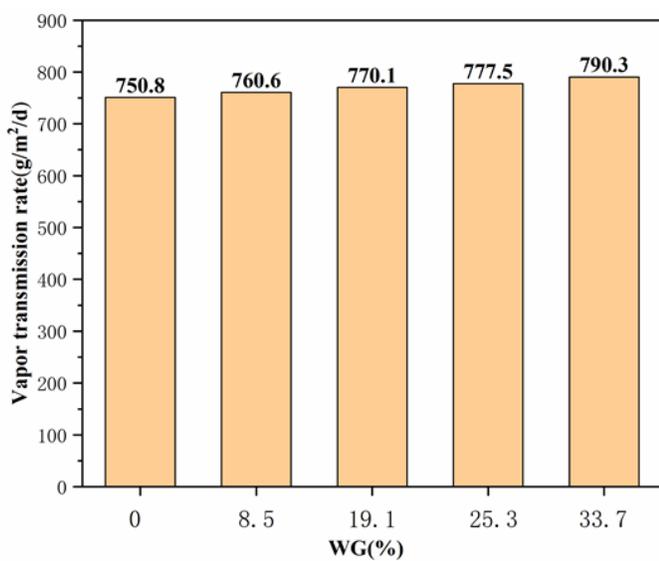
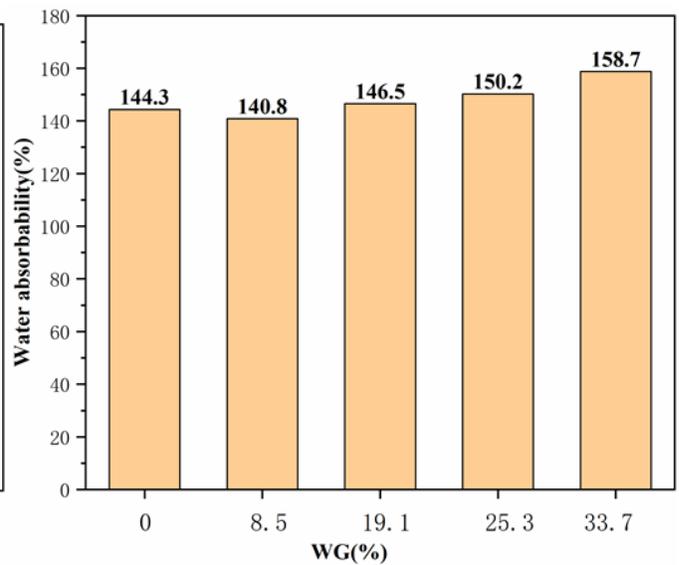


Figure 11

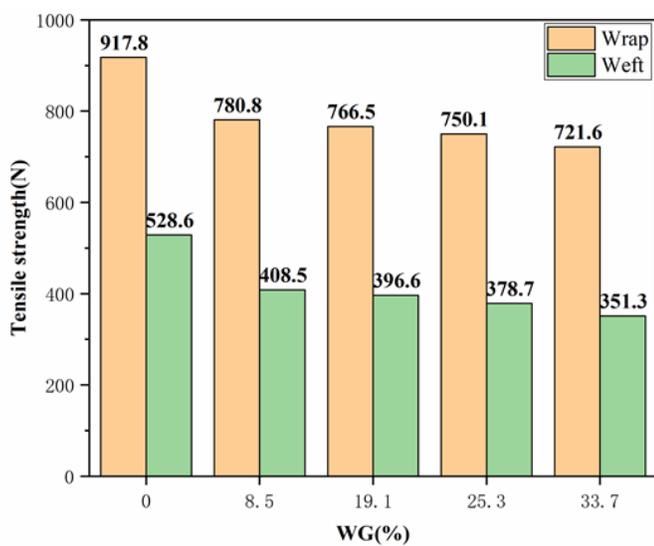
Flexibility of the untreated cotton and treated cotton



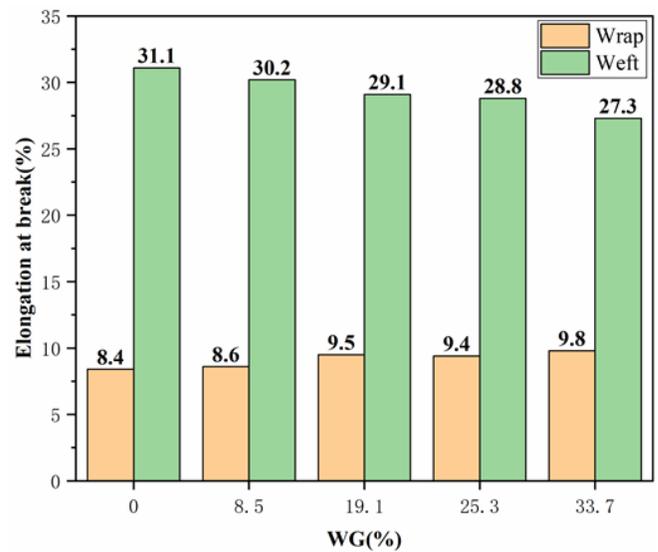
(a)



(b)



(c)



(d)

Figure 12

Vapor transmissibility(a), water absorbability(b), Tensile strength(c), Elongation break(d) of the untreated cotton and treated cotton

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [schema1.png](#)
- [schema2.png](#)
- [schema3.png](#)