

Preparation and application of durable flame retardant antimicrobial finishing agent for cotton fabrics

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1 **Preparation and application of durable**
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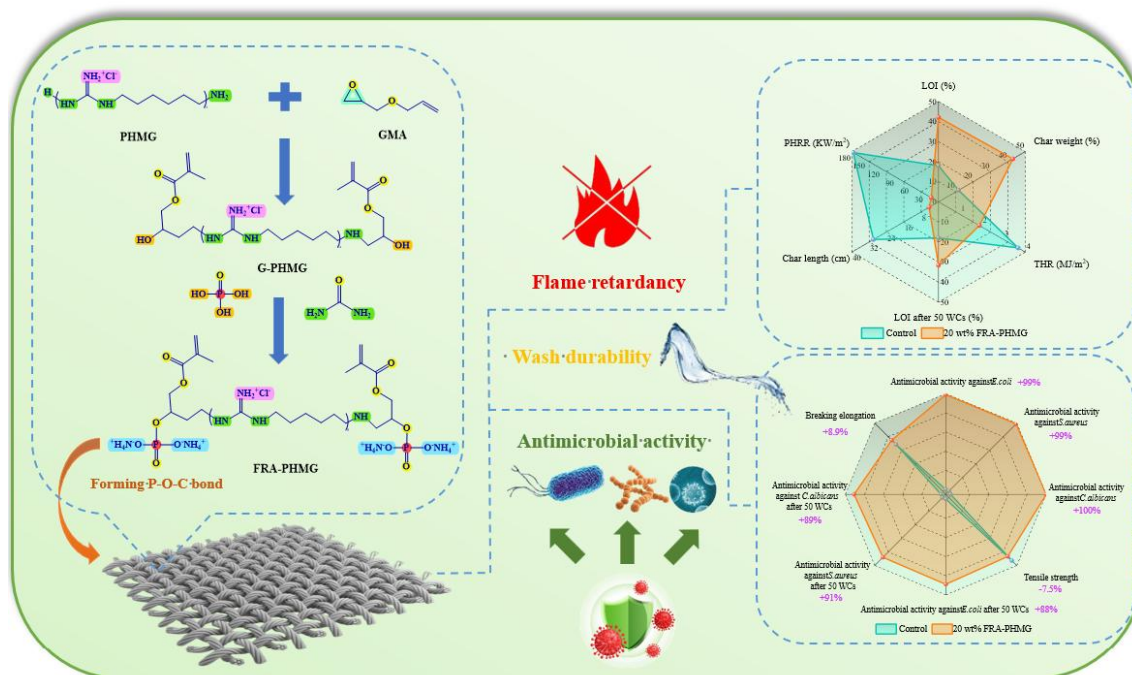
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ABSTRACT: Simultaneously endowing cotton fabrics with flame retardancy and antimicrobial functionality is a key research focus. This study synthesized a finishing agent, FRA-PHMG, using glycidyl methacrylate, polyhexamethylene guanidine hydrochloride, phosphoric acid, and urea as primary raw materials. Cotton fabric modified with a 200 g/L FRA-PHMG solution and cured at 180 °C for 3 minutes exhibited effective flame retardancy, achieving a LOI of 42.1% and a char length of 4.3 cm with no afterflame observed. The modification significantly suppressed heat release, reducing the total heat release by 48.50% and the peak heat release rate by 91.40% compared with the control fabric. Furthermore, the modified cotton demonstrated outstanding antimicrobial activity, achieving 99% against *Escherichia coli*, 99% against *Staphylococcus aureus*, and 100% against *Candida albicans*. The fabric also displayed excellent washing durability, maintaining a limiting oxygen index of 31.6%, a char length of 7.0 cm, and antimicrobial inhibition rates above 85% after 50 laundering cycles, with no detectable leaching of agents, due to robust covalent bonding with the cellulose. The finishing process had a minimal impact on the tensile properties of the fabric.

Keywords: Flame retardant; Antimicrobial; Cotton fabric; Polyhexamethylene guanidine hydrochloride

39 Graphic abstract



40

41

Introduction

Cotton fabric is extensively utilized in apparel, home furnishings, aerospace manufacturing and medical manufacturing due to its inherent properties which include comfort, breathability, excellent moisture absorption and biodegradability (Shi et al. 2024; Zaborniak et al. 2025; Sheng et al. 2025). However, cotton fabric possesses a Limiting Oxygen Index (LOI) of only 18% which indicates its significant flammability. During pyrolysis, it releases volatile combustible gases that conclusively accelerate flame spread. Statistical data reveal that approximately 50% of fire accidents annually originate from textile ignition, a pervasive hazard that results in catastrophic losses of life and property (Martina et al. 2023). Furthermore, while its superior moisture absorption enhances wearing comfort, it simultaneously provides favorable environments for bacterial and microbial proliferation, posing risks to human health. This combination of issues has severely limited the application expansion of cotton fabric in areas like medical protection and public safety (Wang & Zao 2024; Khalaf et al. 2025). Consequently, endowing cotton fabric with both flame retardant and antibacterial functionalities has become a key research focus in cotton functionalization. Some researchers employ bio-based materials (Yuan et al. 2024; Zhu et al. 2025; Yan et al. 2024) as foundational flame-retardant components, achieving a synergistic flame retardant-antibacterial effect through chemical modification. Others concentrate on the construction and functional application of nanocomposites (Shi et al. 2024; Li et al. 2018) to develop novel flame retardant-antibacterial finishing agents for cotton.

Additional research teams focus on phosphorus-based flame retardants as the core component, which are then formulated with antimicrobial agents such as quaternary ammonium salts, to equip cotton fabrics with antibacterial functionality (Li et al. 2026; Shoaib et al. 2024).

Against the backdrop of deep integration towards green, intelligent, and multifunctional textile finishing technologies (Paribha et al. 2021), China's textile industry is accelerating the innovation of related processes. Driven by the urgent demand for enhancing the flame retardancy and antibacterial properties of cotton fabrics, Wang et al. (Wang et al. 2024) modified cotton fabric using dopamine and its in situ-reduced copper ions to form copper nanoparticles, thereby preparing a novel flame-retardant and antibacterial cotton fabric. Liu et al. (Liu et al. 2024) employed γ -ureidopropyltriethoxysilane (TESPR) and phenylphosphonic acid (PPOA) to fabricate a flame-retardant antibacterial cotton fabric via the sol-gel process. Zhu et al. (Zhu et al. 2025) achieved durable antibacterial and flame-retardant performance by synergistically applying an efficient gallic acid-based flame retardant with an N-halamine antibacterial agent to cotton fibers. Both Dong (Dong et al. 2015) and Zhang et al. (Zhang et al. 2020) synthesized biguanide compounds primarily from dicyandiamide through addition reactions, subsequently preparing a novel phosphorus-nitrogen multifunctional flame retardant featuring a biguanide structure via further reactions. However, despite these developments, achieving cotton fabrics that possess outstanding concurrent flame retardancy and antibacterial functionality without

compromising other essential properties such as whiteness, tensile strength, and hygroscopicity remains a significant challenge; as existing research has yet to yield an industrialized or commercialized technology and product meeting these comprehensive requirements.

Polyhexamethylene guanidine hydrochloride (PHMG) is a cationic polymer that exhibits broad-spectrum and highly effective antimicrobial properties. Its core advantages include being non-toxic, environmentally friendly, and low-cost. Research indicates that PHMG's antimicrobial activity primarily stems from the densely distributed positively charged groups on its molecular chains, which electrostatically adsorb to the negatively charged phospholipid bilayers of both Gram-positive and Gram-negative bacteria. This interaction is followed by non-destructive transmembrane transport into the cell, ultimately leading to microbial death through interaction with genetic material (Meng et al. 2025; Finotelli et al. 2025; Shahin et al. 2020). Owing to these characteristics and its ability to maintain non-irritating and non-sensitizing properties towards human skin, PHMG is widely utilized in diverse sectors such as hospital disinfectants, water treatment, and the food and textile industries (Rosin et al. 2008; Kim et al. 2015; Yang et al. 2021). Importantly, since this physical interaction mode between PHMG and bacteria operates, it effectively circumvents the microbial resistance issues commonly associated with traditional chemical biocides. Consequently, numerous researchers have applied PHMG to cotton fabrics. However, as the amino functional groups within PHMG molecules lack chemical bonding

capability with the cellulose molecules of cotton fabric, relying instead on van der Waals forces for surface attachment, PHMG experiences significant leaching from the fabric during washing or detergent laundering. This results in a substantial decline in the fabric's sustained antimicrobial efficacy. To address this limitation, some scholars have attempted to modify either PHMG itself or the cotton substrate to facilitate PHMG grafting onto the fabric thereby imparting durable wash-resistant antimicrobial properties. For instance, Zhou et al. (Zhou et al. 2022) modified PHMG using glycerol triglycidyl ether (GTE) to synthesize the modified antimicrobial agent PHMG-GTE. They then exploited the reaction between the epoxy groups on GTE and the hydroxyl groups on cotton fabric to impart good wash-resistant antimicrobial performance to cotton. Nevertheless, while achieving wash resistance, this study failed to concurrently confer flame-retardant functionality to the PHMG-GTE-treated fabric.

Given the exceptional antimicrobial properties of PHMG, this study undertakes its chemical modification with the aim of imparting dual flame-retardant and antimicrobial functionality. This approach offers a novel strategy for functionalizing cotton fabrics. Accordingly, in this work, PHMG was chemically modified using glycidyl methacrylate (GMA). Subsequent phosphorylation followed by neutralization with urea yielded a flame-retardant and antimicrobial functional finishing agent, designated as FRA-PHMG. This study systematically investigated the flame-retardant and antimicrobial efficacy of FRA-PHMG applied to cotton fabric.

Experimental

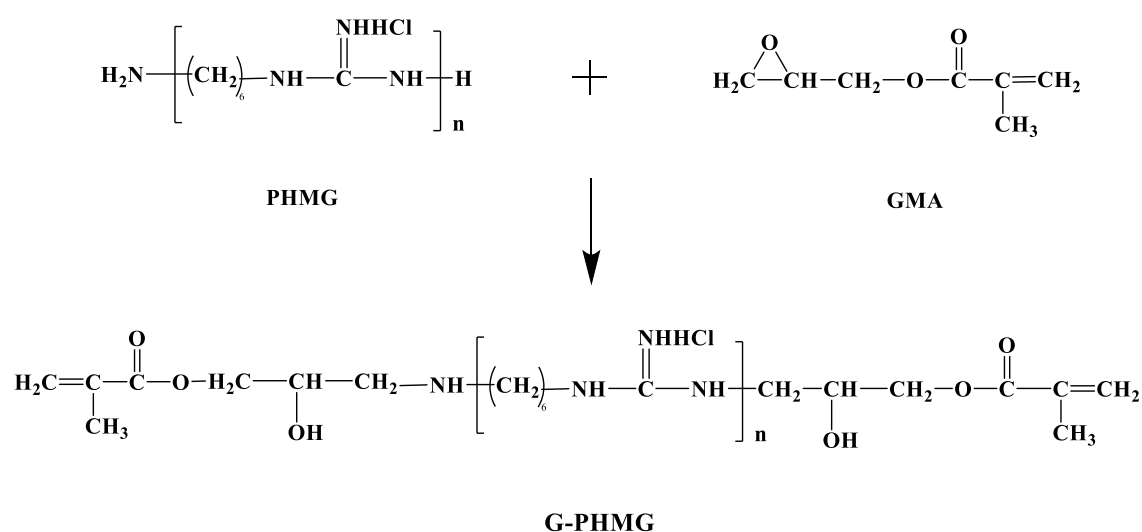
Materials

Bleached plain cotton fabrics (14.75 Tex $\times$ 14.75 Tex, 524 ends/10 cm $\times$ 284 picks/10 cm, 180g/m²) were provided by Zhejiang New Tianlong Group. (Zhejiang, China). Polyhexamethylene guanidine hydrochloride (PHMG, number-average molecular weight at 810) were supplied by Shanghai Gaoju Biotechnology Co., Ltd. (Shanghai, China). Glycidyl methacrylate (GMA, 97%, 1.5–3.0mPa·s) and Orthophosphoric acid (H₃PO₄, 85% in water) were obtained from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Urea ($\geq 98\%$) was supplied by Shanghai Darui Fine Chemicals Co., Ltd. (Shanghai, China). Dicyandiamide (DCD, 98%) and Dimethyl sulfoxide are provided by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Nutrient agar was obtained from Beijing Hongrun Baoshun Technology Co., Ltd. (Beijing, China). *Staphylococcus aureus* (ATCC 29213), *Escherichia coli* (ATCC 25922) and *Candida albicans* (ATCC 752) were supplied by Shanghai Luwei Technology Co., Ltd. (Shanghai, China).

Synthesis of G-PHMG

A measured amount of PHMG was placed in a three-neck flask, and an appropriate volume of dimethyl sulfoxide (DMSO) was added. The mixture was heated to 60 °C with stirring to obtain a homogeneous 40 wt% solution. Subsequently, GMA was introduced into the flask, and the reaction was allowed to proceed at this temperature

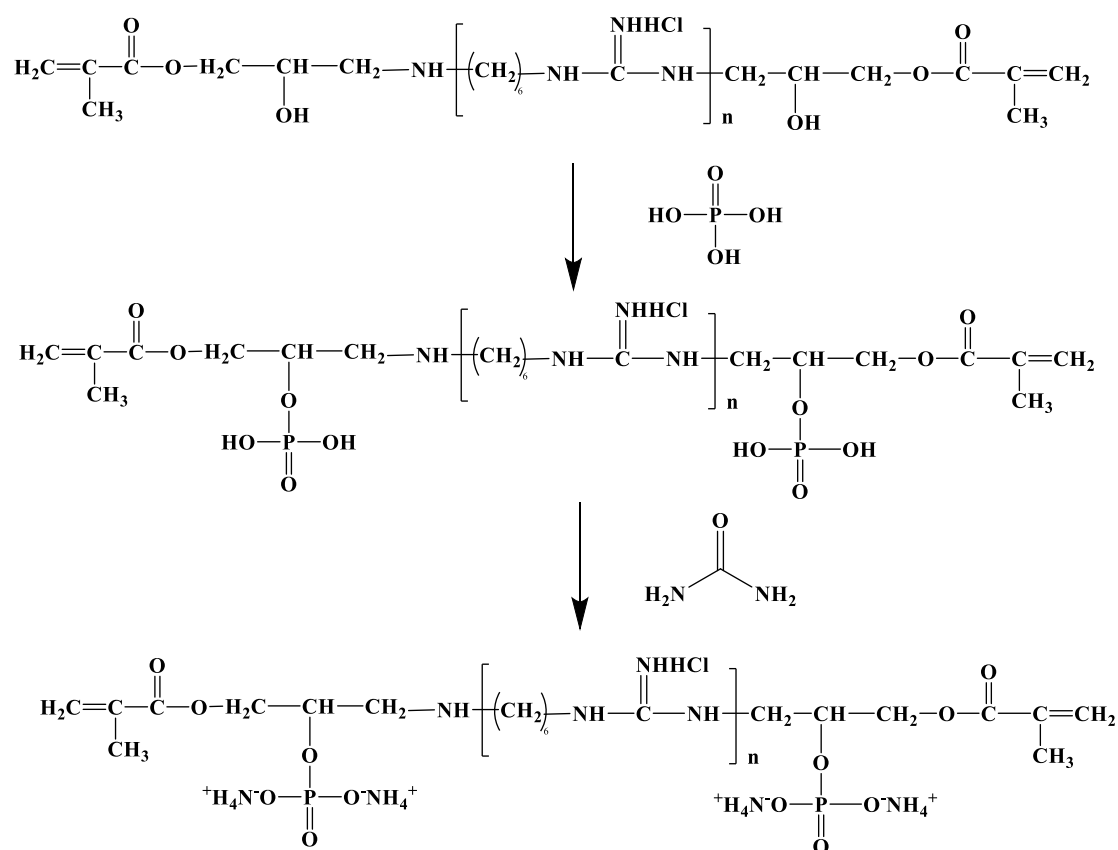
for 75 h under continuous stirring. After completion, acetone was added to the mixture to precipitate the solid product. The resulting solid was thoroughly washed with acetone several times and dried in a vacuum oven at 50 °C for 24 h. The final product was denoted as G-PHMG according to Zhou's and Wei's work (Zhou et al. 2010; Wei et al. 2012). The reaction equation was presented in Scheme 1.



Scheme. 1. Synthesis procedure for G-PHMG.

Preparation of FRA-PHMG

The synthesized G-PHMG and orthophosphoric acid were placed in a four-necked flask and reacted at 140 °C under nitrogen protection for 5 h. An appropriate amount of urea was then added, and the reaction was continued at 150 °C for 2 h to obtain the final product, denoted as FRA-PHMG. The reaction equation was shown in Scheme 2.



FRA-PHMG

Scheme. 2. Synthesis procedure for FRA-PHMG.

Preparation of flame-retardant and antimicrobial cotton fabric

The flame-retardant and antimicrobial agent FRA-PHMG was dissolved in deionized water to prepare working solutions with concentrations of 0, 100, 150, 200, and 250 g/L. An appropriate amount of dicyandiamide and urea was added to each solution. The cotton fabric was immersed in the solution at 70 °C for 5 min with a bath ratio of 1:20. A double-dipping and double-padding process was then performed to achieve a wet pick-up of 110%. The fabric was subsequently dried at 100 °C to remove moisture, followed by curing at 180 °C for 3 min, resulting in the final flame-retardant and antimicrobial cotton fabric. The preparation was presented in Fig. 1. The weight

gain (WG) of the modified cotton fabric (Qin et al. 2024) was calculated using the following formula:

$$WG(\%) = \frac{(M - M_0)}{M_0} \times 100\%$$

Where M_0 and M are the dry weight (g) of the cotton fabrics before and after modification.

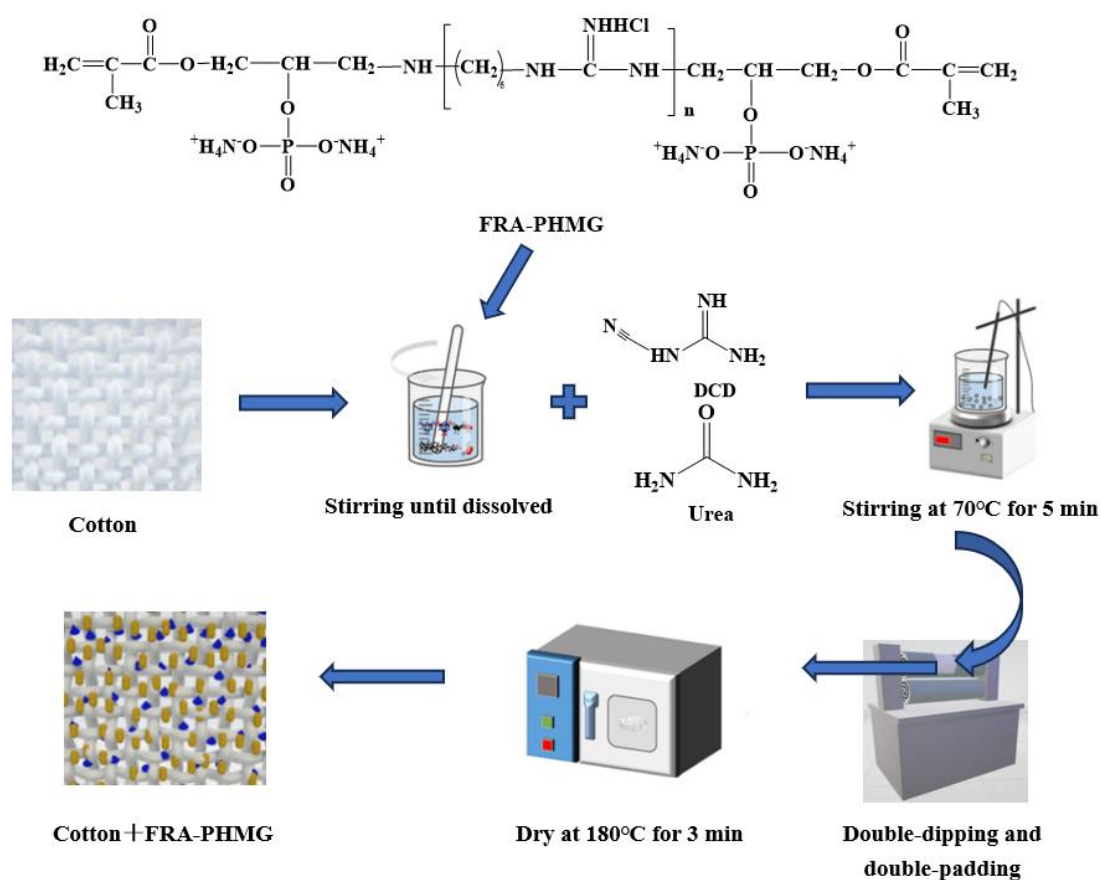


Fig. 1. Synthetic route to flame-retardant and antimicrobial cotton fabric.

Measurement and characterization

The FT-IR spectra of PHMG, FRA-PHMG were analyzed by a Nicolet iS 50 Fourier Transform Infrared Spectrometer (Thermo Fisher Scientific, USA) in the range of 500 to 4000 cm^{-1} with a resolution of 2 cm^{-1} .

¹H NMR spectra were recorded on a Bruker AVANCE III HD 600 MHz NMR spectrometer (Bruker, Germany) at 25 °C. Deuterated water (D₂O) was used as the solvent. Spectra were acquired using the cpmgpr1d pulse sequence with the following parameters: spectral width δ = 20.0276 ppm, time domain (TD) = 64K, acquisition time (AQ) = 2.73 s, number of scans (NS) = 64, relaxation delay (d1) = 10 s, and total acquisition time < 15 minutes.

³¹P NMR spectra were obtained on the same Bruker AVANCE III HD 600 MHz NMR spectrometer using deuterated water as the solvent. The zgpg30 pulse sequence was applied with the following parameters: spectral width (SWH) = 39682.5 Hz, time domain (TD) = 65K, acquisition time (AQ) = 0.825 s, number of scans (NS) = 128, dummy scans (DS) = 4, receiver gain (RG) = 1150, and temperature = 25 °C.

The surface morphology was analyzed using a ZEISS-Sigma 360 scanning electron microscope (SEM, Carl Zeiss, Germany). The elemental analysis (C, N, P, O) of the modified cotton fabric was determined by energy dispersive spectroscopy (EDS) using a ZEISS-Sigma 360 scanning electron microscope (Carl Zeiss, Germany)

According to ASTM D6413-99, the vertical flammability test (VFT) was carried out with a LFY-601A vertical combustion device (Suzhou Zhengbiao Combustion Testing Technology Service Co., Ltd, China). The cotton samples, sized 300 mm × 80 mm, were exposed to a flame for 12 seconds with a flame height of 40 mm. According to GB/T 2919-1998, the limiting oxygen index (LOI) of cotton was determined by a LFY-606B digital limiting oxygen index instrument (Suzhou

Zhengbiao Combustion Testing Technology Service Co., Ltd, China). The sample size was 150 mm × 50 mm.

Thermogravimetric (TG) analysis of the unmodified cotton fabric and modified cotton fabric were performed by an HTG-1 Pyris1 thermogravimetric analyzer (Mettler-Tole, USA) from 30 to 700 °C at a heating rate of 20 °C/min⁻¹ under flowing nitrogen atmosphere.

FTT0007 Cone calorimeter (CCT, Fire Testing Technology, UK) was used to measure combustion behavior of modified cotton fabric according to ISO 5660-1. The sample size was 10 cm × 10 cm, and two pieces were wrapped in aluminum foil under a radiation intensity of 35 kW/m².

According to GB/T 20944.3-2008, the antibacterial activity was evaluated using an oscillation method. Briefly, test cultures of *E. coli* (ATCC 25922), *S. aureus* (ATCC 29213), and *C. albicans* (ATCC 752) were prepared in broth and adjusted to approximately $2.5 \sim 3.0 \times 10^5$ CFU/mL. Sterilized fragments (0.75 g ± 0.05 g) of the antimicrobial test fabric and a control cotton fabric were each incubated with 5 mL of the bacterial suspension and 70 mL of PBS in a conical flask. The flasks were shaken at 150 rpm and 24 ± 1 °C for 18 h. Samples were taken at 0 h and 18 h, serially diluted, and plated on nutrient agar. After incubation, the colonies were counted, and the antibacterial activity was calculated.

The agar diffusion plate method was performed according to GB/T 20944.1-2007. Test cultures of *E. coli* (ATCC 25922), *S. aureus* (ATCC 29213), and *C. albicans*

221 (ATCC 752) were adjusted to $1 \sim 5 \times 10^8$ CFU/mL and incorporated into the upper
222 layer of two-layer agar plates. Circular fabric samples (25 mm diameter) were placed
223 on the agar surface and gently pressed to ensure contact. After incubation at 37°C for
224 18~24 h, the width of the inhibition zone (H) was measured using the formula $H = (D$
225 $- d)/2$, where D is the inhibition zone diameter and d is the sample diameter. Bacterial
226 growth beneath the samples was also examined.

227 The washing durability of modified cotton fabric was determined according to
228 AATCC 61-2013. The modified cotton samples were placed in 250 mL conical flasks
229 containing a 0.15% (wt) detergent solution. The flasks were then subjected to washing
230 in a shaking water bath at 80 r/min and 49 °C for 45 minutes, which corresponds to 5
231 washing cycles (WC).

232 The tensile properties, including breaking strength and elongation at break, of
233 cotton fabrics were measured according to GB/T 3923.1-2013 standard. The test was
234 performed using a LFY-201D electronic fabric tension tester (Shandong Textile
235 Research Institute, China).

Results and discussions

FTIR analysis

The FTIR spectra of PHMG and FRA-PHMG were shown in Fig. 2. In the spectrum of PHMG, the peaks at 3158 cm^{-1} and 1617 cm^{-1} were assigned to the N–H stretching vibration and bending vibration of the NH_2 group, respectively (Zhou et al. 2010). In contrast, the spectrum of FRA-PHMG showed a new absorption band at 3430 cm^{-1} , indicative of an N–H stretching vibration. The peaks at 1592 cm^{-1} and 1435 cm^{-1} were attributed to the bending vibration and the in-plane bending vibration of N–H in the ammonium phosphate group (Zhou & Li 2025). The absorption peaks at 1273 cm^{-1} , 1143 cm^{-1} , 1062 cm^{-1} , and 890 cm^{-1} correspond to the asymmetric vibration of PO_2^- (Tian et al. 2019), stretching vibration of P=O (Yang et al. 2023; Zope et al. 2017), symmetric vibration of the P–O–P bridge, and asymmetric vibration of the P–O–P bond (Zhou 2025), respectively. These presence of these new features confirmed the successful formation of FRA-PHMG.

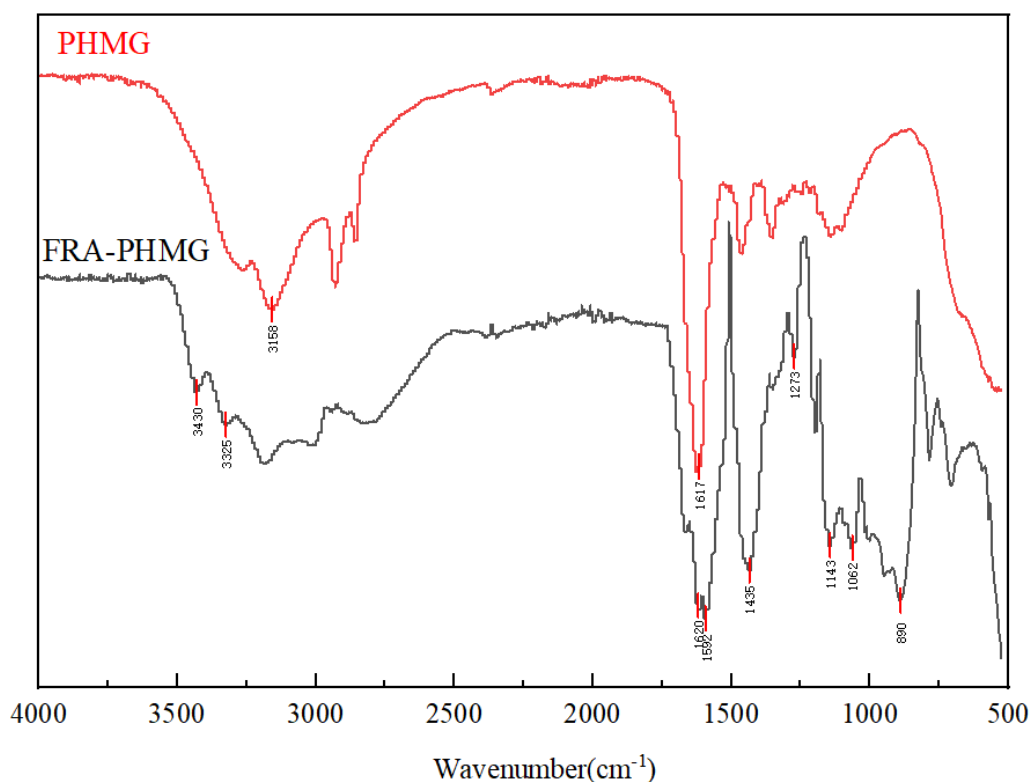


Fig. 2. FTIR spectra of PHMG and FRA-PHMG.

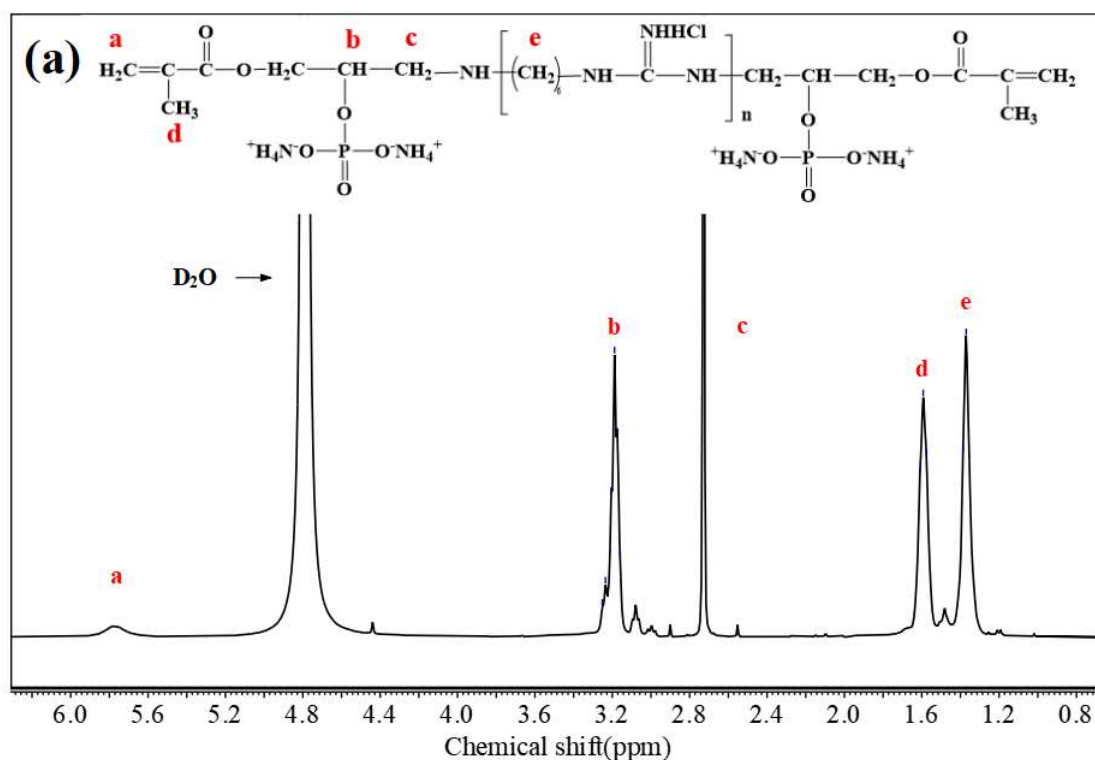
NMR analysis

The ^1H NMR spectrum of FRA-PHMG was presented in Fig. 3a. The singlet at $\delta = 5.69$ ppm was assigned to the hydrogens of the methylene group ($=\text{CH}_2$, site a) (Zhou et al. 2010). A multiplet observed at $\delta = 3.20$ ppm corresponded to the hydrogen of the $-\text{O}-\text{CH}-$ group (site b), while the singlet at $\delta = 2.73$ ppm was attributed to the methylene protons adjacent to the secondary amine (site c) (Zhou et al. 2010). The signal at $\delta = 1.59$ ppm originated from the methyl hydrogens of the methacrylate group (site d). The multiplet at $\delta = 1.38$ ppm was associated with the methylene protons of the long-chain alkane segment (site e). The integration ratios of all characteristic signals were consistent with the theoretical proton ratios expected for the target compound FRA-

PHMG.

The ^{31}P NMR spectrum of FRA-PHMG was shown in Fig. 3b. The characteristic signal at $\delta = 0.33$ ppm corresponded to the phosphorus atom bonded to oxygen in the phosphate structure, while the resonance at $\delta = -9.26$ ppm was characteristic of the phosphorus atom in a P-O-P linkage (Tang 2024). The integrated peak areas matched the theoretical ratios anticipated for the molecular structure.

Collectively, the ^1H and ^{31}P NMR results confirmed the successful synthesis of the target compound FRA-PHMG.



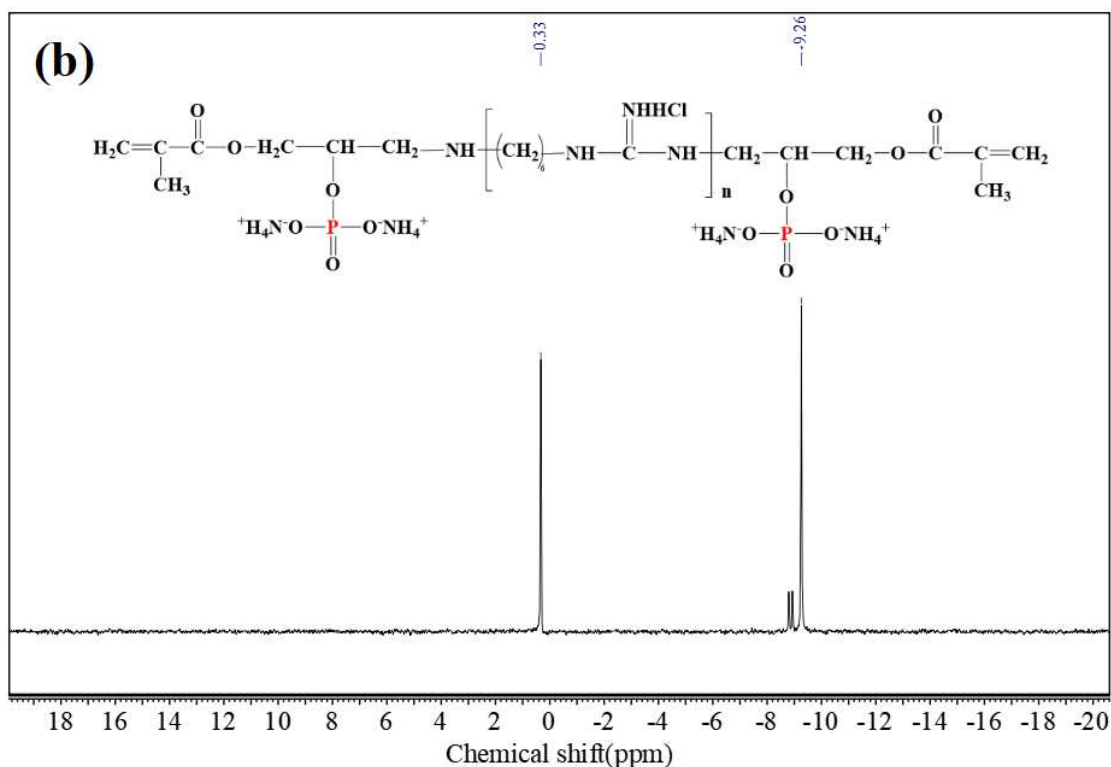


Fig. 3. ^1H NMR(a) and ^{31}P NMR(b) spectra of FRA-PHMG.

Flame retardancy and combustion behavior

As indicated by the data in Table 1, the control cotton fabric was completely consumed after the vertical flame test, leaving only a small amount of fibrous residue, with a low LOI of 18.0%. In contrast, the cotton fabric modified with FRA-PHMG exhibited significantly enhanced flame resistance. As the concentration of FRA-PHMG increased from 0 to 200 g/L, the LOI value of the modified cotton gradually rose. During combustion, a continuous and dense char layer was formed, maintaining the structural integrity of the fabric. Both afterglow and flaming combustion times were reduced to 0 s. Notably, at the concentration of 200 g/L, the LOI reached 42.1%, representing an increase of 24.1% compared to the control sample.

When the FRA-PHMG concentration exceeded 200 g/L, the further increase in LOI became marginal. Within the concentration range of 200~250 g/L, the weight gain rate of the fabric only increased slightly from 22.4% to 22.9%. This plateau effect could be attributed to the saturation of active sites on the cellulose molecules. Below the critical concentration of 200 g/L, the flame-retardant molecules fully occupied active sites such as hydroxyl groups on cellulose, forming a complete coating through intermolecular forces. Beyond this concentration, the surface active sites were saturated, and the adsorption reached a plateau, resulting in limited additional improvement in flame retardancy. In this saturated state, the phosphate groups from FRA-PHMG decomposed at relatively low temperatures into polyphosphoric or metaphosphoric acids, which notably reduced the maximum thermal degradation rate, suppressed the formation of levoglucosan, and catalyzed the dehydration and carbonization of cotton fibers (Wan et al. 2019; Tang et al. 2024). The resulting char layer covered the fiber surface, effectively blocking heat and oxygen transfer, thereby slowing further decomposition of the cotton. Simultaneously, nitrogen elements from the guanidine hydrochloride moiety generated non-flammable gases such as NO, NO₂, and NH₃ during combustion. These gases diluted oxygen concentration in the surroundings and isolate the flame, leading to self-extinguishment.

Table 1 LOI values, WG values and VFT data of different samples

Samples	FRA-PHMG (g/L)	LOI (%)	WG (%)	Afterflame time (s)	Afterglow time (s)	Char length (cm)
Control cotton	0	18	—	40.5	4.6	30
FRA-PHMG	100	34.5	14.6	0	0	7.6
FRA-PHMG	150	38.7	19.3	0	0	5.8
FRA-PHMG	200	42.1	22.4	0	0	4.3
FRA-PHMG	250	42.7	22.9	0	0	4.1

Note. Preparation conditions: Urea, 50g/L; DCD, 80g/L. Curing conditions: 180°C for 3 min.

To verify this flame-retardant effect quantitatively, the combustion behaviors of the control and modified cotton fabrics were further compared under a heat flux of 35 kW/m² using cone calorimetry. The test results were documented in Fig. 4, which presented the dynamic curves heat release rate (HRR), total heat release (THR), total smoke release (TSR), carbon monoxide production (COP), and carbon dioxide production (CO₂P) and photographs of the post-combustion residues, while key combustion parameters were summarized in Table 2.

The cone calorimetry results unequivocally demonstrated the superior fire resistance of the modified fabric, primarily characterized by a drastic reduction in heat release. As shown in Fig. 4c ~ d and Table 2, the modified cotton exhibited

significantly lower HRR and THR values than the control cotton. The control cotton was ignited within 10 s after exposure and reached a peak heat release rate (PHRR) of 176.58 kW/m² at 18 s, indicating rapid decomposition and heat release under high temperatures. In contrast, the combustion of the modified cotton was notably delayed, reaching its PHRR of only 15.18 kW/m² at 64 s, which was 91.40% lower than that of the control. The THR of the modified sample was 1.89 MJ/m², which was 48.50% lower than the control value of 3.67 MJ/m². This suppression effect was attributed to the excellent char-forming ability of FRA-PHMG in the condensed phase. Upon heating, FRA-PHMG grafted onto the cotton surface decomposed and catalyzed the formation of a thin but compact char layer. This layer acted as a barrier against the release of volatile flammable gases and heat diffusion, leading to a rapid decrease in HRR. However, as volatiles accumulated beneath the char, local fractures occurred, resulting in sporadic bursts of heat release and the characteristic fluctuating HRR curve observed in Fig. 4c. This dynamic process confirmed the efficient condensed-phase flame retardant mechanism of FRA-PHMG.

As seen in Fig. 4e, the TSR of the FRA-PHMG modified cotton was significantly higher than that of the control cotton, which could be attributed to the emission of non-flammable gases such as NH₃, NO₂, and NO generated during the decomposition of the flame-retardant system. The increased smoke release diluted the concentration of combustible gases and quenches free radicals, demonstrating the contribution of gas-phase flame retardancy.

The COP and CO₂P rates of the modified cotton were lower than those of the control cotton, as evidenced by the data in Fig. 4f ~ g. The CO₂/CO ratio is often used to evaluate combustion efficiency (Liao et al. 2021); a lower ratio indicates suppressed combustion. It was worth noting that the modified cotton fabric released less CO and CO₂, which appeared inconsistent with some conventional reports. This anomaly could be related to the unique structure of the char layer promoted by FRA-PHMG, which was high density, cross-linked, and of low porosity. This structure limited the pyrolysis rate and escape of flammable gases, thereby facilitating secondary charring. This process converted intermediate products that might otherwise form CO into solid char, reducing toxic CO emission and highlighting the dominance of the condensed-phase mechanism (Shi et al. 2025; Lu et al. 2022) coupled with inhibition of gas-phase processes (Liao et al. 2021).

The results from cone calorimetry, vertical flame testing, and limiting oxygen index collectively demonstrate the synergistic flame-retardant action of FRA-PHMG. The formation of a dense and continuous char layer, as directly evidenced by the residue morphology shown in Fig. 4 a ~ b, provides definitive proof of a condensed-phase mechanism. This char layer is primarily responsible for the dramatic reduction in PHRR and THR by acting as a protective barrier. Concurrently, the observed increase in total smoke release indicates the activity of gas-phase flame inhibition. The synergistic effect of charring and gas-phase inhibition endows the FRA-PHMG modified cotton with excellent flame retardancy.

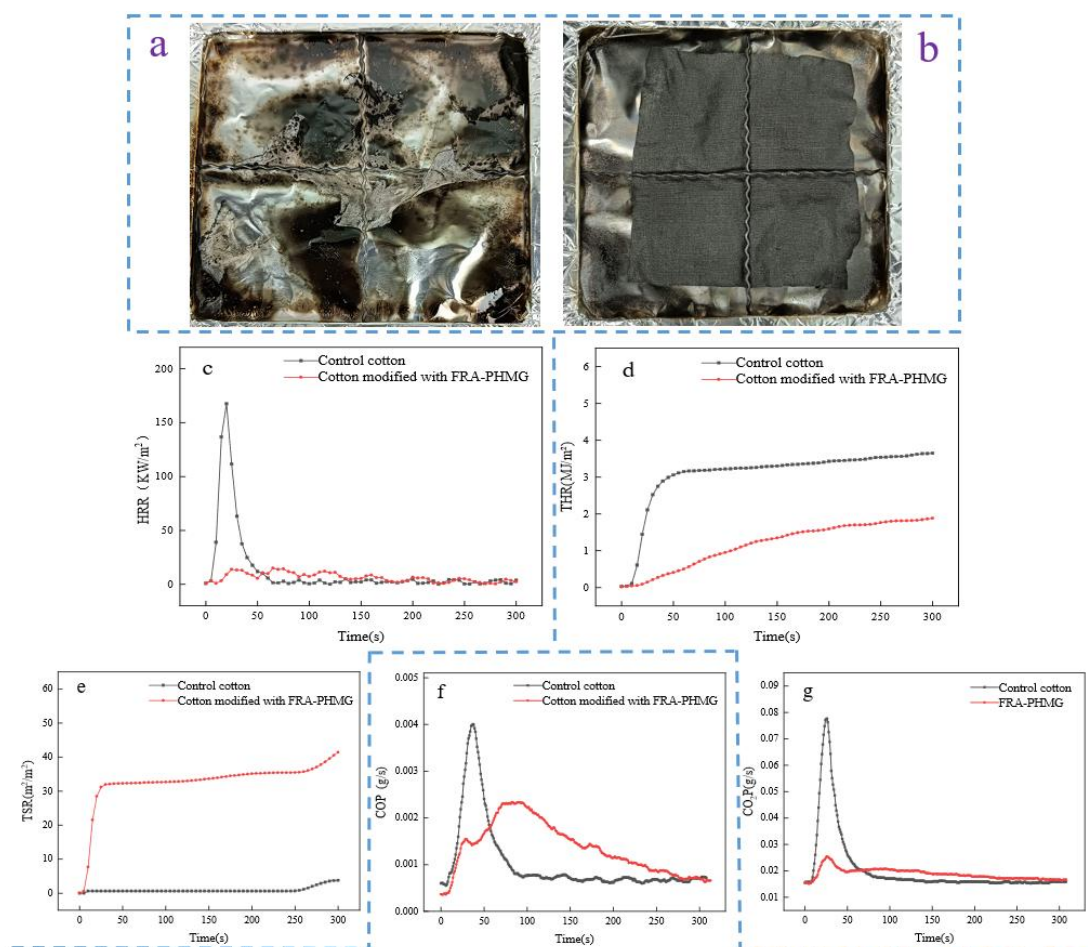


Fig. 4. Photographs of control cotton fabric char residues (a) and the 20 wt% FRA-PHMG modified cotton fabric char residues (b), HRR(c), THR(d), TSR(e), COP(f), CO₂P(g) curves of FRA-PHMG modified cotton fabrics.

Table 2. Cone calorimeter test data of control cotton fabric and FRA-PHMG modified cotton fabric.

Samples	PHRR(kW/m ²)	T _{PHRR} (s)	THR(MJ/m ²)	TSR(m ² /m ²)	Residue (%)
Control cotton	176.58	18	3.67	3.79	2.67
FRA-PHMG	15.18	64	1.89	42.68	21.03

Surface analysis of modified cotton fabrics and char residues

To investigate the modification effect of FRA-PHMG on the cotton fabric surface, the morphology and elemental composition before and after modification were analyzed. Fig. 5a1 ~ f1 presented the SEM images of the cotton fabric before and after modification. As shown in Fig. 5a1 ~ b1, the surface of the original cotton fibers is smooth and structurally regular. In contrast, Fig. 5c1 ~ f1 revealed a uniform and dense reticulated coating on the FRA-PHMG modified cotton fibers, resulting in a significantly roughened fiber surface. This morphological change provides direct visual evidence for the successful grafting of FRA-PHMG onto the cotton fiber surface, which is primarily attributed to the covalent bonding reaction between the phosphoramidate groups in FRA-PHMG molecules and the hydroxyl groups of cellulose.

To further confirm the successful grafting and analyze the elemental characteristics, EDS elemental mapping was performed. The results in Fig. 5a2 ~ f2 showed that, in addition to C and O elements, N and P elements are uniformly distributed on the surface of the modified cotton fibers, indicating the successful and homogeneous attachment of FRA-PHMG. A comparison of the elemental mass fractions before and after grafting is summarized in Fig. 5g ~ h. The data indicate that the mass fractions of N and P on the modified cotton fabric surface are 25.72% and 2.57%, respectively. This result carries important mechanistic implications. The notably high N/P ratio not only confirms the successful grafting of nitrogen-rich PHMG polymer chains onto the cotton fabric via phosphoramidate bridging but also suggests

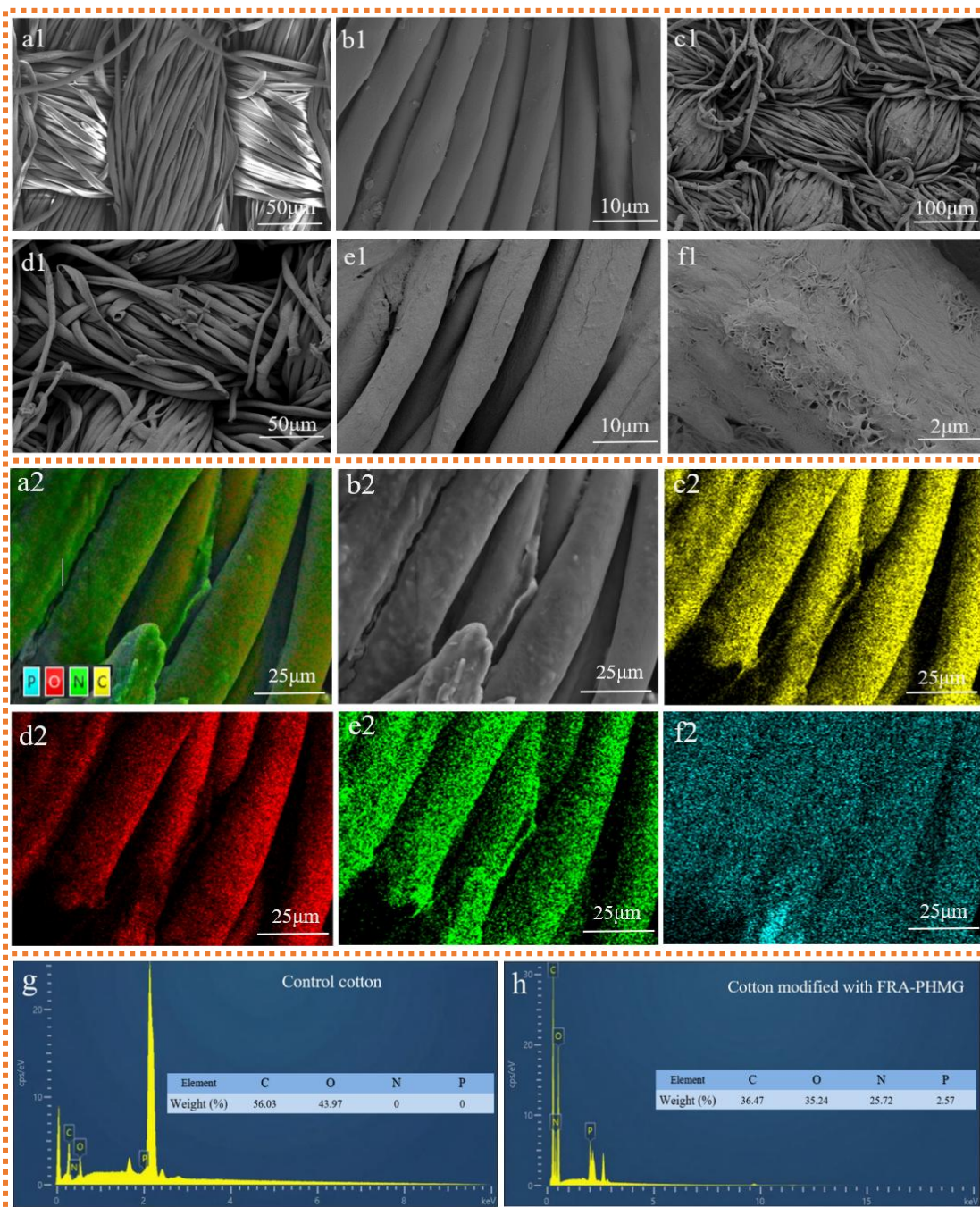
a unique “gas phase-condensed phase” synergistic flame-retardant mechanism. In the gas phase, the high nitrogen content promotes the release of non-combustible gases upon heating, effectively diluting the concentrations of oxygen and flammable gases. In the condensed phase, phosphorus acts as an acid source to catalyze the dehydrative carbonization of cellulose, while nitrogen serves as a blowing agent. Together, they exhibit a significant phosphorus–nitrogen synergistic effect, facilitating the formation of a compact and stable intumescent char layer. This char layer acts as an effective physical barrier, impeding the transfer of heat and oxygen, thereby endowing the material with excellent flame-retardant performance.

The microstructural morphology of the char residues from the cotton fabrics shown in Fig. 4a ~ b was examined to corroborate the proposed flame-retardant mechanism, with the results presented in Fig. 5a3 ~ c3, which depicted the SEM results of the burned control cotton fibers, revealing that the cellulose matrix underwent partial carbonization during pyrolysis, resulting in a discontinuous fracture pattern of the fiber structure. Longitudinal cracks and honeycomb-like pores were visible on the surface of the residual fibers, caused by the release of small-molecule volatiles generated from the thermal degradation of cellulose molecular chains. These morphological characteristics indicated incomplete pyrolysis of the cellulose material in the absence of a flame retardant, leading to a loose and poorly continuous char layer that failed to form an effective thermal barrier.

In contrast, the corresponding images of the FRA-PHMG modified cotton fabric

after combustion, shown in Fig. 5d3 ~ f3, revealed a compact and continuous char layer that retained the original fiber outline. Statistical measurements based on the SEM images indicated that the char residue of the grafted cotton fibers had a diameter of approximately 5.73 μm , whereas that of the control cotton was only about 3 μm , demonstrating that FRA-PHMG treatment significantly promoted char layer thickening. The internal structure of the char layer exhibited uniformly distributed closed-cell pores, which were formed by expansion gases produced during combustion and effectively trapped within the high-viscosity molten char. Compared with the control sample, the modified cotton fabric formed a significantly thicker and denser char residue. The increased thickness and densification of the char layer further improved its thermal insulation capability. This coherent and gradient-porous char structure greatly enhanced the flame retardancy by reducing thermal conductivity and inhibiting oxygen diffusion. This improvement corresponds to the synergistic effect of nitrogen in the gas phase releasing non-combustible gases and phosphorus in the condensed phase promoting carbonization, which is fully consistent with the phosphorus–nitrogen synergistic flame-retardant mechanism described above.

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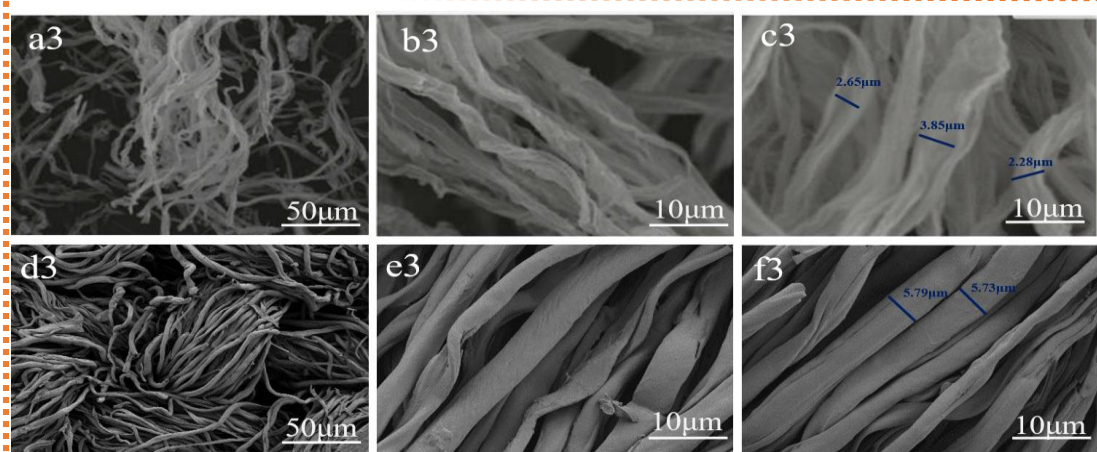


Fig. 5. SEM and EDS characterization of control and FRA-PHMG modified cotton fabrics: SEM images of control cotton fabric (a1, b1); SEM images of FRA-PHMG modified cotton fabric(c1, d1, e1, f1); SEM images of char residues from control fabric after combustion (a3, b3, c3); SEM images of char residues from 20 wt% FRA-PHMG modified cotton fabric (e3, d3, f3); EDS elemental micrograph of modified fabric (a2); SEM image for EDS mapping (b2); EDS distribution maps of C, O, N, and P elements in modified fabric (c2–f2); EDS spectrum of control fabric (g); EDS spectrum of FRA-PHMG modified fabric (h).

TG analysis

The thermal degradation behaviors of control cotton fabric and cotton fabric modified with the FRA-PHMG were investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The corresponding TG and DTG curves are presented in Fig. 6a ~ b, with thermogravimetric analysis showed in Fig. 6c.

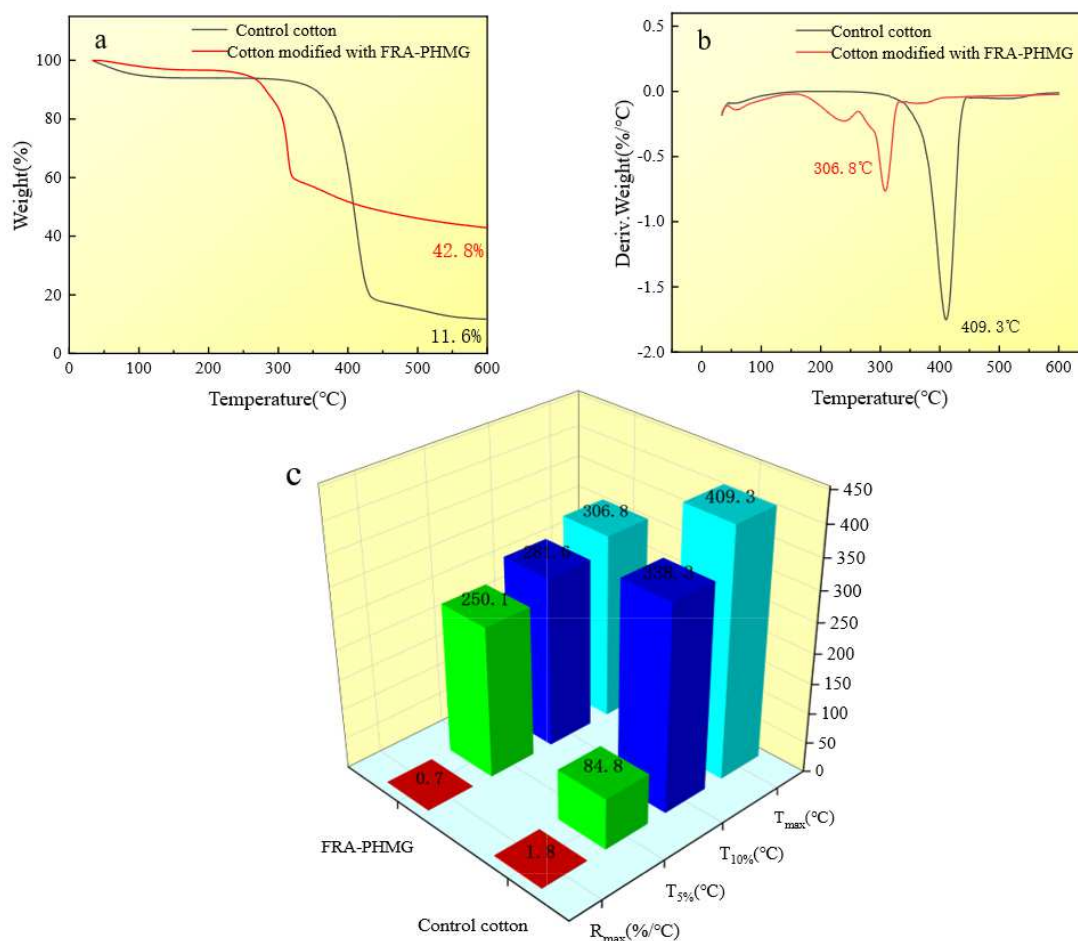
The Control cotton exhibited an initial minor mass loss attributable to the evaporation of surface moisture, followed by a rapid degradation step commencing at approximately 340 °C. The maximum degradation rate (Tmax) was observed at 409.3 °C, which is primarily due to the thermal cleavage of cellulose polymer chains and the release of flammable gases (Ling et al. 2023). As the temperature increased further, the residual char underwent additional reactions, including dehydration and molecular rearrangement, accompanied by the release of gases such as CO₂. This

resulted in a final char yield of only 11.57% at 600 °C.

In contrast, the modified cotton displayed significantly different thermal degradation behavior. The onset of degradation shifted to lower temperatures, with $T_5\%$ and $T_{10}\%$ recorded at 250.1 °C and 281.6 °C, respectively. A substantial mass loss of 35.17% occurred rapidly within the temperature range of 250.1 °C to 320.25 °C, with R_{max} of 1.8 %/°C. The temperature at the T_{max} was 306.8 °C. During this stage, the cleavage of weaker P–O bonds generated phosphoric acid and its polyphosphates, which catalyzed the dehydration and cross-linking of cellulose, thereby promoting char formation. Simultaneously, the scission of chemical bonds such as C–C, N–C, and P=O led to the release of volatile compounds, including NH_3 and H_2O .

Between 500 °C and 600 °C, the mass of the sample gradually stabilized. Within this high-temperature region, the pyrolysis products of cotton fibers follow two competing pathways: one leading to aromatization and the formation of stable aromatic carbon structures, and the other resulting in the generation of aliphatic volatiles. The presence of FRA-PHMG significantly promoted the aromatization pathway, facilitating the conversion of residual aliphatic structures into aromatic carbon while releasing small molecules such as CO, CO_2 , H_2O , and CH_4 (Liu et al. 2021). Consequently, the char residue of the modified cotton at 600 °C was significantly increased to 42.83%. These results demonstrate that FRA-PHMG enhances the thermal stability and char-forming ability of the material by steering the pyrolysis reactions toward carbonization, inducing dehydration at lower temperatures and facilitating the formation of a

464 protective carbon layer.



465
466 **Fig. 6.** TG curves (a), DTG curves (b), Thermogravimetric analysis (c) of cotton fabrics
467 modified with FRA-PHMG in the N₂.

468 Antimicrobial performance

469 The effect of application concentration of FRA-PHMG on the antimicrobial
470 performance of modified cotton fabrics was evaluated against representative microbial
471 species, including *E.coli*, *S.aureus* and *C.albicans*. The shaking flask method was
472 employed for antimicrobial testing, with unmodified cotton fabric used as a control for
473 direct comparison. As summarized in Table 3 and illustrated in Fig. 7a1 ~ a3, the

control cotton fabric supported substantial growth of all three microorganisms after contact, confirming its lack of inherent antimicrobial activity.

In contrast, cotton fabrics modified with FRA-PHMG finishing agent exhibited significant antimicrobial activity against all three tested species. As shown in Fig. 7d1 ~ d3, when the concentration of FRA-PHMG reached 200 g/L, the antimicrobial activity against *E. coli*, *S. aureus*, and *C. albicans* reached 99%, 99%, and 100%, respectively. To address safety considerations related to antimicrobial textiles, the potential diffusion of FRA-PHMG was assessed using the agar diffusion circle method. No distinct inhibition zone was observed around the finished cotton samples as shown in Fig. 7, satisfying the safety criterion that requires an inhibition zone diameter of less than 5 mm. This indicated that the antimicrobial action of FRA-PHMG primarily occurred through a contact-based mechanism rather than by releasing diffusible bactericidal agents.

The outstanding antimicrobial performance was attributed to the guanidine groups in the FRA-PHMG agent. The densely distributed cationic groups on its molecular chain electrostatically adsorb to the negatively charged phospholipid bilayers on microbial surfaces. This interaction disrupted membrane permeability and interfered with lipid synthesis, ultimately blocking respiratory pathways and leading to microbial suffocation and death.

Table 3 Effect of FRA-PHMG concentration on antimicrobial properties of cotton fabrics

Samples	FRA-PHMG (g/L)	Microbial reduction (%)		
		<i>S.aureus</i>	<i>E.coli</i>	<i>C.albicans</i>
Control cotton	0	0	0	0
FRA-PHMG	100	96	97	97
FRA-PHMG	150	97	98	100
FRA-PHMG	200	99	99	100

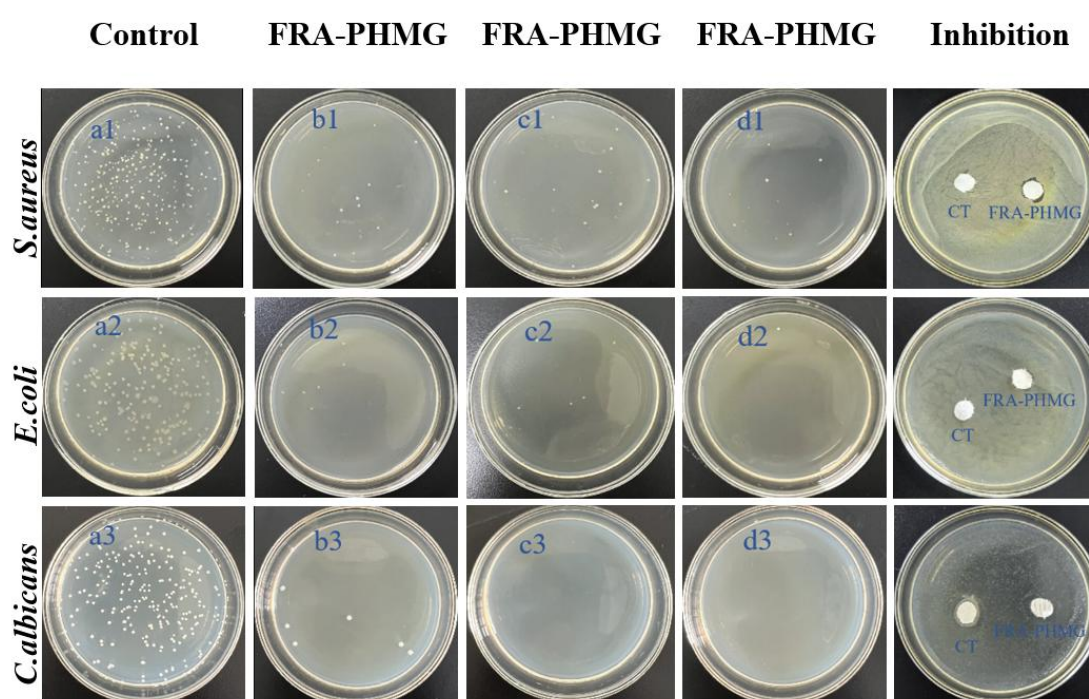


Fig. 7. Inhibition zone images and antimicrobial activity against *S.aureus* (a1~d1), *E.coli*(a2~d2), and *C.albicans* (a3~d3) at FRA-PHMG concentrations: Control cotton fabric (a1, a2, a3); 100 g/L (b1, b2, b3); 150 g/L (c1, c2, c3); 200 g/L (d1, d2, d3).

Washing durability

The long-term stability of the flame retardant and antimicrobial properties of

cotton fabric modified with 200 g/L FRA-PHMG was evaluated under accelerated washing cycles (WC).

As shown in Fig. 8, the flame retardancy exhibited a decline during the initial washing phase. After five washing cycles, the LOI of the modified cotton decreased markedly from 42.1% to 35.2%, the weight gain rate dropped from 22.4% to 16.3%, and the damaged char length increased from 4.3 cm to 6.5 cm. This reduction in performance was primarily attributed to residual compounds from the FRA-PHMG treatment bath, such as urea, a swelling agent, and dicyandiamide, which acted as a catalyst, in addition to competitive ion exchange between metal ions present in the wash solution and the modified fabric during laundering. Notably, once the system reached a dynamic equilibrium, the fabric demonstrated outstanding flame retardant durability: even after 50 washing cycles, the weight gain rate remained at 15.7%, the LOI was sustained at 31.6%, and the char length increased only marginally to 7.0 cm. Results from VFT confirmed that all samples, irrespective of washing history, exhibited self-extinguishing behavior without afterflame or afterglow, and the residual char length was consistently short.

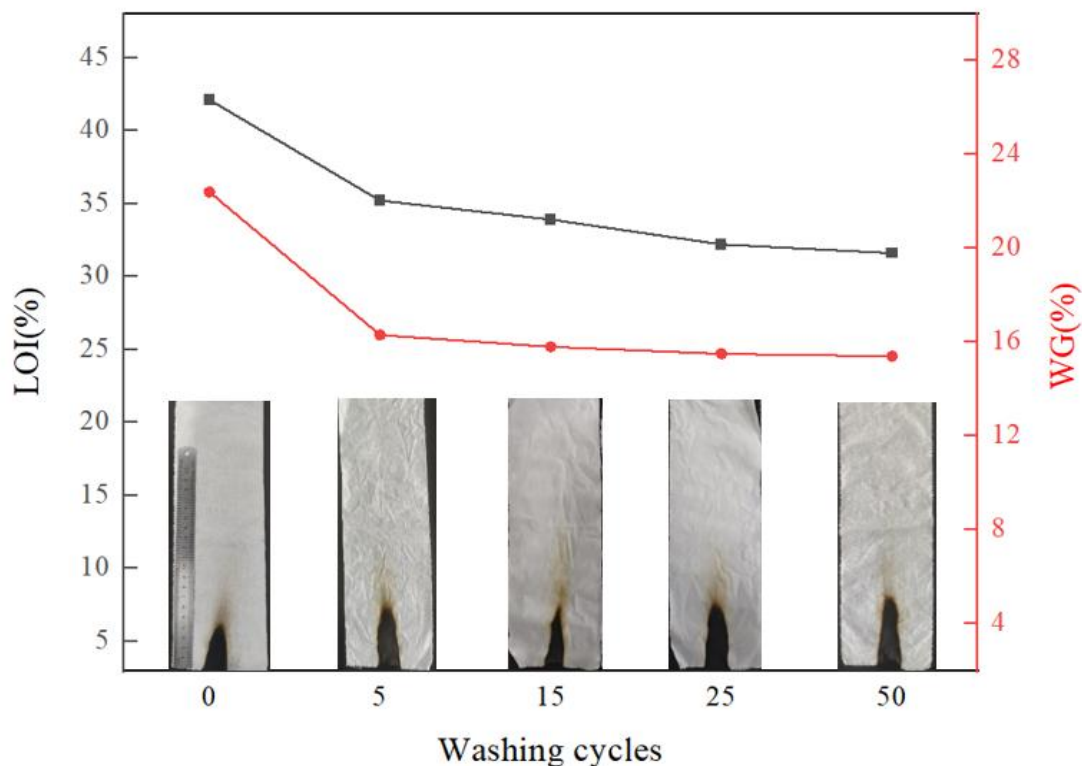


Fig. 8. WG and LOI values of cotton fabric modified with 200 g/L FRA-PHMG after different washing cycles.

Meanwhile, the laundering durability of the antimicrobial properties further underscored the excellent wash fastness of the finishing system. This high stability originated from the highly reactive $-P(=O)(O^-NH_4^+)_2$ groups generated during phosphorylation and subsequent neutralization with urea. These groups underwent esterification with hydroxyl groups on the cellulose chains, forming stable P–O–C covalent bonds that firmly anchor the antimicrobial polymer to the fiber (Xu et al. 2021). As depicted in Fig. 9b1 ~ b3, after 5 washing cycles, the finished fabric still exhibited substantial antimicrobial activity against *E. coli*, *S. aureus*, and *C. albicans*. More importantly, as shown in Fig. 9d1 ~ d3, even after 50 stringent washing cycles, the

antimicrobial activity against these three microorganisms remained as high as 89%, 88%, and 91%, respectively, meeting the AAA antibacterial standard. This superior long-term antimicrobial efficacy confirmed the successful incorporation of a high density of surface-grafted PHMG sites during treatment, which ensured durable and effective contact-killing antimicrobial activity.

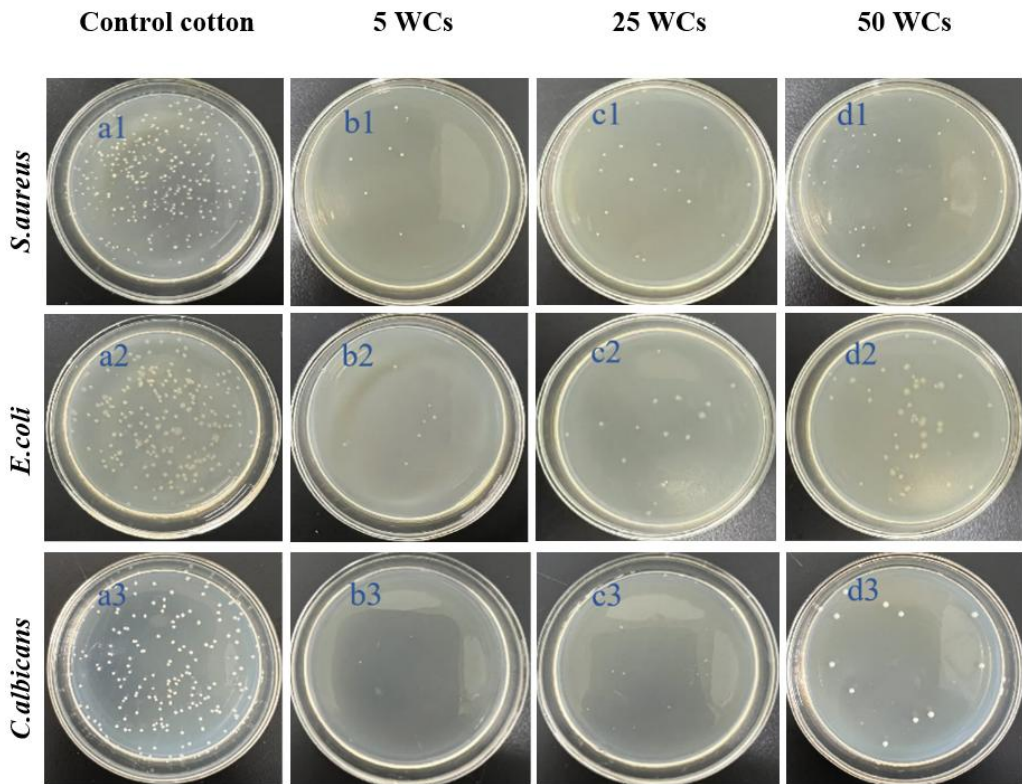


Fig. 9. Antimicrobial activity against *S.aureus* (a1 ~d1), *E.coli* (a2 ~d2), and *C.albicans* (a3 ~d3) for cotton fabric modified with 200 g/L FRA-PHMG after cyclic laundering: Control cotton fabric (a1, a2, a3); 5 washing cycles (b1, b2, b3); 25 washing cycles (c1, c2, c3); 50 washing cycles (d1, d2, d3).

Tensile of cotton fabric

In order to investigate the degree of damage of FRA-PHMG modified cotton

fabrics, the tensile test of control cotton fabrics and modified cotton fabrics were shown in Fig. 10. The results demonstrated that the control cotton fabric exhibited a warp breaking strength of 369.4 N and a weft breaking strength of 141.6 N. After the flame-retardant and antimicrobial treatment with 200 g/L FRA-PHMG, the warp breaking strength of the modified fabric decreased to 342.9 N, with a strength retention rate of approximately 93.1%, while the weft breaking strength decreased to 130.2 N, with a strength retention rate of approximately 91.9%. This indicated that the FRA-PHMG treatment caused only a minor reduction in the strength of the cotton fabric, preserving a high proportion of its original mechanical robustness. Additionally, an increase in the breaking elongation of the modified fabric was observed. It is suggested that this phenomenon may be attributed to the introduction of the FRA-PHMG agent, which reduced the crystallinity of cellulose molecules within the cotton fibers, thereby enhancing the mobility of molecular chains and ultimately leading to an improvement in the macroscopic breaking elongation of the fabric.

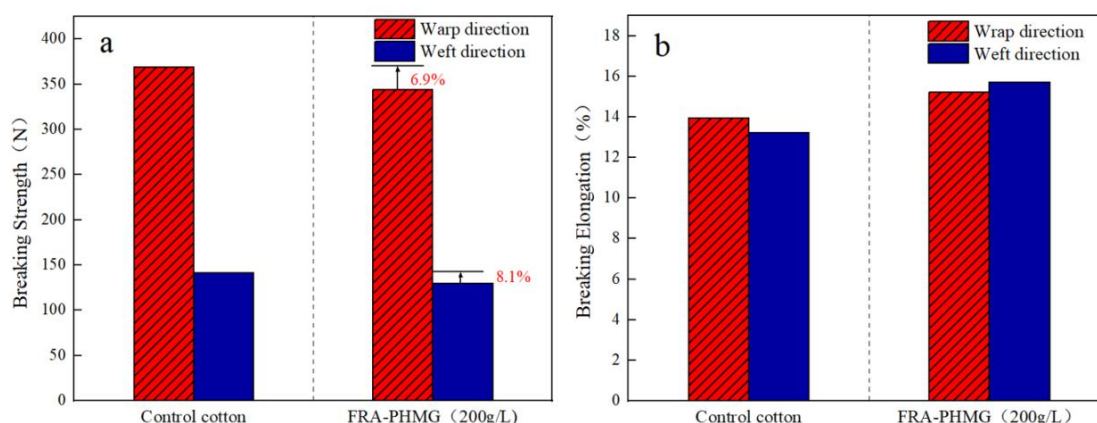


Fig. 10. Tensile strength(a) and breaking elongation (b) of control cotton fabric and cotton fabric modified with 200 g/L FRA-PHMG.

Conclusions

This study synthesized a dual-functional finishing agent FRA-PHMG with both flame-retardant and antimicrobial properties. The process involved the preparation of a G-PHMG intermediate via a ring-opening addition reaction using GMA and PHMG as primary materials. Following purification, the intermediate underwent sequential phosphate esterification and neutralization with urea. Experimental results indicated that cotton fabric modified with a 200 g/L FRA-PHMG solution, cured at 180 °C for 3 min, achieved a LOI of 42.1% and a char length of 4.3 cm, with no afterglow or afterflame observed. Thermogravimetric analysis revealed that the modified cotton commenced thermal decomposition at a lower temperature, while its residual char yield significantly increased from 11.57% to 42.83%. The cone calorimetry test data further confirmed significant suppression of heat release during combustion, with the THR decreasing by 48.50% and the PHRR decreasing by 91.40% compared to the unmodified fabric. The modified fabric also exhibited broad-spectrum antimicrobial activity, achieving inhibition rates of 100%, 99%, and 99% against *S. aureus*, *E. coli*, and *C. albicans*, with no detectable leaching of the antimicrobial agent. Furthermore, the modified fabric maintained excellent durability after 50 laundering cycles according to the AATCC 61-2013 2A standard. Even after this rigorous washing, the char length remained at 7.0 cm, the LOI was sustained at 31.6%, and maintained antimicrobial activity above 85% against all three microbes. This work presents a one-pot synthetic strategy for a multifunctional finishing agent, achieving a synergistic combination of

580 flame retardancy and antimicrobial performance. The modified cotton fabric
581 approaches the flame-retardant grade with an LOI exceeding 42%, shows significantly
582 suppressed key heat release parameters, and demonstrates highly effective, non-
583 leaching antimicrobial activity against three common pathogens. Its maintained
584 performance after repeated laundering provides an efficient and viable technical
585 solution for developing safe, durable, and multifunctional cotton textiles, indicating
586 considerable application potential and promising prospects for industrialization in the
587 field of functional fabrics.

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