

Construction of Biological Flame Retardant Layer on Cotton Fabric via Photografting of Nucleotide/Amino Acid Monomers

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Research Article

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Abstract

The 5'-adenylic acid (AMP- Na_2) is modified to introduce unsaturated double bonds for photografting onto cotton fabrics together with L-cysteine (L-Cys) monomer to prepare synergistic flame-retardant cotton fabrics. The chemical structure of AMP- Na_2 /L-Cys monomers, the surface morphology, residual carbon morphology, thermal property and flame retardant property of photografted flame retardant cotton fabrics are analyzed. FT-IR and ^1H NMR spectra verified the AMP- Na_2 and L-Cys monomers with unsaturated double bonds. Scanning electron micrographs revealed the carbon residue of photografted fiber maintains a natural curled and fibers shape. TGA showed the major pyrolysis temperature of photografted cotton fabric declined by 42°C , with the weight loss reduced by 21.6%, proving that good charring effect. The continuous burning and smoldering time of photografted cotton fabric are decreased to 0s. The experimental results indicate that AMP- Na_2 /L-Cys monomers can reveal good durability and remarkable flame retardancy property to cotton fabrics via facile treatment of photografting.

Highlights

- A novel adenine nucleotide (AMP- Na_2) monomer with unsaturated double bond was synthesized.
- The durable flame retardancy of cotton fabrics was obtained via photografting of AMP- Na_2
- Flame retardancy improved significantly by the combination of AMP- Na_2 / L-Cys monomers.

Introduction

Cotton fiber has plenty high properties and advantages, like moisture absorption, dyeability, softness, and a wide range of sources[1–3]. Therefore, cotton fabrics are used in various fields, such as civil and medical applications. In contrast, LOI of cotton fiber is 18.4% and ignition temperature is only 350°C , are a flammable material. When the relative humidity is $\leq 30\%$, they will be a serious fire source[4, 5]. As a result, cotton fabric is easy to burn and fire, threatening personal safety, so the fire resistance of cotton fabric has certain requirements.[6]. Therefore, the development and utilization of flame retardants for cotton fibers have brought into focus.

In recent years, due to the advantages of green environmental protection and halogen-free, intumescent flame retardant (IFR) has received extensive attention[7]. Typically, IFR includes carbon, acid, gas sources. [8]. Among them, intumescent flame retardant systems composed of APP, MEL and PER are the most common[9]. Shao et al.[10], Li et al.[11] employed ammonium polyphosphate, melamine mixt and pentaerythritol as intumescent flame retardant materials. Cotton fabrics are photografted by pad-bake method. Although flame retardant properties of cotton fabrics is improved well, most of the salts formed are small molecules. This results in poor thermal stability, low carbon formation rate, and some limitations in application[12]. When PER itself decomposes, it produces not only water, but also combustibles like formaldehyde and ethanol[8]. Therefore, the natural intumescent bio-based flame retardant materials become the research focus of flame retardant. Nucleotide or nucleic acid built by

nucleotide unit is composed of phosphoric acid, ribose and nitrogenous base. As bio-based intumescent flame retardant, it can well combine condensed phase flame retardation and gas phase flame retardation to produce synergistic flame retardation. In 2013, Alongi et al. used DNA as a novel flame retardant system for enhancing flame retardant properties of cotton fabrics. As a result of cotton fabrics being impregnated with the DNA suspension, the DNA coating was easy to come off and the cotton fabric had poor durable flame retardancy[13]. Carosio et al. employed DNA and chitosan solution, and made the flame retardant cotton fabric by Layer by Layer assembly, giving it remarkable flame retardant. Their study shows that the deposition of 20 BL does increase carbon residue (88%). The flame-retardant composite multilayers usually show better flame-retardant effect when the number of assembled cycles is high[14]. In 2015, Jenny Alongi et al. found that DNA underwent the transformation of multi-cavity, foam and thermal insulation materials at low temperature, and such expansion residues would be transformed into highly thermally stable ceramic-like materials at high temperature[15]. Annalisa et al. applied DNA and chitosan to construct a flame retardant system on cotton fabrics by the layer-by-layer approach and subsequent to UV-curing. As a result, the water resistance of the coating structure is enhanced, and the flame self-extinguishing time is short, which shows good flame retardant effect[16]. Therefore, the fire-retardant finishing methods of cotton fabrics include dip drying method, layer by layer method and UV-curing method. The UV-curing method is more beneficial to improve the durability. However, the direct use of DNA or RNA units as flame retardants has not been reported.

Nucleotide, as the structural unit of DNA or RNA, is a kind of small molecule expansive flame retardant with three sources, which can further reduce the cost of raw materials. Therefore, in this study, AMP- Na_2 was used as a biological flame retardant, and unsaturated double bond was introduced and then treated on cotton fabric by photografting to improve its flame retardancy. The introduction of amino acid monomer (modified L-Cys) can not only reduce the steric hindrance of nucleotide monomer during graft polymerization, but also play the role of co-effective flame retardant. The chemical structure of biological flame retardant monomers and the surface morphology, carbon residue morphology, thermal and flame retardant properties of photografted flame retardant cotton fabric were analyzed.

Experimental

2.1 Material

Pure cotton fabric was obtained from Dalian Market (Dalian, China). AMP- Na_2 was supplied by Huaxia Crop. (Chengdu, China). L-Cys was supplied by Bailingwei Technology Co. Ltd. (Beijing, China). Allyl bromide (AB) and TPO were purchased from Sigma-Aldrich. Dichloromethane, ethyl acetate, methanol, ether analytical grade were supplied by Tianjin Komiou Chemical Reagent Co. Ltd. (Tianjin, China). Ethanol and analytical grade were supplied by Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjin, China).

2.2 Synthesis of AMP- Na_2 monomer

The AMP-Na₂(98%) was dissolved in DMSO, then AB (98%) was added dropwise while stirring magnetically. Then sodium hydrogen was slowly added. The mixture was reacted at 75 °C for 6 h. The ethyl acetate was added into the mixture to precipitate the AMP-Na₂ monomer. Then the monomer was washed with dichloromethane and ether and dried at 50 °C to get AMP-Na₂ monomer. Figure 1 shown the synthesis reaction of the AMP-Na₂ monomer.

2.3 Synthesis of L-Cys monomer

L-Cys (99%) and deionized water were mixed under magnetic stirring for 20 min. Then sodium hydroxide solution was added under ice bath. Then, AB (98%) was slowly added several times and heated at 20°C for 14 h. The reaction solution was poured into a crystallization dish and HCl was added dropwise to the isoelectric point. The raw product was precipitated, and the white product (L-Cys monomer) was obtained after suction filtration and freeze drying. Figure 2 shown the synthesis reaction of the L-Cys monomer.

2.4 Flame-retardant finishing of cotton

AMP-Na₂ monomer and L-Cys monomer were dissolved in deionized water. In addition, TPO as photoinitiator was added. Cotton fabrics were immersed into the above solution to make the mass fraction of monomers reach 50%. Then, it was exposed to ultraviolet radiation for 5 minutes and dried at 110°C for 50 min. Figure 3 shown the photografting of AMP-Na₂/L-Cys monomers onto cellulose.

The grafting yield (W_G) of the cotton fabric after treatment was calculated using Eq. (1):

$$W_G(\%) = (W_2 - W_1) / W_1$$

Where, W_1 and W_2 are the weight of control cotton and the treated cotton, respectively.

2.5 Characterization and measurement

The infrared spectra of AMP-Na₂ monomer, L-Cys monomer were measured with a Spectrum One-B infrared spectrometer (PerkinElmer Inc., Waltham, MA, USA). The spectra of ¹H NMR of monomers were obtained using a Bruker AV III I 600 spectrometer (Bruker Corporation, Billerica, MA, USA). Laser Raman spectroscopy measurements of char residue were conducted with a InVia Raman spectrometer (Renishaw Co., UK). The surface of the cotton fabric and char residue were observed by scanning electron microscopy (SEM)(JEOL JSM-6460LV). The elemental composition of raw and photografted cotton fabrics were tested by energy-dispersive X-ray spectroscopy (EDX) (JEOL 6300 F) using a high beam voltage (10 kV). Vertical burning tests were conducted on a vertical burning test instrument (YG815-type) with fabric dimensions of 80×200 mm according to GB/T 5455 – 2014. The thermal properties of the samples were measured using the HCT-4 thermogravimetric analyzer.

Results And Discussion

3.1 FT-IR analysis

FT-IR spectra of AMP-Na₂ monomer and AMP-Na₂ are displayed in Fig. 4. For the modified AMP-Na₂, The peak at 2927 cm⁻¹ represents the deformation vibration of CH₂ in CH₂ = CH-CH₂-. The characteristic absorption peaks of C = C appears at 1511 cm⁻¹; Out-of-plane deformation vibration peak at 955 cm⁻¹ corresponds to CH₂ in CH₂ = CH-. The appearance of three new characteristic peaks indicates that C = C and CH₂ have been found on the AMP-Na₂ monomer due to the substitution reaction of AMP-Na₂ with AB.

FT-IR spectra of L-Cys monomer and L-Cys are shown in Fig. 5. The stretching vibration peak of terminal unsaturated = C - H is generally located at 3090 ~ 3075 cm⁻¹, which is weak but easy to identify. Thus, in the spectra of L-Cys monomer, the band at 3082 cm⁻¹ is assigned to the absorption of = C - H bond[17]. Out-of-plane deformation vibration peak at 919 cm⁻¹ corresponds to = CH₂[17]. The above peaks confirm that L-Cys monomer of contains -CH = CH₂ group.

3.2 ¹H NMR analysis

The molecular structure of the AMP-Na₂ monomer/ L-Cys monomer flame retardant is characterized by ¹H NMR in Fig. 6. The peak at 6.13 ppm is assigned to hydrogen atoms in CH₂=-. The peak at 5.14 ppm corresponds to hydrogen atoms in = CH-. Thus, Allyl modification is introduced into AMP-Na₂. The peak at 5.76 ppm is assigned to hydrogen atoms in - CH₂-. The peak at 3.14 ppm is assigned to hydrogen atoms in = CH-, The peak at 3.8 ppm is assigned to hydrogen atoms in -CH₂-. It can be deduced that L-cysteine reacts with AB, and the reaction site of L-cysteine is in sulfhydryl group (-S-H).

3.3 Fabric surface and Char morphology

SEM and EDX obtained the surface morphology and elemental composition of the photografted cotton fabric. SEM images of the raw cotton, photografted cotton before and after combustion in Fig. 7. The surface of raw cotton fibers in Fig. 7a is fairly complete and smooth. The surface of photografted cotton in (Fig. 7b,c) appears some striate protrusions and adhesions between the fibers. The flame-retardant cotton fabrics have a blocky covering. The fiber surface of photografted cotton fabric with AMP-Na₂ and L-Cys monomer is rough and covered with strips. Compared with photografting AMP-Na₂ monomer, photografted fabric with AMP-Na₂ and L-Cys monomer has more coverings on its surface. The reason is that modified L-Cys plays a synergistic role in reducing the steric hindrance of nucleotide monomer during graft polymerization in (Fig. 7c).

As shown in Fig. 7d, a small amount of residual carbon of raw cotton fabric remains with a loose structure, porous surface and no fiber skeleton. The cotton residue of photografted cotton fibers maintain the integrity of the cotton fabric structure and the fiber shape shown in Fig. 7e and Fig. 7f. Some cotton fiber carbon residue shows the effect of expansion. A few white particulate matter and tiny bubbles are

found for char residue of photografted cotton fabric with AMP-Na₂/L-Cys monomers. The white particles may be caused by the change of the catalytic carbonization process, and the composition of the carbonization residue with addition of L-Cys monomer. On the side, there are a few bubbles on the surface of cotton fiber are due to the fact that N and S element easily forms released gases, preventing the cotton fabric from further combusting[1].

The elemental compositions of the photografted flame fabric was investigated by EDX. The EDX diagrams of the photografted cotton fabric with AMP-Na₂ monomer (Fig. 8) reveals the presence of the elements C, N, O, P and Na. The EDX diagrams of photografted cotton fabric with AMP-Na₂/L-Cys monomers (Fig. 9) appear the elements C, N, O, P, Na and S. Table 1 indicates that the N and P contents of the photografted cotton fabric with AMP-Na₂ monomer are 0.62% and 1.20%, respectively. The N and P contents of the photografted cotton fabric with AMP-Na₂/ L-Cys monomer are 0.55% and 0.58%, respectively. Combined with the analysis of the combustion effect of grafted cotton fabric, the ratio of N to P is more favorable to the formation of carbon when the ratio of N to P is 1:1 than 1:2. EDX indicated that the mentioned elements were evenly distributed on the grafted cotton to show relatively even grafting.

Table 1
Summary of EDS data of photografted cotton fabric

Elements	Atomic (%)		Weight (%)	
	Photografted cotton fabric with AMP-Na ₂ monomer	Photografted cotton fabric with AMP-Na ₂ /L-Cys monomers	Photografted cotton fabric with AMP-Na ₂ monomer	Photografted cotton fabric with AMP-Na ₂ /L-Cys monomers
C	63.35	62.78	56.16	55.52
O	35.41	36.06	41.82	42.48
N	0.60	0.54	0.62	0.55
P	0.52	0.25	1.20	0.58
S	0	0.37	0	0.87

3.4 Analysis of Raman spectra

Raman spectra of residual carbon and the ratio of intensity of the D and G bands (I_D/I_G) in Fig. 10 and Table 2. When L-Cys monomers were added into photografted cotton fabric with AMP-Na₂ monomers, the I_D/I_G decreased from 3.01 to 2.9. Briefly, the lower the ratio of I_D/I_G , the higher graphitization degree of char residue. The two peaks of carbon residue of the raw and photografted cotton fabrics indicate that their carbon layers are graphitized to some extent. In the expanded carbon layer, the larger the I_D/I_G value is, the smaller the carbon hole is, the better the corresponding barrier to gas and heat is. The I_D/I_G value of carbon residue of photografted cotton fabric is higher than that of raw cotton, which indicates a thicker

carbon layer with smaller pores and a flame-retardant effect. Comparing to higher I_D/I_G value of photografted cotton fabrics with AMP- Na_2 monomer, a more porous structure highly graphitized layer appeared for photografted fabric with AMP- Na_2 /L-Cys monomers, enhancing heat and persistency.

Table 2
 I_D/I_G of carbon residue of raw and photografted cotton fabrics

sample	Raw cotton	Photografted cotton fabric with AMP- Na_2 monomer	Photografted cotton fabric with AMP- Na_2 / L-Cys monomers
I_D/I_G 2.77		3.01	2.9

3.5 Thermal Stability

The thermal degradation behavior of raw and photografted cotton fabrics was analyzed by TGA (Fig. 11a). When the weight loss rate reaches 10%, the decomposition temperature, of raw cotton fabric, photografted fabric with AMP- Na_2 monomer and AMP- Na_2 /L-Cys monomers are 259.2 °C, 235.6 °C, and 217.4 °C, respectively. The decomposition temperature of 42 °C lower than that of the raw fabric and the weight loss dropped from 98.5–76.9% indicate significant improvement in the thermal stability of cotton fabrics after photografting of AMP- Na_2 /L-Cys monomers. It can be seen from the DTG curve in Fig. 11 (b) that the mass rate of weight loss of photografted cotton fabric with AMP- Na_2 /L-Cys monomers is also slower than that of raw cotton fabric and photografted cotton fabric with AMP- Na_2 monomer. The photografted polymer of AMP- Na_2 monomer decomposes before the cellulose molecular chain during the heating process to generate phosphoric acid. As the temperature rises, phosphoric acid is dehydrated and polymerized into polyphosphoric acid, which promotes the carbonization of cellulose and inhibits the formation of combustible pyrolysis products, and thus achieved excellent flame retardancy. N atom components in the graft polymer will be heated to produce a non-flammable gas, which dilutes the oxygen and to expand the carbon layers inhibit combustion to achieve a synergistic flame-retardant effect.[18].

3.6 Flame retardancy

Table 3 and Fig. 12 show flame retardancy of raw cotton fabric and photografted cotton fabrics with AMP- Na_2 /L-Cys monomers. Amount of L-Cys increases, the steric hindrance between the modified AMP- Na_2 molecules decreases. It is advantageous for the graft polymerization reaction. When the mass ratio of modified AMP- Na_2 /L-Cys decreases, the grafting ratio and flame-retardant properties of the flame-retardant cotton fabric show a first increasing and then decreasing trend. It can be deduced that addition of a certain amount of L-Cys decreases the steric hindrance of AMP- Na_2 monomer. At the mass ratio of AMP- Na_2 /L-Cys of 1.8:0.2, the higher grafting ratio results in no burning and smoldering time after igniting and a more complete carbon residue, which reflects the synergistic flame retardancy of AMP- Na_2 /L-Cys. The synergistic flame-retardant effect of AMP- Na_2 /L-Cys monomers is reflected in shortening burning time and more obvious promotion of char formation.

Table 3
Vertical flammability results of cotton samples

Samples(AMP-Na ₂ monomer/L-Cys monomer)	graftingratio(%)	After-flame time(s)	Afterglow time(s)
Raw cotton	0	4.8	41.2
1.7/0.3	7.5	0.6	0.1
1.75/0.25	7.7	0.4	0
1.8/0.	8.3	0	0
1.85/0.15	7.6	0.8	0
1.9/0.1	5.8	1.8	0
2/0	3.6	1.2	0

Conclusions

RNA unit, AMP-Na₂, is a natural green bio-flame retardant that integrates three sources. AMP-Na₂ monomer with double bonds combined with L-Cys monomer are photografted to prepare eco-friendly flame-retardant cotton fabric. The introduction of L-Cys monomer improves the grafting ratio and produces a synergistic flame retardant effect. The main pyrolysis temperature of photografted flame-retardant cotton fabric with AMP-Na₂/L-Cys monomers decreased by 42°C. The weight loss decreased by 21.6%, and the amount of carbon residue increased significantly. The complete fibrous carbon residue after burning implies a good char-forming effect. The photografted flame retardant cotton fabric mass rate of AMP-Na₂/L-Cys monomers of 1.8/0.2 has no continuous burning and smoldering time, indicating that AMP-Na₂/L-Cys bio-monomers have a good flame retardant effect on cotton fabrics via a facile treatment of photografting.

Declarations

Funding

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Conflicts of interest/Competing interests

It's our honor to submit the enclosed manuscript entitled Construction of biological flame retardant Layer on cotton fabric via photografting of nucleotide/amino acid monomers, which we wish to consider for publication in industrial crops and products. No conflict of interest exists in the submission of this manuscript and the work described was original research that has not been published previously, and not

under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

Availability of data and material

Not applicable

Code availability

Not applicable

Authors' contributions

Xiao Wang, Writing - review and editing, Funding acquisition, Resources. Zhenbao Li, Methodology, Formal analysis and investigation. Ju Wei, Formal analysis and investigation, Resources. Bing Du, Formal analysis and investigation, Resources.

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Figures

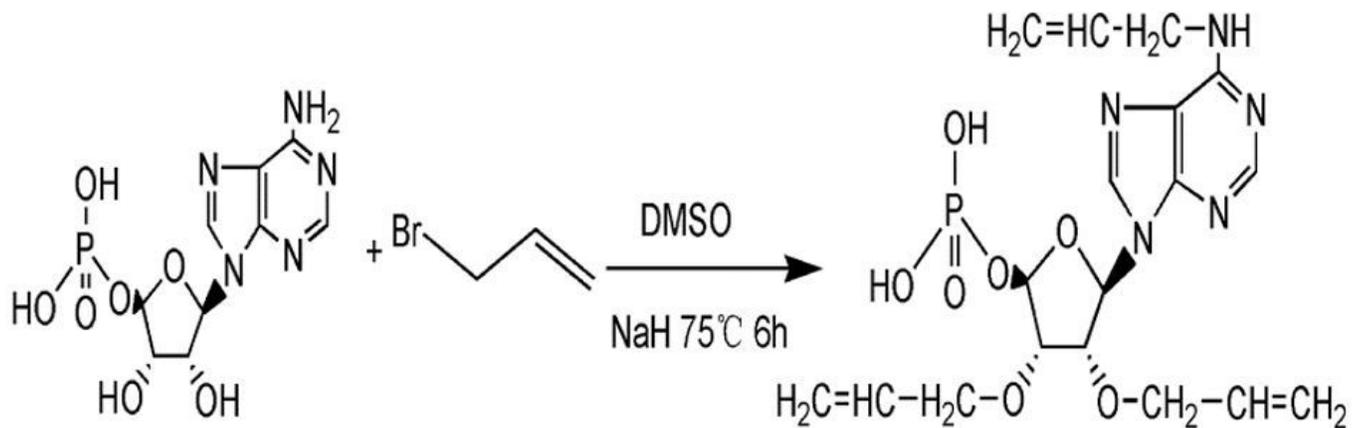


Figure 1

Synthesis of AMP- Na_2 flame retardant monomer

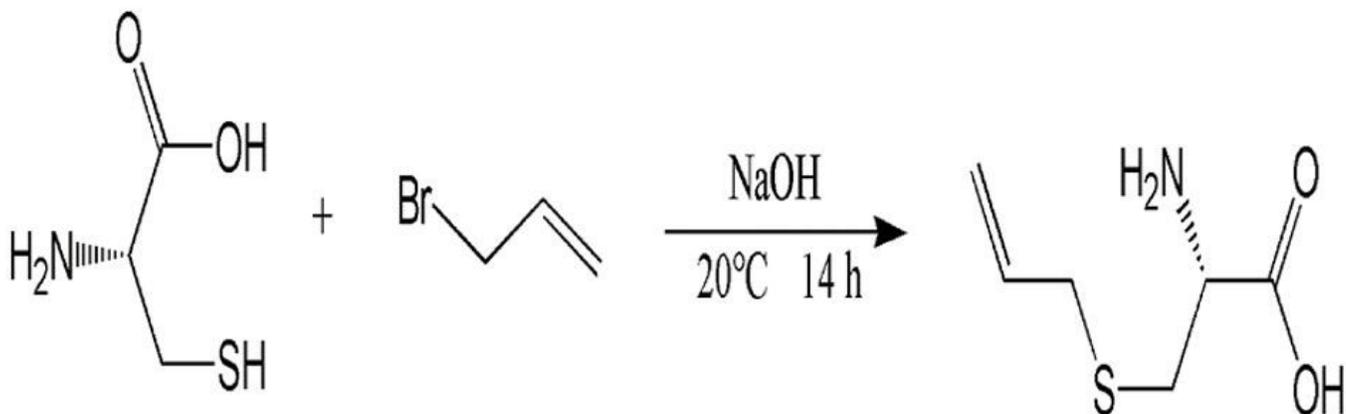


Figure 2

Synthesis of L-Cys monomer

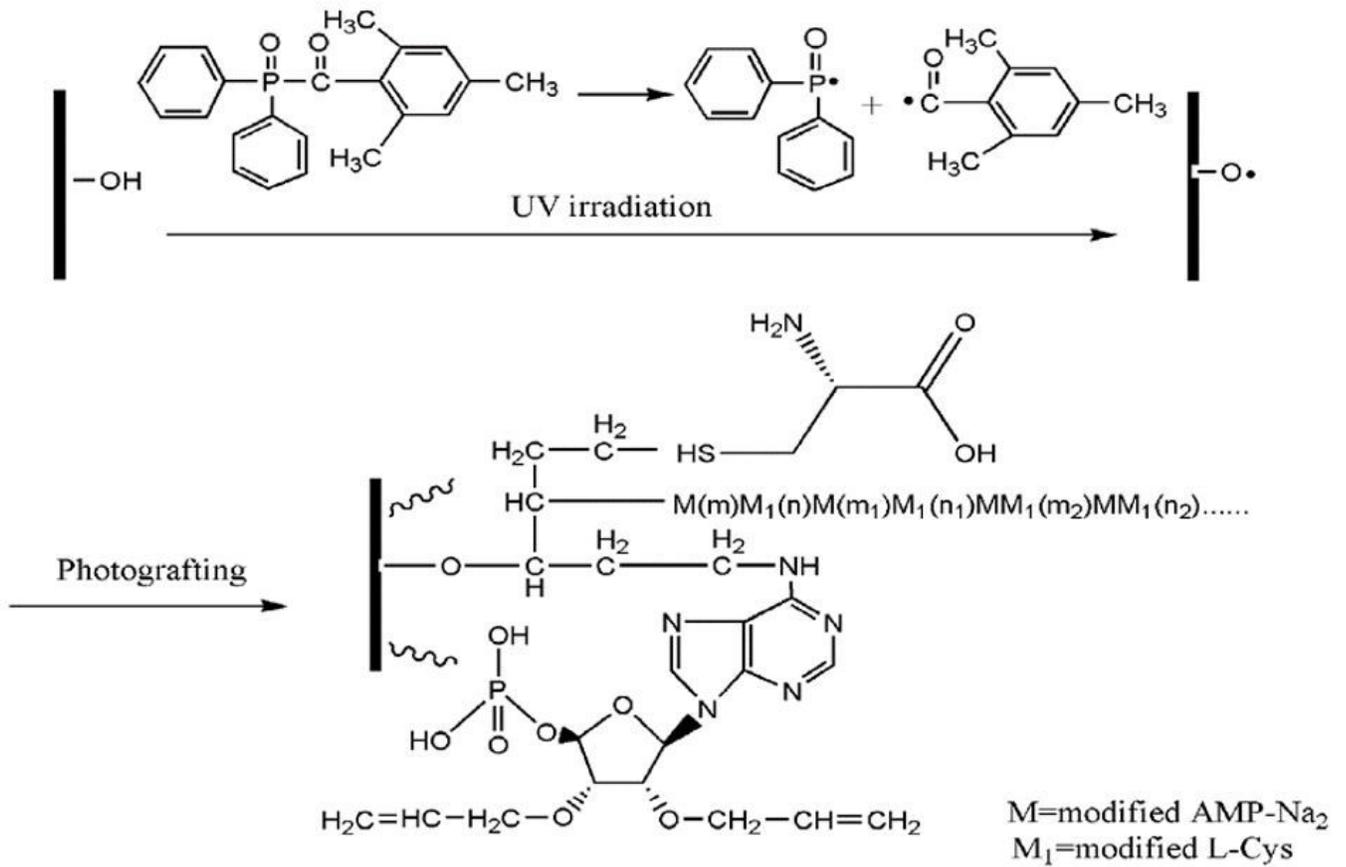


Figure 3

Preparation of flame-retardant cotton fabric via photografting of AMP-Na₂ monomer and L-Cys monomer

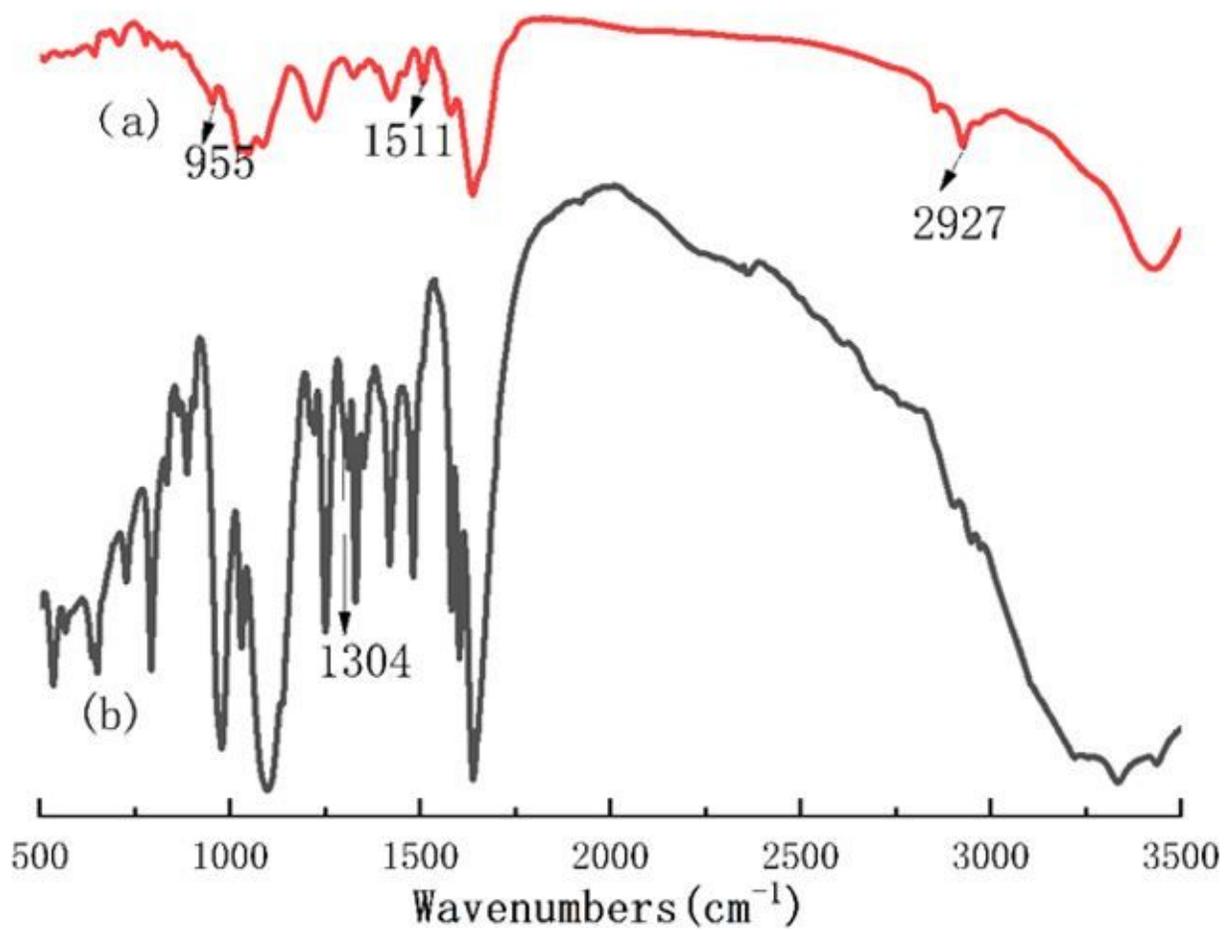


Figure 4

Infrared spectra of AMP-Na2 monomer(a) and AMP-Na2(b)

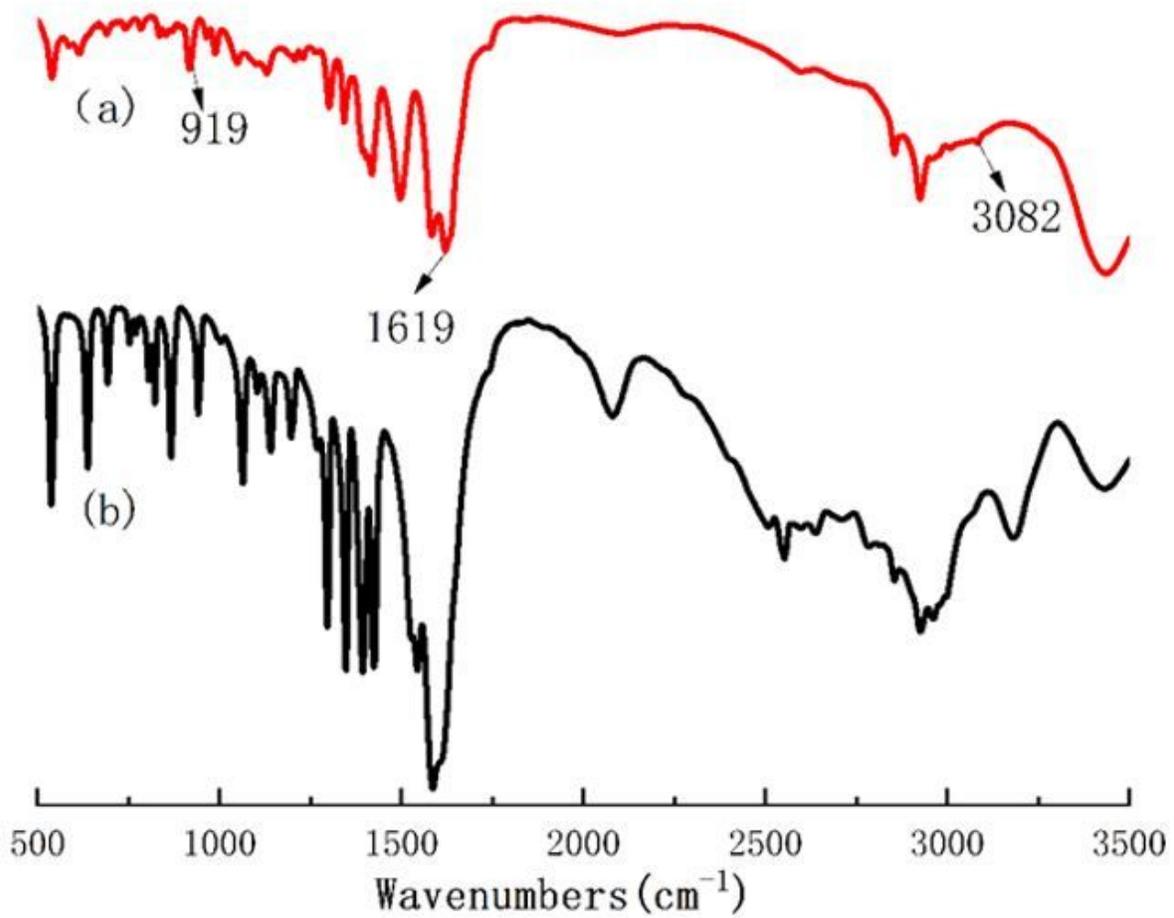


Figure 5

Infrared spectra of L-Cys monomer(a) and L-Cys(b)

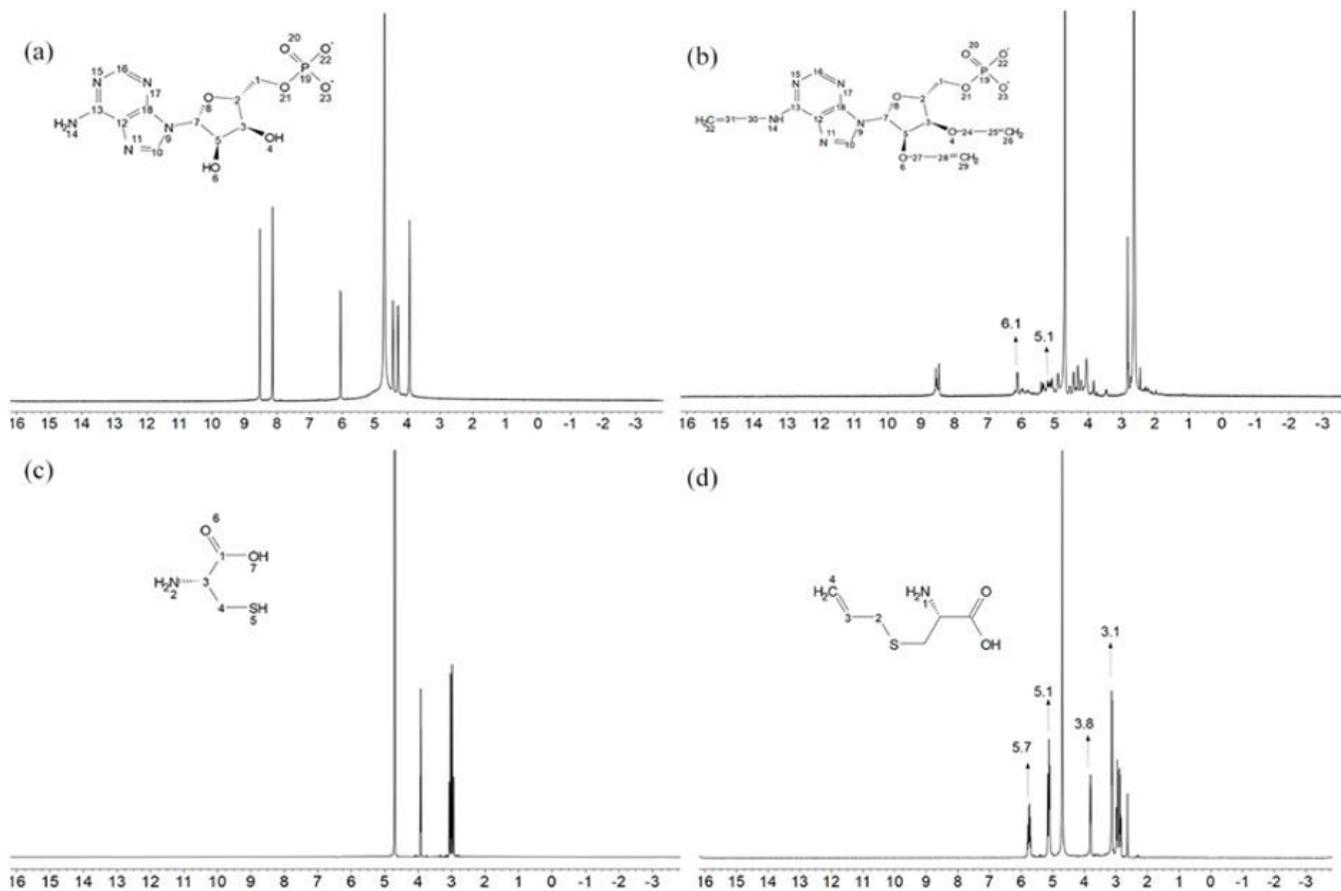


Figure 6

^1H NMR spectra of AMP-Na₂(a), AMP-Na₂ monomer(b), L-Cys(c) and L-Cys monomer(d)

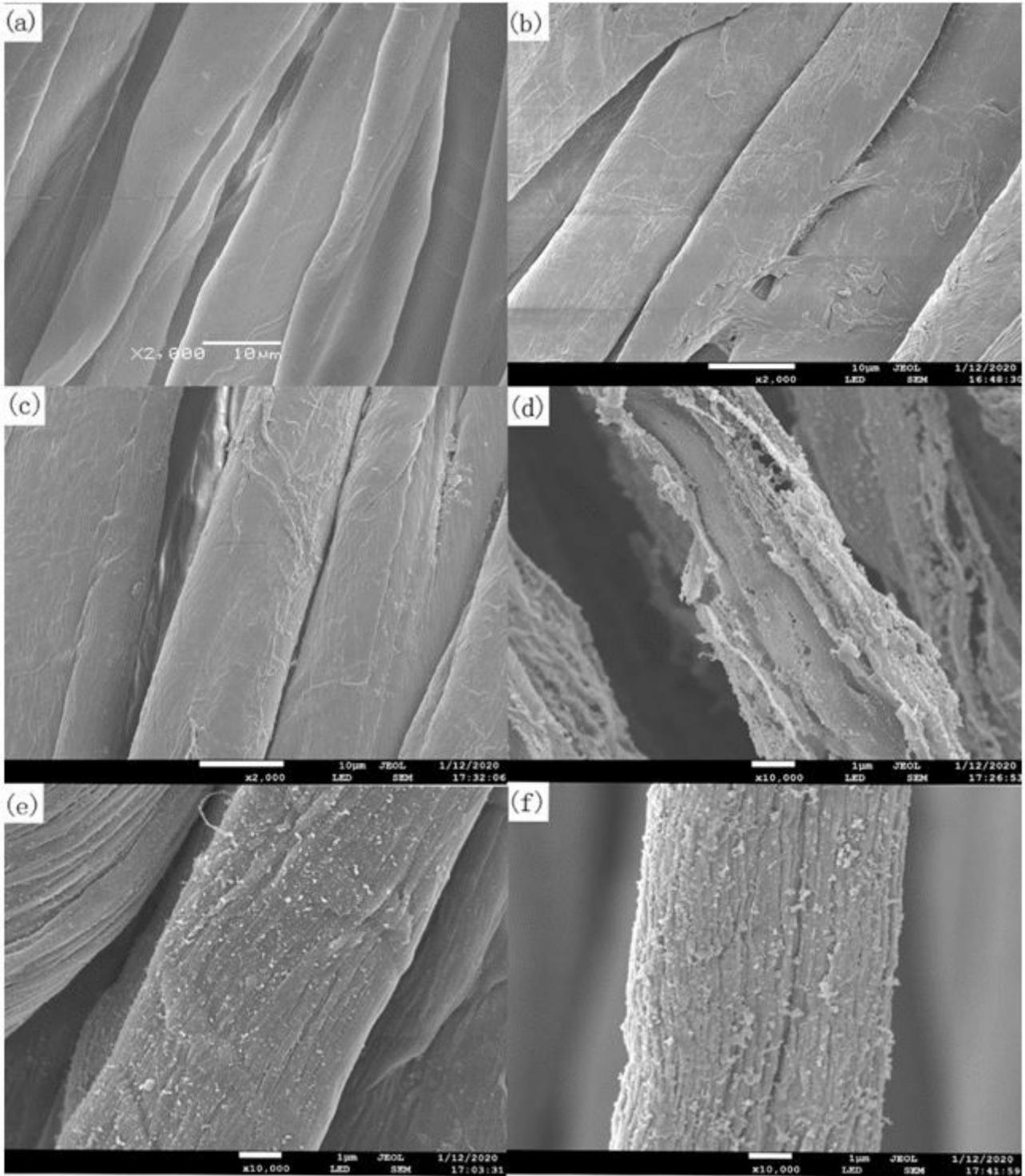


Figure 7

SEM images of the raw cotton fiber (a), photografted cotton fabric with AMP-Na₂ monomer cotton fiber (b), photografted cotton fabric with AMP-Na₂/L-Cys monomers cotton fiber (c), raw cotton fibers after combustion(d), photografted cotton fabric with AMP-Na₂ monomer cotton fiber after combustion(e) and photografted cotton fabric with AMP-Na₂/L-Cys monomers cotton fiber after combustion(f)

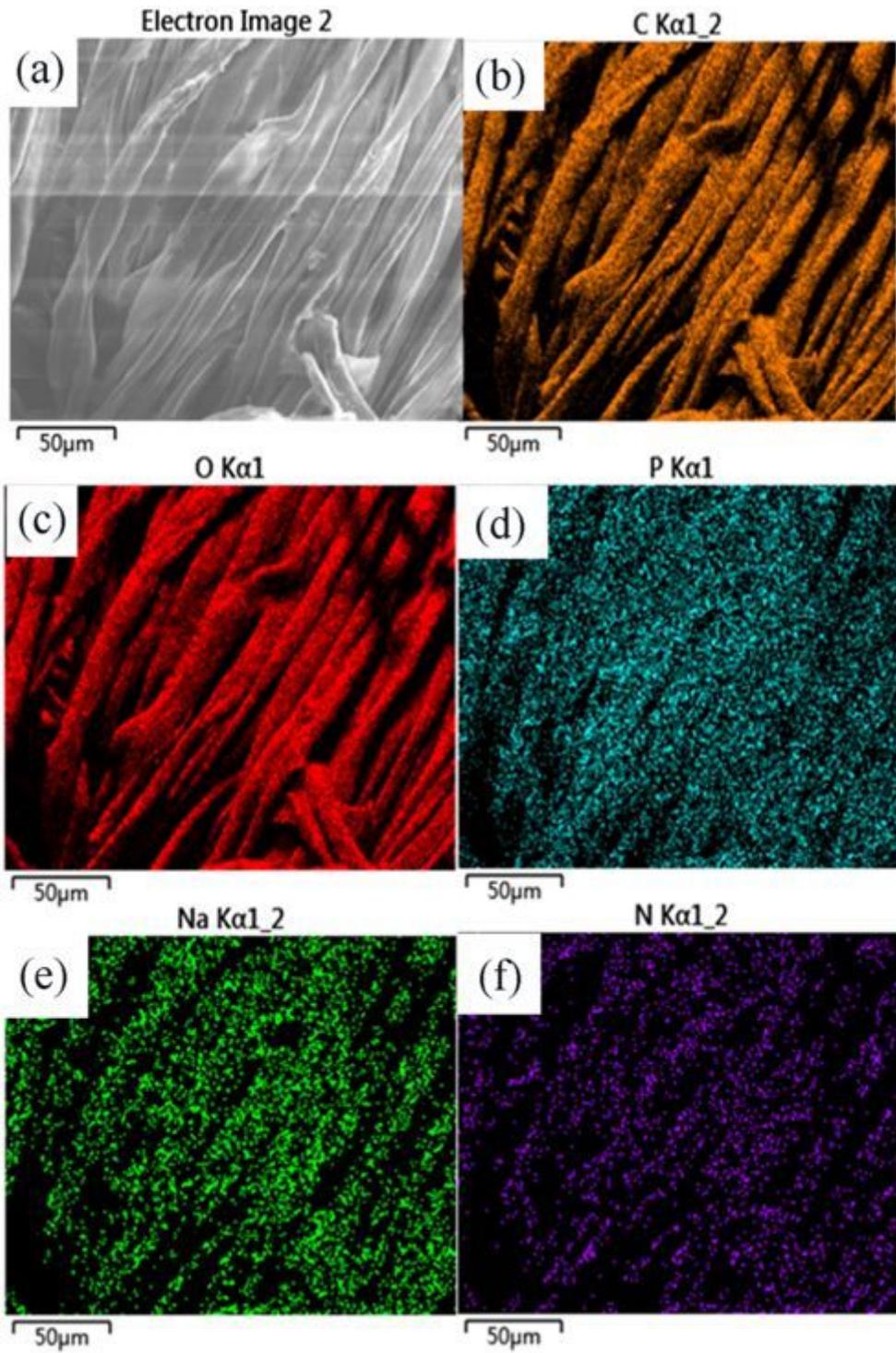


Figure 8

EDX results of photografted cotton fabric with AMP-Na₂ monomer. SEM micrograph(a); elemental distributions of C(b), O(c), N (d), P(e), and Na(f)

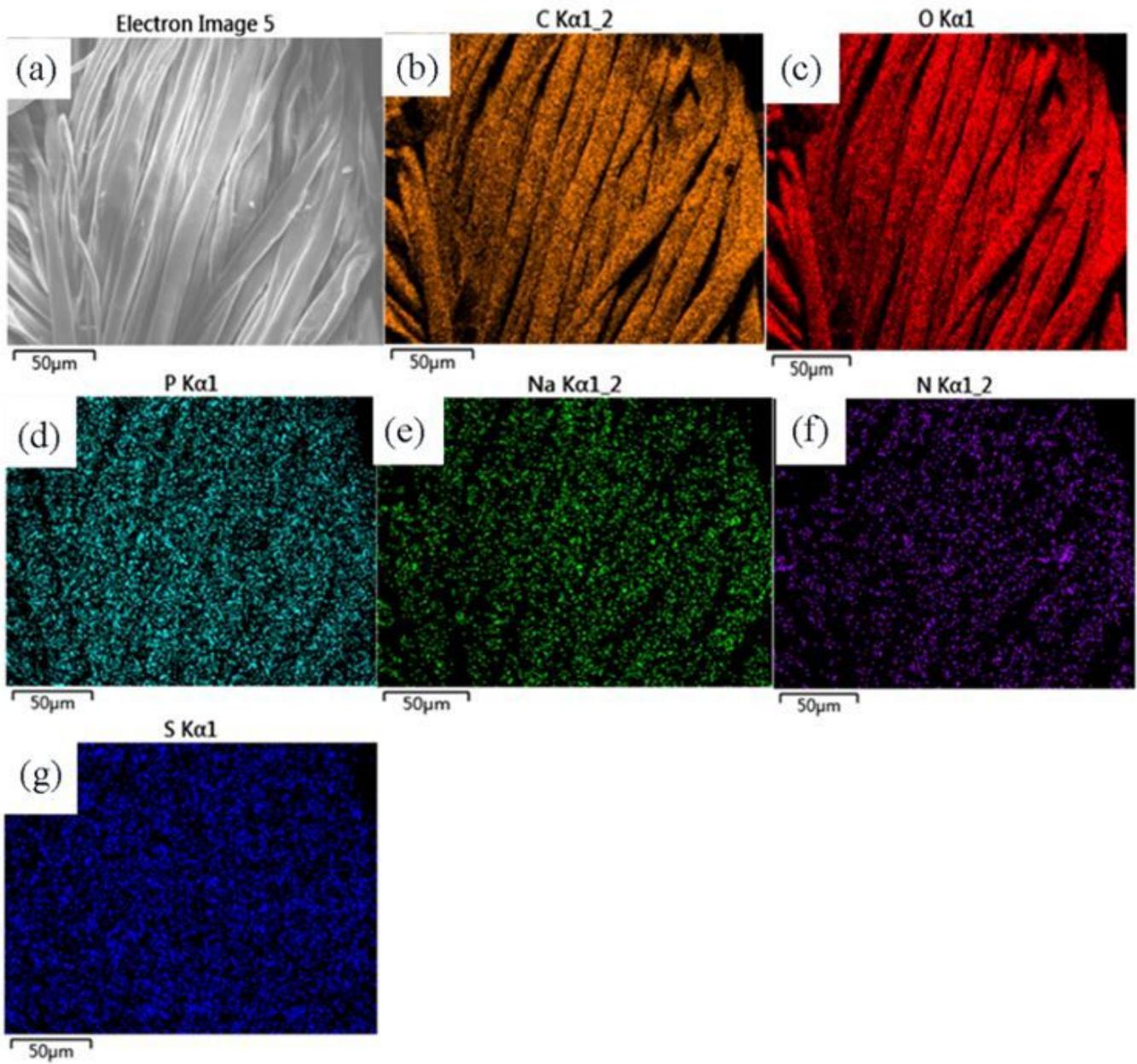


Figure 9

EDX results of photografted cotton fabric with AMP-Na₂/L-Cys monomers. SEM micrograph(a); elemental distributions of C(b), O(c), N(d), P(e), Na(f) and S(g)

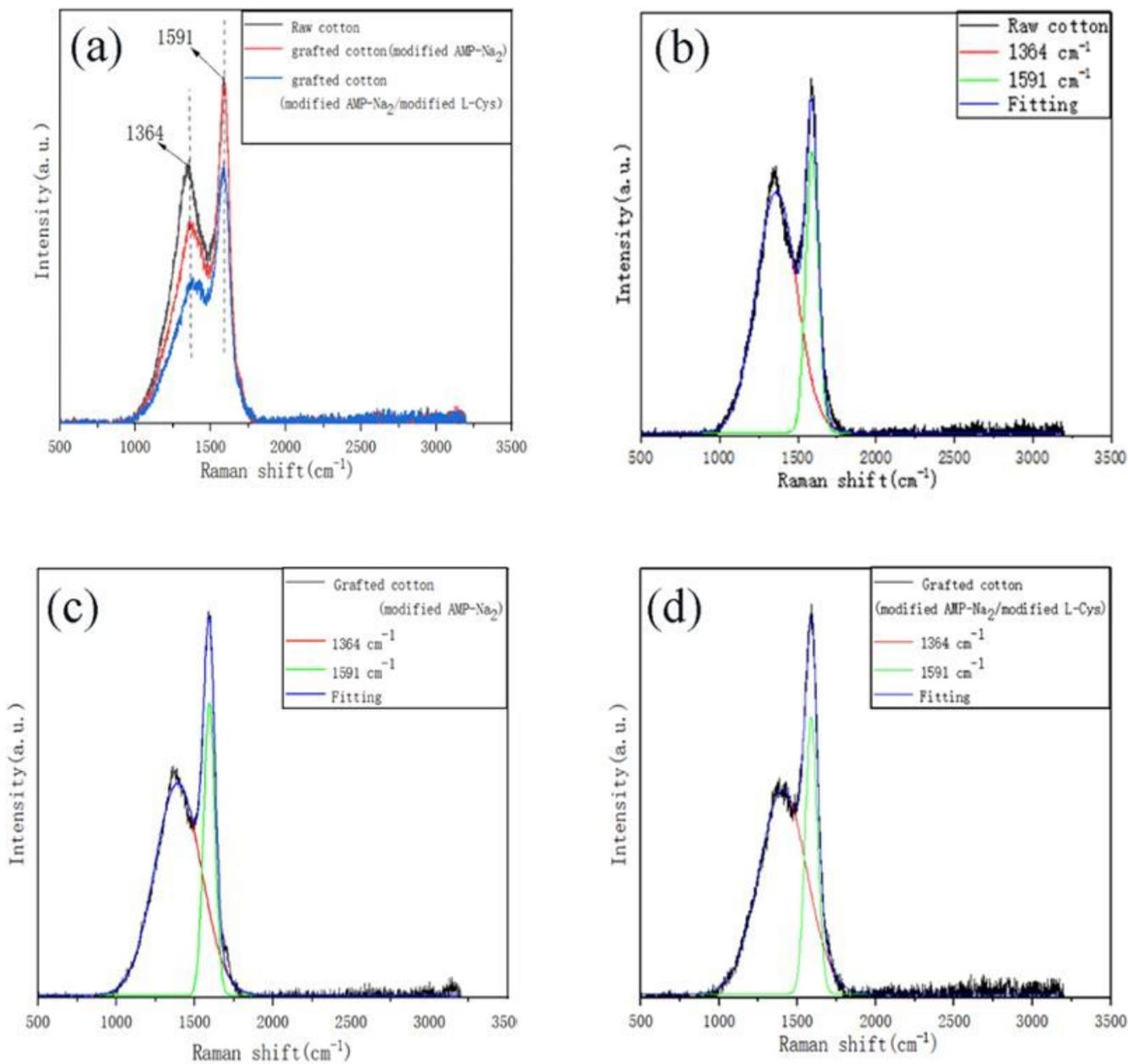


Figure 10

Raman spectra of char residue of raw cotton fabric(a), photografted cotton fabric with AMP-Na₂ monomer(b), and photografted cotton fabric with AMP-Na₂/L-Cys monomer(c)

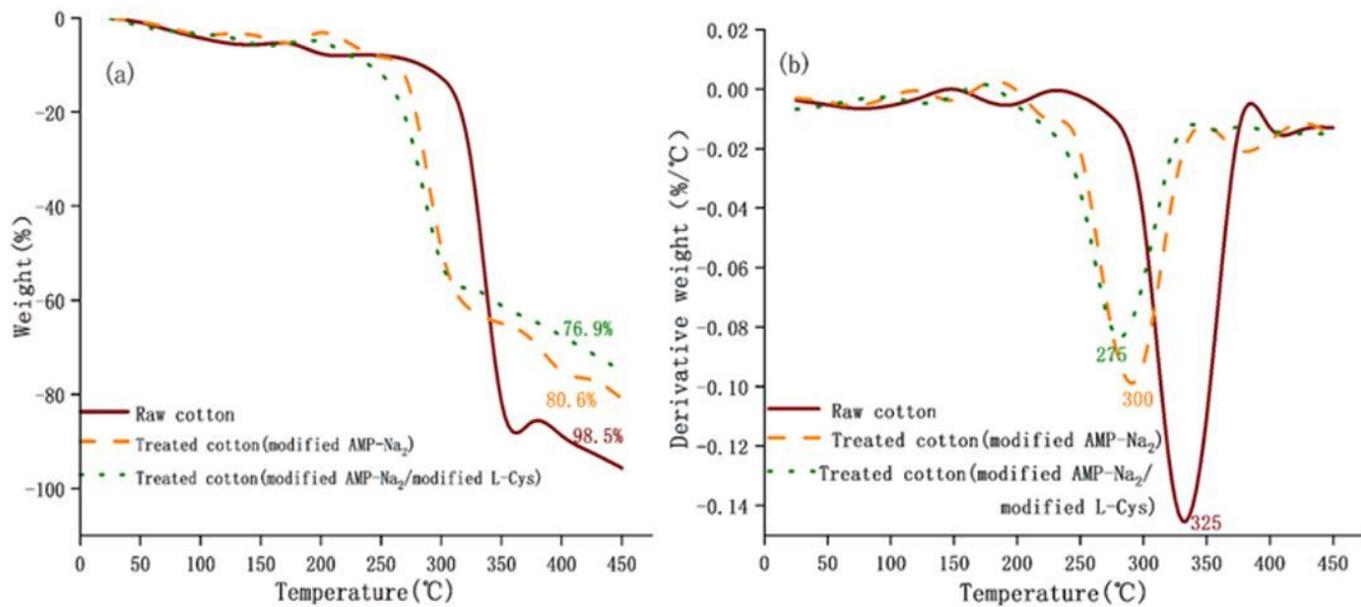


Figure 11

TGA and DTG curves of raw and photografted cotton fabrics

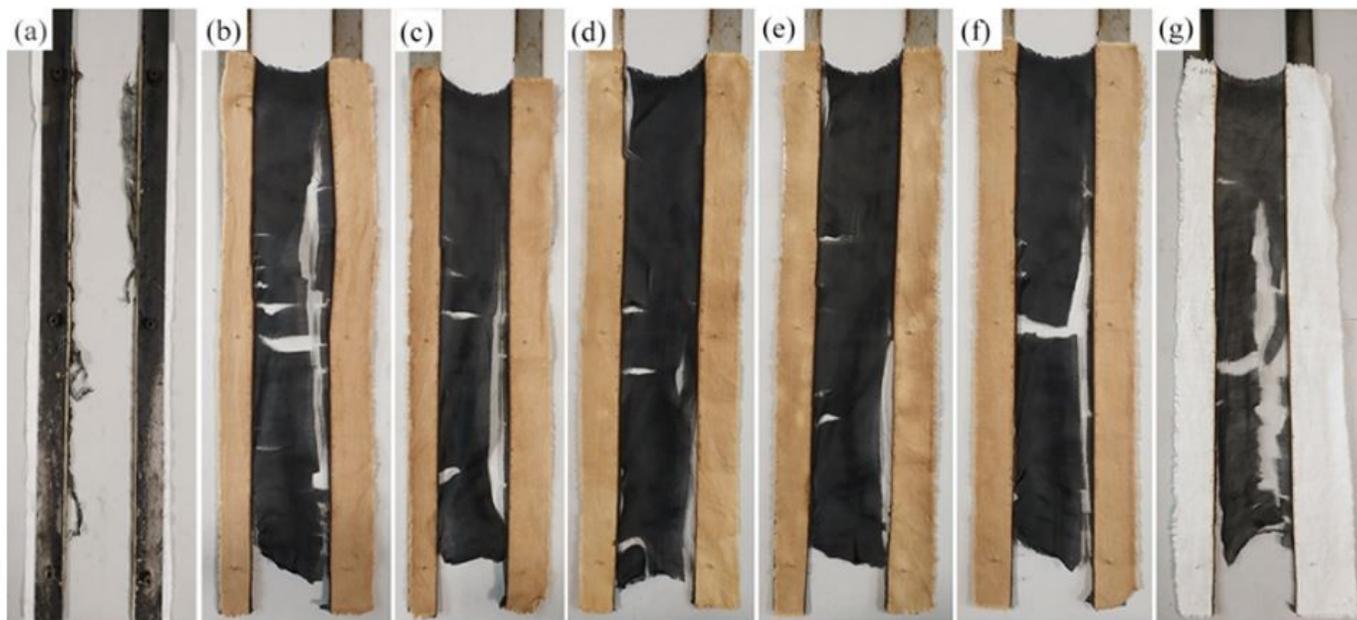


Figure 12

Results of vertical flammability testing of raw cotton fabric (a), photografted cotton fabrics with the mass ratio of AMP-Na₂ monomer and L-Cys monomer of 1.7/0.3 (b), 1.75/0.25 (c), 1.8/0.2 (d), 1.85/0.15 (e), 1.9/0.1 (f), and 2.0/0 (g)