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Flame retardancy and thermal degradation of cotton textiles based on UV-curable flame retardant coatings

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ABSTRACT

The flame retardant coatings were prepared through UV-curable technique using tri(acryloyloxyethyl) phosphate (TAEP) and triglycidyl isocyanurate acrylate (TGICA). Results from FTIR-ATR spectroscopy and scanning electron microscopy (SEM) showed that flame retardant coatings were successfully coated onto the surface of cotton fabrics. The flame retardancy of the treated fabrics was studied by Micro-scale Combustion Calorimeter (MCC) and limited oxygen index (LOI). The cottons coated flame retardant coatings had the lower peak heat release rate (PHRR), heat release capacity (HRC), total heat of combustion (THC) and higher LOI value compared with untreated cotton. The results from TGA test showed that the flame retardant coatings lowered the decomposition temperature of treated fabric. The thermal decomposition of cottons was monitored by real time FTIR analysis and thermogravimetric analysis/infrared spectrometry (TGA-IR). The enhanced flame retardant action might be caused by thermal decomposition of TAEP structure, producing acidic intermediates, which could react with fabrics to alter its thermal decomposition process.

1. Introduction

Currently, both synthetic and natural polymers have been widely used in textile and clothing products. Among various textile materials, cotton is one of the most commonly used materials for textiles and clothing. Compared with some synthetic polymer fibers, the main drawback of cotton fibers is its high flammability, and therefore it cannot be used for special textiles [1]. It is very important for public safety to find ways to render this material less flammable. Hence there have been a large number of studies to understand the combustion of cotton and ways to make it more flame resistant in the past.

Many people frequently use halogen-free phosphorus-compounds as flame retardants for cotton textiles. They are cheap to manufacture, are less volatile, have good thermal stability and promote char formation during the burning process. Some studies [2,3] have shown that, phosphorus-compounds can catalyze char formation and reduce the flammability of cotton textiles.

Phosphorus-based flame retardants impart flame retardancy to cotton by the following mechanism. Firstly, they release polyphosphoric acid on heating, which phosphorylates the C-6 hydroxyl group in the anhydro glucopyranose moiety and simultaneously they serve as an acidic catalyst for the dehydration. The first reaction could reduce formation of laevoglucose, which will further break down to flammable volatiles. This can increase the char yield by altering the chemical reactions yielding carbonaceous char rather than CO or CO_2. The acidic catalytic effect of the released polyacid could further accelerate the rate of this reaction [4].

Many of the phosphorus-based flame retardants which evoke these effects also contain nitrogen-based flame retardants. This observation has led to the proposal of a synergistic effect between phosphorus and nitrogen. Several studies [5–7] have demonstrated that the flame retardant containing phosphorus and nitrogen compounds are more efficient flame retardants due to the char formation increases.

As one of the easiest and most efficient ways, flame retardant coatings have been employed widely to protect a substrate against fire [8–10]. It can prevent heat from penetrating and flames from spreading [11,12].

As improvement of living standards and society for human, a novel flame-retardant coating, UV-curing coating, is gradually developing. UV-cured coatings have many advantages, such as very rapid curing, lower energy consumption, less environmental pollution, lower process costs, high chemical stability and lower VOCs

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[13,14]. This technology is satisfying new requirements for traditional or advanced applications, since it can offer a broad range of the changes in formulation and curing conditions.

In this paper, we introduce a method to prepare flame retardant cotton, UV-curable technology. This way is flame-retardant monomer polymerization on the surface of cotton textiles. To our knowledge, the study on flame retardancy and thermal degradation of cotton based on UV-curable flame retardant coatings has not been reported.

In the present work, we investigated the polymerization processes taking place on the surface of cotton textile through ATR spectroscopy and SEM. The flame retardant effect and thermal stability were investigated and discussed here. Furthermore, the changes of chemical structure for fabrics during the thermal degradation were monitored by real time FTIR analysis.

2. Experimental

2.1. Materials

Phosphorus oxychloride ($POCl_3$) and triethylamine (TEA) were distilled before use. 2-Hydroxylethyl acrylate (HEA), supplied from Dong-fang Chemical Co., Beijing, China, was distilled at reduced pressure and dried over 4 Å molecular sieves before use. Acetone, ethyl ether, dioxane and acrylic acid were purchased from Shanghai Chemical Reagents Company in China. Triglycidyl isocyanurate was purchased from Anhui Taida New Materials Co., Ltd. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173) was used as a photoinitiator. The ultrasonic treatment was carried out by a KS-900 ultrasonic generator (Ningbo Kesheng) at room temperature under air atmosphere. UV irradiation equipment was made by Lantian Co. in China (80 W cm^{-2}). Plain-weave cotton fabrics were from the market with an areal density of 156 g^{-2}. Cotton fabrics were pre-treated in the solution containing 18 wt% NaOH and rinsed with distilled water then air-dried at room temperature.

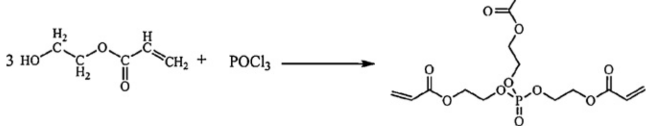
2.1.1. Preparation of tri(acryloyloxyethyl) phosphate (TAEP) [15]

HEA (17.75 g, 0.153 mol), TEA (18.05 g, 0.18 mol) and 60 mL ethyl ether were placed into a 250 mL round-bottomed flask with a calcium chloride drying tube. A mixture of 7.86 g $POCl_3$ (0.05 mol) and 20 mL of ethyl ether was slowly added into the above flask at 0 °C using an ice bath, and then kept at ambient temperature for 12 h. The triethylamine hydrochloride salt by-product was removed by filtration. The obtained filtrate was twice extracted by HCl (1 M), $NaHCO_3$ (10%) and NaCl (saturated) aqueous solution. After drying over sodium sulfate, the solvent was removed under vacuum, obtaining a colorless liquid product, named TAEP. The synthetic route of TAEP is shown in Scheme 1.

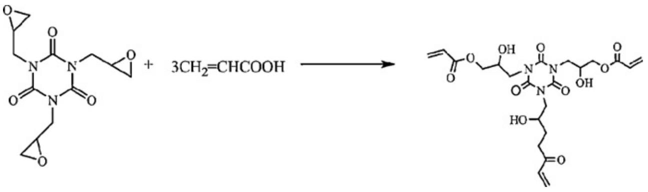
$$\mathrm{IR\,(KBr)\,(cm^{-1}):\ 1265\,(—P{=}O);\ 1058\ and\ 980\,(—P—O—C);}$$
$$\mathrm{1727\,(—C{=}O);\ 1635;\ 1410;\ 810\,(—C{=}C).}$$

2.1.2. Preparation of triglycidyl isocyanurate acrylate (TAEP) [16]

TGIC (29.75 g, 0.1 mol), AA (21.6 g, 0.3 mol), and 100 mL dioxane were placed in a 250-mL four-necked round bottom flask, which was equipped with a mechanical stirrer, reflux condenser, and thermometer. And triethylamine (0.3 mL, as catalyst), 4-methoxyphenol (0.3 g, as polymerization inhibitor) were also added. And then, the temperature was raised to 105 °C, kept at this temperature for 3 h. After that, the solution was placed in a rotary evaporator to remove any unchanged reactants and solvent. A colorless sticky liquid product was obtained, named TGICA. The schematic process of the reaction was presented in Scheme 2.



Scheme 1. The synthetic route of TAEP.



Scheme 2. The synthetic route of TGICA.

$$\mathrm{IR\,(KBr)\,(cm^{-1}):\ 3448\,(—OH);\ 1731\,(C{=}O);\ 1061\,(—C—O—C—);}$$
$$\mathrm{1636;\ 1409;\ 810\,(—C{=}C).}$$

2.2. Preparation of flame retardant cotton

In the first step, pieces of bleached cotton fabrics were immersed in an acetone solution containing 50 g/L, 100 g/L and 200 g/L of the flame retardant monomers (as shown in Table 1) (FR (g)/acetone (L); FR: TAEP/TGICA = 1/1, by weight; 4% (w/w) of the photoinitiator (Darocur1173)) at room temperature for 30 min, respectively. Each mL of these solutions contains 0.05 g, 0.10 g, 0.20 g reactive compounds, respectively. And then ultrasonic treatment was carried out for 10 min. And finally, these impregnated fabrics were removed from the solution, placed onto glass plates and irradiated on both sides each 10 s under UV-source in an air atmosphere. (80 W cm^{-2}; the distance between the light source and the sample is 8 cm.). After radiation, the fabric was firstly washed with acetone, and then extracted by tetrahydrofuran for 48 h to remove the generated homopolymers. Finally, the fabric was dried in air, then under vacuum until no weight lost could be detected.

2.3. Measurements

2.3.1. ATR measurements

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry was performed using a Thermo Nicolet Avatar 6700 FTIR equipped with an attenuated total reflectance device.

2.3.2. Microscale Combustion Calorimeter (MCC)

GOVMARK MCC-2 Microscale Combustion Calorimeter was used to investigate the combustion of cotton fabrics. In this system, about 5 mg sample was heated to 700 °C at a heating rate of 1 °C s^{-1} in a stream of nitrogen flowing at 80 cm^3 min^{-1}. The volatile, anaerobic thermal degradation products in the nitrogen gas stream are mixed with a 20 cm^3/min stream of pure oxygen prior to entering a 900 °C combustion furnace. Measured during the test is the heat release rate dQ/dt (W) and sample temperature as a function of time at constant heating rate [17,18]. The specific heat release rate HRR (W/g) is obtained by dividing dQ/dt at each point in time by the initial sample mass. A derived quantity, the heat release capacity HRC (J/g K) is obtained by dividing the maximum value of the specific heat release rate by the heating rate in the test. The heat release capacity is a molecular level flammability parameter that is a good predictor of flame resistance and fire behavior when only research quantities are available for testing [19].

Table 1
The formulations, MCC data and LOI test of samples.

Sample	Composition FR[a] (g)/ acetone (L)	LOI	PHRR (W/g)	HRC (J/g K)	THC (kJ/g)	T_{max} (°C)
Cotton 0	0	21	183.0	181	8.8	371
Cotton 1	50	22.5	165.8	167	5.1	336
Cotton 2	100	23	138.2	137	4.1	326
Cotton 3	200	24.5	119.7	121	3.6	321

[a] TAEP/TGICA = 1/1, by weight.

2.3.3. Laundering procedures

Laundering procedures was done according to GB/T17595-1998, and the water temperature of laundering was approximately 50 °C.

2.3.4. limited oxygen index (LOI)

LOI tests were measured according to ASTM D2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 150 mm × 58 mm.

2.3.5. Scanning electron microscopy (SEM)

The cottons and char formed after MCC testing were first sputter-coated with a conductive layer, and then its morphologic structures were observed by scanning electron microscopy Hitachi X650.

2.3.6. Dry weight pickup

Weighing measurements were used to monitor how much the flame retardant was coated on the fabric. Dry weight pickup is determined as follows:

$$\text{Dry weight pickup} = \frac{M2 - M1}{M1}$$

where, M_1 and M_2 are the weights of the cotton samples before and after dipping process, respectively.

2.3.7. Determination of nitrogen concentration of the treated fabrics

Element analyzer (Elemental analysis Instrument Company, Germany, VARIO ELIII) was used to test the nitrogen concentration of the treated fabrics.

2.3.8. Determination of phosphorus concentration of the treated fabrics

Approximately 0.4 g of the samples and 10.0 mL concentrated HNO_3 (65%) were placed into an Erlenmeyer flask with reflux condenser. The mixture was kept under reflux for about 8 h, and then some perchloric acid (about 10 drops) was added into above mixture. The reaction was maintained at the same temperature until no white smoke was released. And then, the clear solution were transferred to a 25 mL volumetric flask, and then diluted with distilled/deionized water. The phosphorous content in the solution was measured with an Atomscan Advantage ICP-AES (Thermo Jarrell Ash Corporation, USA).

2.3.9. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) was carried out on the TGA Q5000 IR thermogravimetric analyzer (TA instruments) using a heating rate of 20 °C/min under nitrogen and air atmosphere, respectively.

2.3.10. Real time Fourier transforms infrared spectra (RT-IR)

Real time Fourier transform infrared spectra (RT-IR) was recorded using the Nicolet 6700 FT-IR spectrophotometer equipped with a ventilated oven having a heating device. The cotton sample was mixed with KBr powders, and the mixture was pressed into a disc, which was then placed into the oven. The temperature of the oven was raised at a heating rate of about 10 °C min^{-1}. RT-IR spectra were obtained in situ during the thermo-oxidative degradation of the sample.

2.3.11. Thermogravimetric analysis-infrared spectrometry (TGA-IR)

Thermogravimetric analysis/infrared spectrometry (TGA-IR analysis) of the cured sample was performed using the TGA Q5000 IR thermogravimetric analyzer that was interfaced to the Nicolet 6700 FT-IR spectrophotometer. The heating rate was as 20 °C min^{-1} (nitrogen atmosphere, at flow rate of 45 mL min^{-1}).

3. Results and discussion

3.1. Surface characterization of cotton fabrics

3.1.1. ATR study for samples

ATR spectra of untreated (a) and treated (b) cotton (Cotton 3) fabrics are shown in Fig. 1. The treated cotton fabrics have the new absorption band at around 1741 cm^{-1} and 1464 cm^{-1}, which are attributed to the carbonyl stretching vibration of the acrylic polymer. This can be demonstrated that flame retardant monomers have been coated onto the surface of cotton fabrics. It is not easy to identify the absorption bands for P=O and P—O—C of flame retardant coatings on the treated fabrics, as the vibrations of the primary and secondary —OH deformation of the cotton appear in the same region at about 1057, 1370, and at 1162 cm^{-1} [4]. It is very clear that the —OH stretching vibration present on untreated cotton is still visible in the treated fabrics, which indicates that the thickness of the deposited polymer layer is less than 1 μm [9].

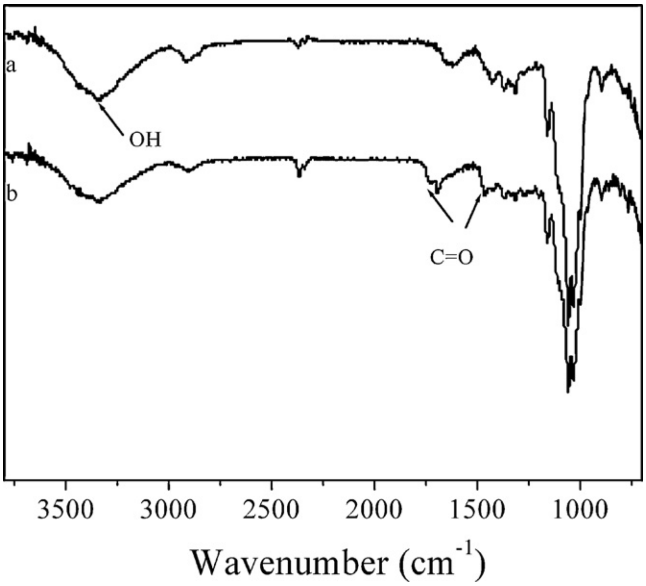


Fig. 1. ATR analyses of Cotton 0 (a) and Cotton 3 (b).

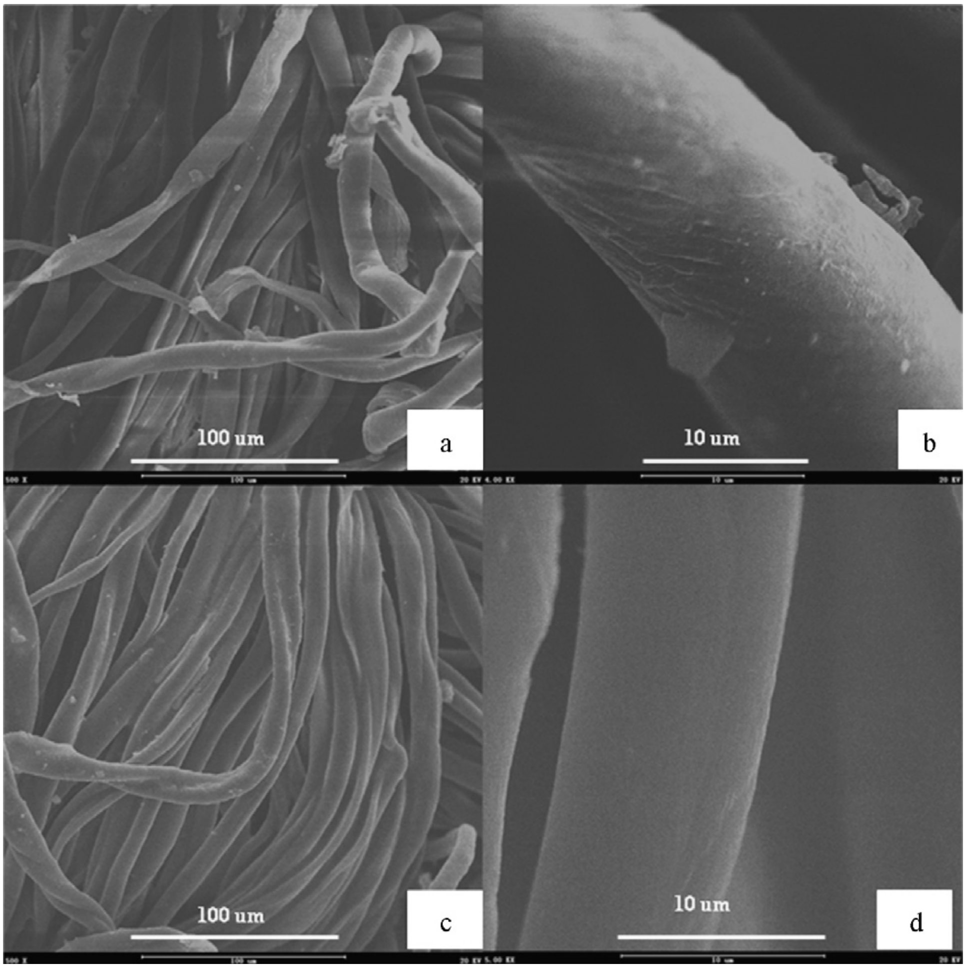


Fig. 2. SEM micrographs of cotton fabrics: Cotton 0 (a, b); Cotton 3(c, d).

3.1.2. *Scanning electron microscopy (SEM)*

The surface morphologies of fabrics before and after treatment are shown in Fig. 2. From SEM pictures, it can be seen that the surface of virgin cotton textile (Cotton 0) (Fig. 2(a) and (b)) is rough with many veins while the treated fabric (Cotton 3) (Fig. 2(c) and (d)) is smooth. This shows that polymer coatings have been present on the surface of the treated cotton fabrics. However, the fine structure of the untreated cotton surface can be still seen in the treated sample. This suggests that the polymer coatings on the treated cotton are very thin.

3.2. *Flame retardancy of the treated cotton fabrics*

The Micro-scale Combustion Calorimeter (MCC) is one of the most effective bench scale methods for investigating the combustion properties of polymer materials. Treated cotton textiles samples are tested on the MCC instrument to determine the heat release rate (HRR), total heat of combustion (THC) and temperature of maximum HRR ($T_{\max}$). As shown in Table 1 and Fig. 3, all treated fabrics have lower HRR, $T_{\max}$ and THC values compared with pure cotton textile. This may be caused by the catalytic action of phosphorus compounds, which enables fabrics to dehydrate at the lower temperature, and accelerates the formation of char and reduces the release of combustible gas. The lower THC values further indicate FR could reduce fire risk of cotton textiles.

Moreover, the positive effect of the FR coating on flame retardancy for cotton fabrics can be proved from the LOI data directly, which was listed in Table 1. With the increase of FR content, LOI value rose from 21% to 24.5%. It is in agreement with MCC data.

3.3. *Laundering procedures*

Fig. 4 and Table 2 show MCC results of sample after laundering. It can be seen that the flame retardant cotton still has the lower HRR, THC, which proves flame retardant coating good durability to laundry.

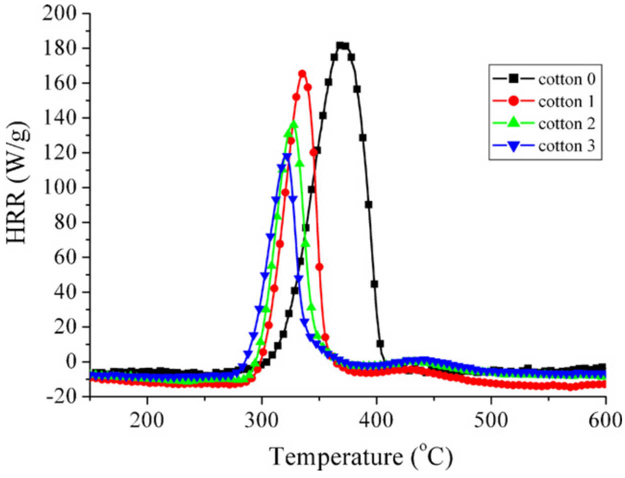


Fig. 3. MCC curves of cotton textiles.

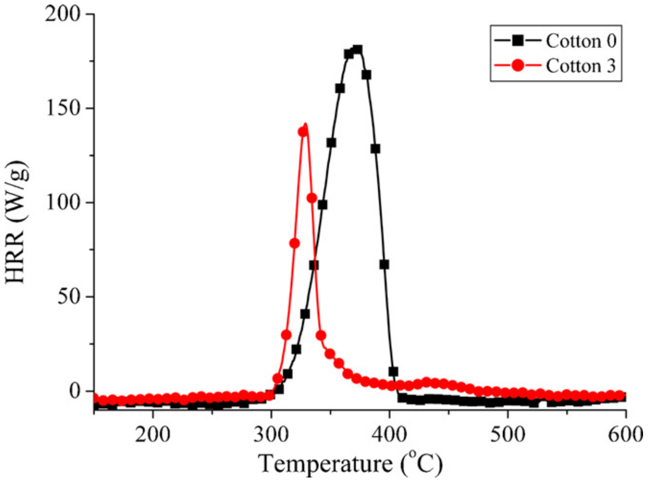


Fig. 4. MCC curves of cotton textiles after laundering.

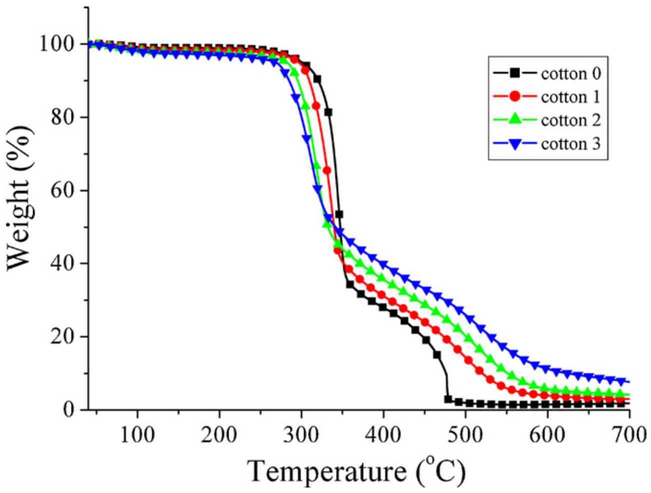


Fig. 6. TGA curves of cotton textiles under air.

Table 2
The MCC data after laundering.

Sample	PHRR (W/g)	HRC (J/g K)	THC (kJ/g)	T_{max} (°C)
Cotton 0	183	181	8.8	371
Cotton 3	142	142	4.0	329

3.4. Surface morphology of chars

Fig. 5 shows SEM pictures of chars formed from the virgin cotton (a) and treated cottons (b, c). The treated fabrics (Fig. 5(b) and (c)) maintain the morphology of fibers after the burning, while that of virgin cotton is very loose. The predominant chars may contribute to efficiency of flame retardants and improve the flame retardancy of substrates. This may be cause by formation of polyphosphoric acid inside the fiber resulting in more crosslink structures in the char, which works like a shield to protect the cotton during the burning process [20]. In other words, phosphorus-based flame retardants promote a tendency for char formation and nitrogen compounds favorably provide an enhancement of thermal stability of the char, resulting in a high efficiency of char formation.

3.5. Dry weight pickup

Weighing measurement is very effective method to characterize the dipping process. As shown in Table 3, the amount of flame retardant coating increases with increase of the monomer concentration. The highest amount attains at about 29.7%

3.6. The phosphorus and nitrogen content

The phosphorus and nitrogen content are shown in Table 3. The investigations on textile fixed phosphorus and nitrogen can show that the phosphorus and nitrogen on all materials is in the range of 0.19–0.72% and 0.3–1.8%, respectively. Moreover, the phosphorus and nitrogen concentrations are directly proportional to the add-on, indicating that the fixed UV-cured product does not significantly change its composition-regardless from the textile substrate [21].

3.7. Thermal behavior

3.7.1. Thermal oxidation degradation behavior

The thermal stability of the flame retardant materials is very important. TGA is one of the most widely used techniques for rapid evaluation of the thermal stability for various polymers. Fig. 6 shows the TGA curves of untreated and treated cotton using various amounts of flame retardant monomer in air atmosphere. The decomposition temperature at 5% weight loss ($T_{-5\%}$) and final char yields at 700 °C are summarized in Table 3. The TGA curve for untreated cotton reveals that the pyrolysis of cotton fabric includes three stages: the first region around 100 °C corresponding to the release of physically adsorbed water; the second region around −400 °C, the weight loss is very fast and significant, this is the main pyrolysis stage and it is attributed to the dehydration and decarboxylation reactions which produce combustible gasses like aldehydes, ketones, ethers, etc.; the third region around −500 °C, which corresponds to the decomposition of char formed in the second stage [6,22,23]. The pyrolysis of the treated fabrics also shows three stages, but all the treated fabrics decrease in ini-

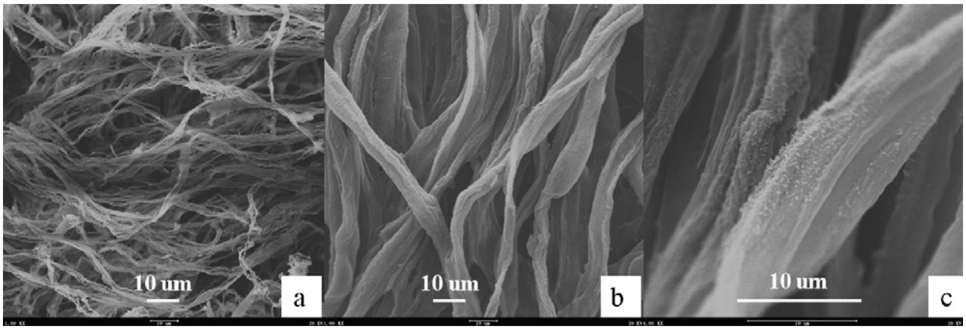


Fig. 5. SEM images of char left after MCC test: the virgin cotton (a); treated cottons (b, c).

Table 3
The dry weight pickup and TGA data of samples.

Sample	Dry weight pickup (added-on) (%)	Phosphorus (%)/Nitrogen (%)	$T_{-5\%}$		Char yield (%) at 700 °C (air)	Char yield (%) at 700 °C (nitrogen)
			Air	Nitrogen		
Cotton 0	0	0/0	300.6	304.1	1.9	12.1
Cotton 1	3.0	0.19/0.3	296.3	306.1	3.0	19.4
Cotton 2	11.6	0.63/1.6	281.7	288.7	4.2	23.5
Cotton 3	29.7	0.72/1.8	268.3	270.2	7.7	31.1

tial and maximum decomposition temperatures. The early thermal degradation is mainly attributed to facile catalytic dehydration and cross-linking of fabrics by phosphoric acid generated during pyrolysis of phosphorus-containing compounds (TAEP). Treated cotton fabrics have more residue than that of the untreated cotton (1.9%) at 700 °C. Cotton 3 gives the highest char yield (7.6%), followed by Cotton 1 (3. 0%) and Cotton 2 (4.2%).

3.7.2. Thermal degradation behavior

Fig. 7 shows the TGA curves of samples in nitrogen atmosphere. It shows that environment atmosphere does not influence the degradation behavior of cottons, except at high temperature region. The residuary weights of these samples are almost constant above 500 °C in N_2. The weight loss at high temperature in air could be ascribed to the further oxidation degradation of unstable char layer, resulting in more char residue in nitrogen than in air. Cotton 3 leaves the highest char yield (31.1%) at 700 °C, followed by Cotton 1 (19.4%) and Cotton 2 (23.5%).

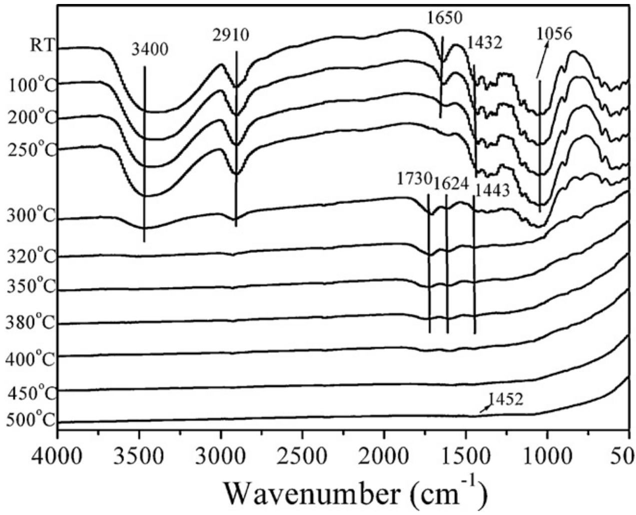


Fig. 8. FTIR spectra of Cotton 0 during the thermal degradation in the range of RT-500 °C.

3.8. The analyse of real time Fourier transform infrared spectra (RT-IR)

In order to further investigate the thermal oxidative degradation of treated fabrics at air atmosphere, Cotton 0 and Cotton 3 samples are chosen for measuring the changes in spectra of real time FTIR, as shown in Fig. 8 and Fig. 9 respectively.

It can be seen from Fig. 8 that the relative intensities of the characteristic peaks of virgin cotton (Cotton 0) change negligibly around 100 °C except the peak at 1650 cm^{-1}, which is attributed to H—O—H of physical adsorbed water. The absorptions at 3400 cm^{-1} (stretching vibration of OH), 2910 cm^{-1} (stretching vibration of C—H), 1432 cm^{-1} (in plane bending vibration of C—H) cm^{-1} and 1056 cm^{-1} (stretching vibration of C—O—C) disappear at 350 °C, indicating that cotton fabrics decompose and carry on the dehydration reactions of cotton fabric. Meanwhile, the appearance of the new peaks at 1730 cm^{-1}, 1443 cm^{-1} (attributed to C=O absorption) and 1624 cm^{-1} (attributed to C=C absorption) above 250 °C, further indicates that the system is carrying out dehydration reaction and producing aldehydes, ketones and other olefin compounds. But with an increase of temperature, the relative intensity of the absorption peaks (the absorptions of C=O) continues to weaken, which indicates the system is carrying out decarboxylation reaction and producing combustible gasses like aldehydes, ketones, etc. All peaks almost disappear at 500 °C except the absorption at 1452 cm^{-1} (condensed aromatics), indicating that virgin cotton decomposes completely and forms the comparatively stable char layer.

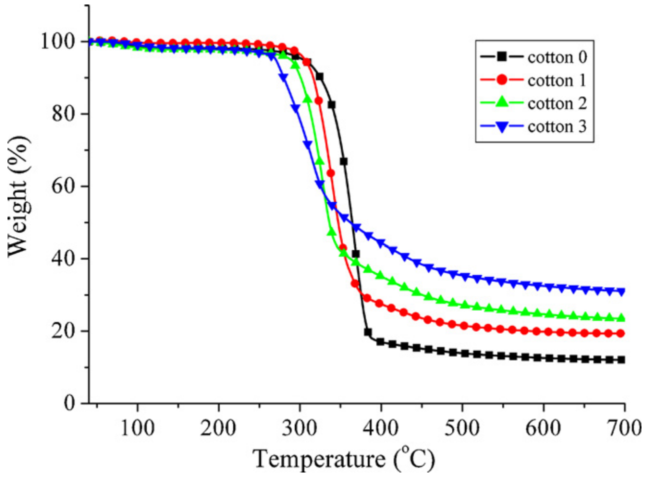


Fig. 7. TGA curves of cotton textiles under nitrogen.

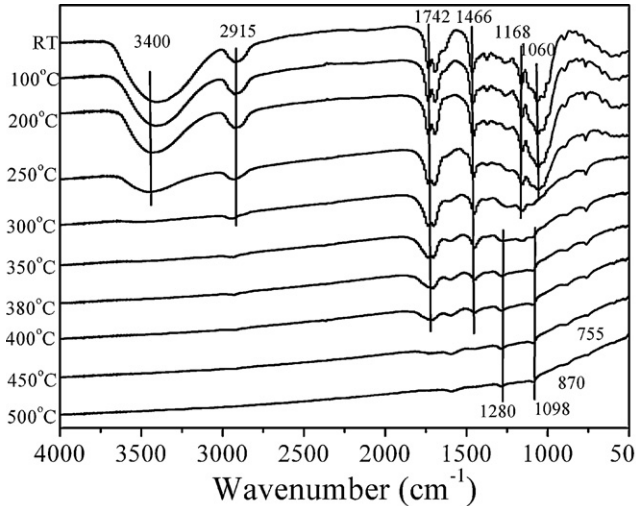


Fig. 9. FTIR spectra of Cotton 3 during the thermal degradation in the range of RT-500 °C.

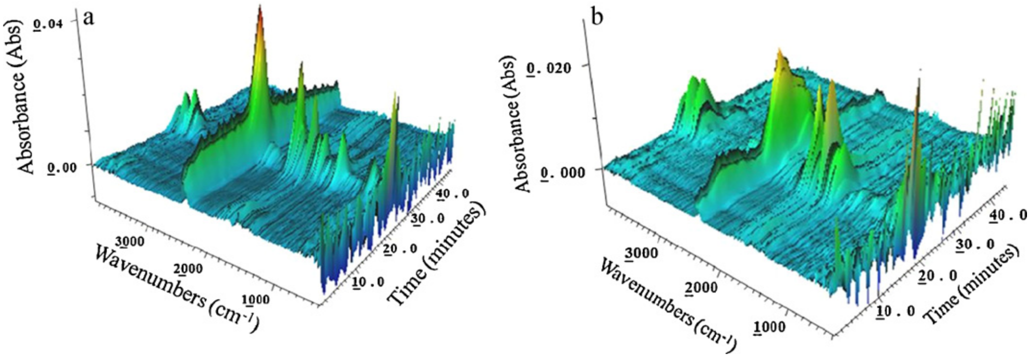


Fig. 10. The 3D surface graph for the FTIR spectra of the evolved gases produced by Cotton 0 (a) and Cotton 3 (b).

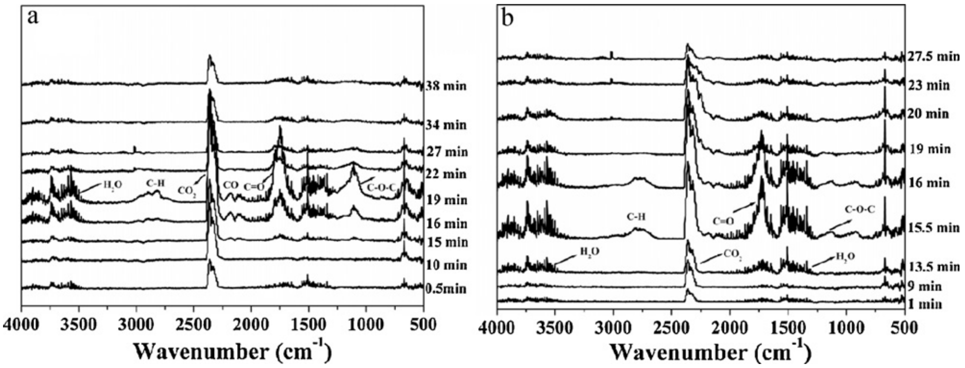


Fig. 11. FTIR spectra of pyrolysis products for Cotton 0 (a) and Cotton 3 (b).

The thermal degradation process of treated cotton (Cotton 3) is shown in Fig. 9. The absorption at 3400 cm^{-1} disappears earlier compared with untreated cotton, indicating treated cotton could finish the dehydration reaction early. Meanwhile, the peak at 1060 cm^{-1} ascribed to P—O—C absorption (TAEP) decreases quickly with increasing temperature and then disappears completely above 300 °C, indicating the degradation of P—O—C occurred. Furthermore, the new peaks at 1098 and 870 cm^{-1} (the symmetric and asymmetric stretching vibration of P—O—P band) [24] appear above 300 °C. This indicates that poly (phosphoric acid) (PPA) is formed, which can catalyse the decomposition of cotton fabric, resulting in the dehydration reaction occurring earlier. The peaks at 1742 and

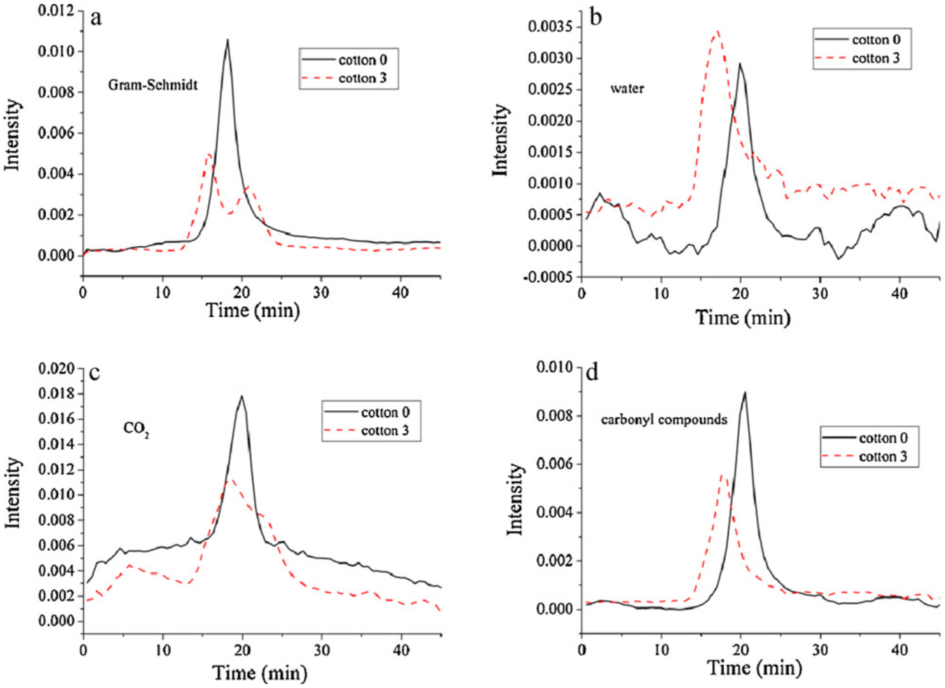


Fig. 12. Absorbance of pyrolysis products for Cotton 0 and Cotton 3 vs time: (a) Gram-Schmidt; (b) H_2O; (c) CO_2; (d) carbonyl compounds.

1466 cm^{-1}, assigned to the vibration of C=O group, start to decrease from about 200 °C and almost disappear around 450 °C.

The appearance of new peak at 1280 cm^{-1} in the FTIR spectra [25] indicates that the phosphate group deviates from the aliphatic structure and then forms PPA or re-links to the aromatic structures at the temperatures over 300 °C. The appearance of new peak at 759 cm^{-1} implies aromatic structures are formed [26].

3.9. The evolved products of treated and untreated fabrics

In this work, TGA-FTIR was used to analyze the gas products during the thermal degradation process of Cotton 0 and Cotton 3.

Fig. 10 shows 3D TGA-IR spectra of gas phase in thermal degradation of Cotton 0 (a) and Cotton 3 (b). In Fig. 10, peaks in the regions of around 3400–4000 cm^{-1}, around 2250–2400 cm^{-1}, around 2100–2200 cm^{-1}, and around 1600–1900 cm^{-1} are noted. The spectra fit well to the reported FTIR features of gas products such as H_2O (3400–4000 cm^{-1}), CO_2 (2250–2400 cm^{-1}), carbonyl compounds (representing aldehydes, ketones, carboxylic acids, 1633–1839 cm^{-1}). As this figure shown, the process of thermal degradation for Cotton 0 is different from Cotton 3.

Some FTIR spectra are shown in Fig. 11. It can be drawn that the pyrolysis products for Cotton 0 (Fig. 11(a)) at the beginning (from about 15 min) are mainly composed of a small amount of H_2O. With the increase of temperature (above 19 min), lots of water, hydrocarbons, CO_2, CO, carbonyl, compounds containing ether, etc. are released. However, Cotton 3 (Fig. 11(b)) starts degradation at the earlier time (from about 13.5 min) compared with Cotton 0. And it releases the similar gas products with Cotton 0.

The change for the intensity of the total evolved products versus time is shown in Fig. 12(a). It can be seen that the intensity for Cotton 3 is lower than that of Cotton 0. It can be interpreted that flame retardant can catalyze the thermal decomposition of cotton textiles to form the stable char layer, which can protect the fabric from further decomposition.

In order to further study the difference between Cotton 0 and Cotton 3, some IR evolution curves of the identified gaseous species are shown in Fig. 12(b). For example, H_2O, CO_2 and carbonyl compounds are easily identified by their characteristic absorption. The data obtained from Cotton 0 and Cotton 3 can be compared quantitatively as the weight of sample during the testing of each sample was kept constant (1 mg). As shown in Fig. 12(b), Cotton 3 has the lower temperature for the peak release rate of water vapor. Cotton 0 has the lower intensity of peak release rate of water. Lower temperature of the peak release rates and higher intensity of absorption for Cotton 3 clearly indicate their superior dehydrating action [6].

Release of CO_2 and carbonyl compounds during the thermal decomposition of treated and untreated fabrics is also shown in Fig. 12(c) and (d). The rate of release of CO_2 and carbonyl compounds is lowered as compared with the untreated fabric.

4. Conclusions

This paper has shown that tri(acryloyloxyethyl) phosphate (TAEP) and triglycidyl isocyanurate acrylate (TGICA) monomers could be easily polymerized on the surface of cotton under UV radiation in the presence of Darocur1173. The results of ATR and SEM showed that TAEP and TGICA polymer coatings were formed on the surface of cotton fabric. The MCC results showed that the flame retardant effect correlated with the concentration of the monomer. Hence, Cotton 3 had the lowest PHRR (119.7 W/g), THC (3.6 kJ/g) and higher LOI value. Surface morphology of chars indicated that treated cotton fabric maintained fiber integrity after burning and revealed the formation of a layer of nonflammable coating on surfaces of the burned cotton fibers, which might insulate the inner layers more efficiently during combustion. TGA results reflected that with increase of concentration for flame retardant monomer, the thermal stability for cotton textiles could enhance. Cotton 3 gave the highest char yield, 7.7% in air and 31.1% in nitrogen. TGA-IR results showed that Cotton 3 had the lower temperature for the peak release rate of water vapor, CO_2 and carbonyl compounds, higher intensity of absorption for water, and lower intensity of absorption for CO_2 and carbonyl compounds as compared with Cotton 0.

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