

Synergistic Flame-Retardant Finishing of Cotton Using Dichlorotriazinyl Phosphonate and Triethanolamine

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Abstract: Dichlorotriazinyl phosphonate (DCTP), a formaldehyde-free flame retardant (FR), was steam-cured with triethanol amine (TEA) to impart synergistic flame-retardancy to cotton fabrics. While the DCTP treatment alone showed very limited resistance less than five laundering cycles (LC), TEA addition increased the laundering durability of the FR cotton up to ten LC. More enhanced washing performance up to fifteen LC was observed with epichlorohydrin (ECH) after-treatment. The TEA and ECH extended the washing resistance via nucleophilic substitution and addition reactions of DCTP and cotton respectively producing the densely crosslinked networks of DCTP and cellulose. With increasing molar ratio of TEA to the DCTP up to 0.5, the flame retarding effectivity and the synergistic effectiveness improved up to 3.8 and 2.2 respectively. The pyrolysis and combustion behaviors of the FR-cotton were verified with TGA and micro combustion calorimetry. The FR cotton decomposed at lower maximum pyrolysis and combustion temperatures with decreased peak pyrolysis and heat release rate, yielding higher char contents. The synergistic DCTP and TEA formulation coupled with ECH post-treatment seemed to follow a solid-phase flame-retarding mechanism.

Keywords: Formaldehyde-free, Flame retardant, Crosslinking, Synergy, Laundering durability

Introduction

Cotton fibers contain the purest form of cellulose, the most abundant polymer in nature, having the highest molecular weight among all plant fibers, and the economic impact of cotton in the global market is appreciated by its majority share in textile goods [1]. However, the fibers are very flammable because of low pyrolysis and ignition combustion temperatures of 350 °C and low limiting oxygen index of 18.4 [1,2]. Therefore, the modification of its thermal behaviors has been carried out for reducing ignition and combustion of cotton by both academic and industrial institutions, ensuring the security and protection of peoples such as workers under flammability hazard and firefighters in the fire accidents. Flame retardants (FR) for cotton should have reactive groups which can be covalently linked to the substrate to withstand repeated laundering cycles, without damaging the physicochemical and environmental features such as strength, handle, appearance, and toxic influences on humans during application and service.

Some organophosphorous compounds have been used commercially for cotton fibers as durable flame retardants such as *N*-Methylol dimethyl phosphonopropionamide (Pyrovatex) or Tetrakis(hydroxymethyl) phosphonium salt/urea condensates (Proban polymer) [3,4]. However, since both FR processes may release carcinogenic formaldehyde from the finished apparel, more eco-friendly FRs need to be developed to meet increasingly tougher regulations on hazardous and toxic chemicals throughout the lifecycle of the FR cotton fabrics.

Several studies on formaldehyde-free flame-retardant (FR) finishing of cotton containing phosphorous and nitrogen has been carried out including UV curable flame retardants (FR) [5,6], hybrid organic-inorganic FR [7], polymeric FR [8], phosphoramidate derivatives FR [9], and triazine-based FR. Among them, the triazine-based organophosphorous FRs have been extensively studied because they may have potentially high laundering durability resulting from the strong C-O-C bond formation via nucleophilic substitution between chlorotriazinyl groups and the hydroxyl groups of anhydroglucopyranose in cellulose [10]. The phosphorous-containing chlorotriazine FRs can be classified into monochloro-triazine FRs and dichloro-triazine FRs depending on the number of chlorine in the triazine ring, which is the same reactive group of the reactive dyes for cotton. The monochloro-triazine FR can be synthesized from cyanuric chloride and various nucleophilic phosphonates, producing derivatives of Bis(dimethyl hydroxymethyl phosphonate) [11,15], Bis(diethyl phosphonate) [10,12], and Bis(diethyl aminoethyl phosphonate) [13]. Also there have been many dichloro-triazine FR derivatives of Diethyl phosphonate [10], Diethyl aminoethyl phosphonate [13], Aminoethyl hydrogen phosphite [14], Dimethyl or diethyl hydroxymethyl phosphonate [10,15], and Dihydroxyethylamino sulfatoanilino phosphonate [16]. While most of the chlorotriazine FRs exhibited outstanding flame-retarding performances, the study on the washing durability prerequisite for FR textiles was rather limited. The water resistance of the FR-cotton under alkaline condition can be improved using a Bis(diethyl phosphonate monochloro-triazine) crosslinked with Neopentyl glycol, nevertheless, it was only durable to five repeated washing [17]. Therefore the laundering durability of the triazine-based FR treatment of cotton still

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need to be enhanced.

This study was carried out to improve the durability against repeated domestic washing by *in situ* formation of the crosslinked Diethyl 4,6-dichloro-1,3,5-triazin-2-yl phosphonate (DCTP) and cellulose using triethanolamine as a FR crosslinker, combined with an cellulose crosslinker epichlorohydrin. The flame retarding effectivity and synergistic effectiveness of the FR cotton fabrics increased with increasing TEA application. The thermogravimetric and microcalorimetric analyses were carried out to evaluate the pyrolytic and combustion behaviors including char content of the FR cotton. The laundering durability was examined in relation with the addition of the additives including atomic composition change assessed with EA and ICP.

Experimental

Fabrics and Materials

Scoured and bleached cotton fabrics of plain weave (115 g/m², warp: 35 threads 16.5 tex/cm, weft: 31 threads 14 tex/cm) were used. As supplied from Sigma Aldrich, cyanuric chloride (CAS no. 108-77-0) and triethyl phosphite (CAS no. 122-52-1) were used to synthesize diethyl (4, 6-dichloro-1,3,5-triazine-2yl) phosphonate (DCTP) using toluene (CAS no. 108-88-3) as a solvent. Triethanolamine (TEA) and epichlorohydrin (ECH) were used as crosslinkers for DCTP and cellulose respectively.

Synthesis of (4,6-Dichloro-1,3,5-triazine-2yl) Diethyl Phosphonate (DCTP)

DCTP was synthesized with cyanuric chloride and triethyl phosphite as shown in Scheme 1 [10]: 0.1 mole of cyanuric chloride was dissolved in 250 ml of toluene in a three-necked flask with a stirrer, a thermometer and a condenser. Triethyl phosphite of 0.1 mole was dropwise added into the reaction flask using a dropping funnel within 2 hours and the reaction mixture was refluxed at 70 °C for 6 hours.

Flame-Retardant Finishing and Cellulose Crosslinking

The cotton fabrics was first padded with an aqueous alkaline solution of 10 % Na₂CO₃ containing different amounts of TEA, and subsequently squeezed to 100 % wet pick up using a padding mangle. The pretreated cotton fabrics were dipped into the aqueous 30 % DCTP solution and then squeezed to same pick up. The impregnated

samples were cured under steam at 120 °C for 10 minutes, rinsed with running water and dried under vacuum. The TEA was added for the crosslinking of DCTP during the steam curing. In order to improve the laundering durability by cellulose crosslinking, the FR-treated cotton was dipped in an aqueous solution containing 9 % epichlorohydrin and 15 % Na₂CO₃, and then squeezed to 80 % pick up. The impregnated sample were dried at 80 °C for 5 minutes and cured at 120 °C for 3 minutes [18].

The add-on (A%) were calculated from the following formula:

$$A(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the weight of the untreated cotton and W_2 is the weight of the cured fabric after water rinsing.

Elemental and ICP Analysis

The nitrogen and phosphorus contents of the finished fabrics were analyzed by elemental analyzer (Flash 2000, Thermo Fisher) and inductively coupled plasma atomic emission spectrometer (Optima 7300DV, Varian).

FT-IR and FE-SEM Analysis

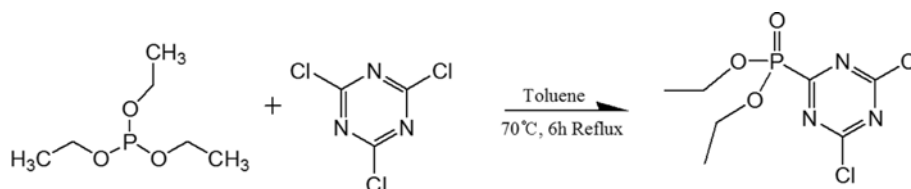
FT-TR (ATR 300E, JASCO) analysis was performed using KBr pellet to observe the molecular changes in cotton fabrics before and treatment. In addition, FE-SEM (JSM 6500F, JOEL) was used to observe the surface microstructure of the FR cotton.

Thermogravimetric Analysis

To confirm the thermal behavior of flame-retardant cotton fabrics, the weight loss rate were measured from room temperature to 600 °C with a thermogravimetric analyzer (TGA Q500, TA Instruments) at a heating rate of 20 °C /min. Also, to evaluate the contribution of the flame retardant to the residual char formation of cotton, the residue number (Nr) was calculated from the following equation:

$$\text{Residue number } (N_r) = \left(\frac{R_r}{F}\right) / R_u$$

where R_r and R_u represent the weight percentages of the residual carbonaceous char of the treated and untreated fabrics after pyrolysis respectively and F is the weight fraction of the cotton in the treated fabrics.



Scheme 1. Synthesis of DCTP by Michaelis-Arbuzov rearrangement.

Microscale Combustion Calorimetry (MCC)

The flammability was assessed using a Pyrolysis-Combustion Flow Calorimeter (PCFC, Fire Testing Technology Ltd). The heating rate was 1 °C/sec, the pyrolysis temperature range 75-750 °C and the combustion temperature 900 °C. The flow was 100 cm³/min at a O₂/N₂ mixture of 20/80 and the sample weight 6±0.5 mg. The peak heat release temperature and the maximum specific heat release rate (Peak HRR) as well as the total heat release (THR) were derived from the calorimetric measurements, which was repeated three times.

LOI and Synergistic Effectiveness

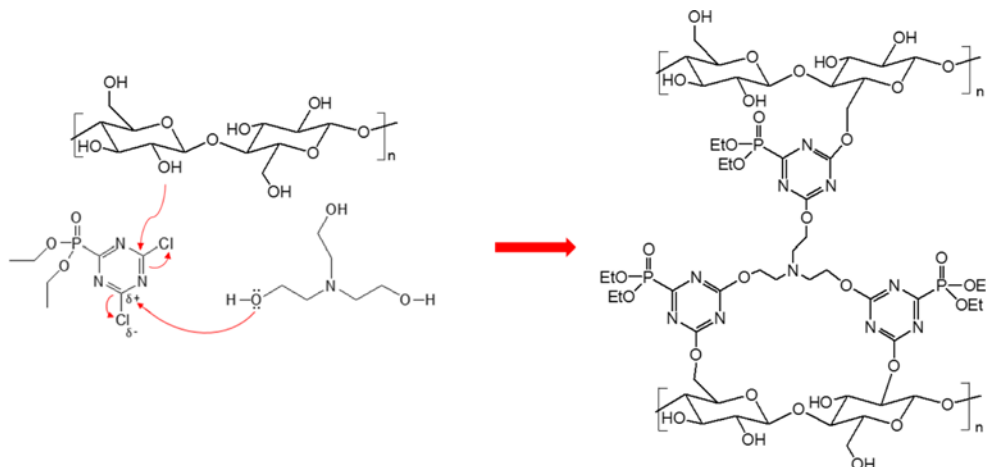
Using a limiting oxygen detector (Yasuda Seiki Seisakusho, Japan), the flame retardant property of the treated cotton fabrics was evaluated quantitatively by limiting oxygen index (LOI), which is the minimum oxygen volume ratio required for fiber samples to sustain combustion in accordance with ISO 4589: 2000. Flame retarding effectivity (EFF) is the increment in LOI for 1 % P element in the FR cotton. Synergistic effectiveness (SE) is the ratio of the measured LOI of the treated fabric with FR mixture (FR+A) to the LOI sum of the cotton fabrics finished with each component (FR or A) in the formulation according to the following equation [5]:

$$SE = \frac{[LOI(F+FR+A) - LOI(F)]}{[LOI(F+FR) - LOI(F)] + [LOI(F+A) - LOI(F)]}$$

where LOI(F) is the LOI of the fiber alone, LOI(F+FR), LOI(F+A) and LOI(F+FR+A) are the LOIs of the fabrics treated with flame retardant (FR), the additive (A), and both the flame retardant and additive, respectively.

Laundering Durability Test

The laundering durability of the FR cotton fabrics was evaluated by AATCC test method 61-2006 2A using a Launder-O-meter (Daelim, Korea).



Scheme 2. Proposed crosslinking mechanism of DCTP with TEA.

Results and Discussion

Effect of TEA Addition on the FR-Treatment with DCTP

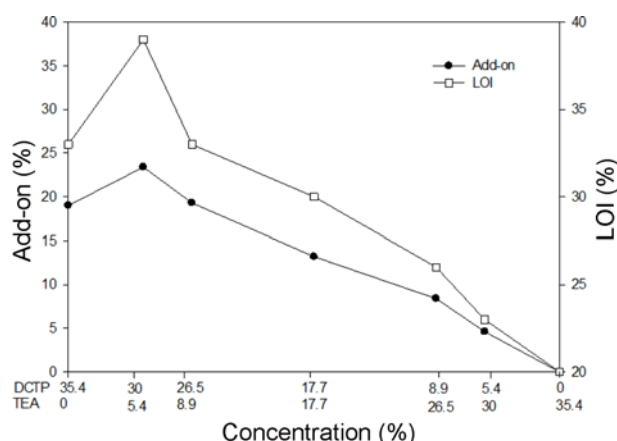
Dichlorotriazinyl group of DCTP can react with two hydroxyl groups of cellulose via alkali-catalyzed nucleophilic substitution, which can yield covalently-linked cellulose with the DCTP containing a phosphonate moiety. Preliminary study showed that the DCTP treatment was most effective at 30 % (w/w) DCTP concentration, producing a LOI of 29 with an add-on of 19.1 %, which levelled off above the application level. However it showed very limited laundering durability showing a LOI of 22 after ten laundering cycles (LC), which is not suitable for durable flame-retardant finishing. In order to improve the laundering durability, one mole of the added TEA with a functionality of 3 can react with three moles of DCTPs by the nucleophilic substitution reactions as shown in Scheme 2. Therefore the TEA is expected to enhance the washing resistance of the FR-cotton fabrics by incorporating the Y-shaped crosslinks of the DCTPs which linked to cotton celluloses.

The effect of TEA addition in the DCTP treatment was shown in Table 1. With increasing TEA addition, the add-on increased up to a molar ratio of 0.5 to DCTP with higher LOI reaching as much as 40, which was enough to claim self-extinguishing property of the finished cotton fabrics. The effect of the molar ratio of TEA to DCTP shows that the add-on and LOI levelled off above the molar ratio of 0.33. Also the P content of the finished cotton increased substantially from 2.9 % to 5.2 % as well as the N content from 3.7 % to 8.1 % upon TEA addition. Accordingly the flame retarding effectivity (EFF) also increased from 3.1 to 3.8 with increasing TEA, indicating the synergistic FR effect of the DCTP and TEA system. The synergistic effectiveness (SE) increased up to 2.2 meaning that a synergy occurred, which is more synergistic compared with the Pyrovatex and trimethylol melamine system with a SE of 1.75 [19].

The synergistic performance of the FR finish was

Table 1. EA and ICP data of FR-finished fabrics

Fabric	Molar ratio	Add-on (%)	P (%)	N (%)	N+P (%)	LOI	EFF	SE
Cotton	-	-	-	-	-	20	-	-
D30+T0	0.00	19.1	2.9	3.7	6.6	29	3.1	-
D30+T3.1	0.20	22.6	3.2	4.1	7.3	31	3.4	1.2
D30+T3.9	0.25	23.5	4.3	7.3	11.6	36	3.7	1.8
D30+T5.4	0.33	25.5	5.0	7.4	12.4	39	3.8	2.1
D30+T7.8	0.50	26.1	5.2	8.1	13.3	40	3.8	2.2
D30+T5.4+ECH9	0.33	30.8	5.4	8.4	13.8	39	3.5	-

**Figure 1.** Effect of DCTP and TEA concentrations on add-on and LOI.

investigated in depth as shown by Figure 1. While the FR treatment of cotton with 35.4 % DCTP alone gave a LOI of 33 with an add-on of 19.5 %, the TEA treatment alone did not show any improvement in add-on and LOI. All the mixtures of DCTP and TEA produced some synergy compared with the expected values by simple addition. Particularly the synergy increase was most pronounced in the mixture of 30 % DCTP and 5.4 % TEA, corresponding 3: 1 mole ratio of DCTP to TEA. The crosslinking of DCTP seemed to be most efficient at the mole ratio of 0.33 or more because one TEA can connect three DCTPs as suggested in Scheme 2. However the higher TEA concentration above 0.33 may increase the DCTP crosslinking but with lower degree of reaction with cellulose as expected from the fixed numbers of the dichlorotriazinyl groups. While the FR

performance of 30 % DCTP-treated cotton reduced significantly to LOI 22 with the decreased add-on by 89 % after ten laundering cycles (Table 2), the TEA incorporation imparted higher resistance against the repeated washing as shown by higher add-on and LOI after the ten laundering cycles (LC) probably resulting from the persistence of the DCTP crosslinks. Also the EFF of the treated cotton with both DCTP and TEA system was also higher compared with the DCTP treatment alone due to the larger amount of the remaining P and N contents after the ten LC.

Effect of ECH Crosslinking on the Durability of the FR Cotton

The laundering durability of the FR fabrics can be improved by the post-treatment of epichlorohydrin (ECH) as a cellulose crosslinker after the DCTP and TEA treatment. The ECH is known to form crosslinks between cellulose molecules: the diepoxide react with the hydroxyl groups in cellulose and the unreacted TEA by alkali-catalyzed nucleophilic reaction. The ECH after-treatment can retain the FR performance after ten laundering cycles as indicated by lower decreases of add-on and LOI. Even after fifteen laundering cycles, the FR-cotton showed superior resistance to the washing exhibiting a LOI of 28 with an add-on of 12.5 %, implying that the cellulose crosslinking was effective in increasing the laundering durability of the FR cotton with DCTP and TEA up to fifteen laundering cycles. However the excessive ECH treatment has some detrimental influences on mechanical strength of the crosslinked FR-cotton.

IR and SEM Analyses

Infrared spectroscopy were used to verify the reactions of

Table 2. EA and ICP data of FR-Finished fabrics after 10 laundering cycles

Fabric	Add-on (%)	P (%)	N (%)	N+P (%)	LOI	EFF	SE
D30+T0	2.1	1.0	2.4	3.4	22	2.0	-
D30+T5.4	12.5	2.6	5.8	8.4	28	3.1	4.0
D30+T5.4+ECH9	17.5	3.7	5.6	9.3	31	3.0	-
D30+T5.4+ECH9*	12.5	2.8	3.4	6.2	28	2.9	-

*Indicates the data obtained after 15 laundering cycles.

the DCTP and TEA in the FR-finished cotton as shown in Figure 2. The DCTP shows the stretching peaks of C=N and P=O appeared at 1574 cm^{-1} and 1250 cm^{-1} respectively and P-O-C vibration located at 1035 cm^{-1} and 948 cm^{-1} with C-

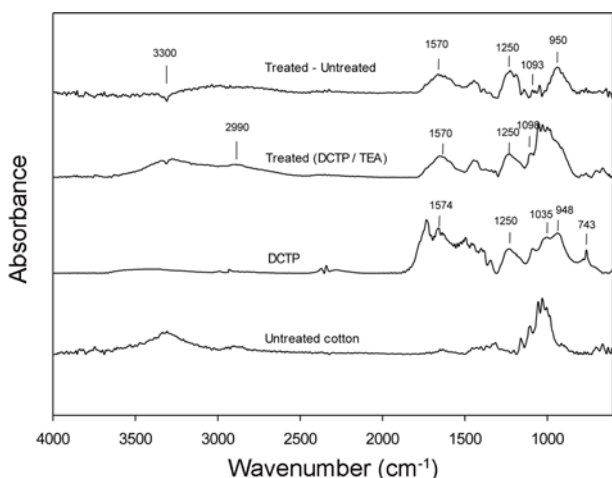


Figure 2. Infrared spectra of FR-Finished fabrics.

Table 3. TGA data of FR-finished fabrics

Treatment	DTGA peak ($^{\circ}\text{C}$)	Char yield at 600°C (%)	F	N_r
Cotton	375	8.5	1.00	1.00
D30+T0	323	30.1	0.90	3.93
D30+T5.4	286	40.6	0.82	5.86
D30+T5.4+ECH9	353	43.0	0.76	6.67

Cl at 743 cm^{-1} . The nucleophilic substitution of DCTP after the steam curing can be proved by the disappearance of the C-Cl and the O-H peaks with the intact phosphonate group.

As shown in Figure 3(b or c), the SEM images of the FR-finished cotton fabrics with DCTP or DCTP/TEA system appeared similar surface structures with negligible coating layers to that of untreated cotton (a), indicating that the substitution and crosslinking reactions occurred mainly at the fiber interior rather than on the fiber surface. However, with ECH post-treatment, some coated layers of the FR cotton (d) can be found not only on the fiber surfaces but also between the fibers as interfiber bonding.

Pyrolysis Behavior of FR-Finished Cotton

The thermal behavior of the FR-finished fabrics was investigated by thermogravimetric analysis, which was shown in Figure 4 and Table 3. While maximum pyrolysis temperature occurred at 375°C for untreated cotton, the temperatures were reduced to 323°C or 286°C for the finished fabrics with either 30 % DCTP or 30 % DCTP+5.4 % TEA respectively. The maximum pyrolysis rates of cotton fabrics were significantly decreased with the increased residual char contents at 600°C . The amount of residual char of the FR-finished fabrics with either 30 % DCTP or 30 % DCTP and 5.4 % TEA increased to 30.1 % or 40.6 %, respectively compared with 8.5 % for the untreated cotton. Therefore, it can be said that the FR finishing promotes the dehydration or crosslinking reaction of the cellulose during pyrolysis, thereby reducing the amount of combustible materials and reducing the overall exothermic reactions. The residue numbers (N_r) were calculated to verify the flame retarding mechanism of the FR-finished

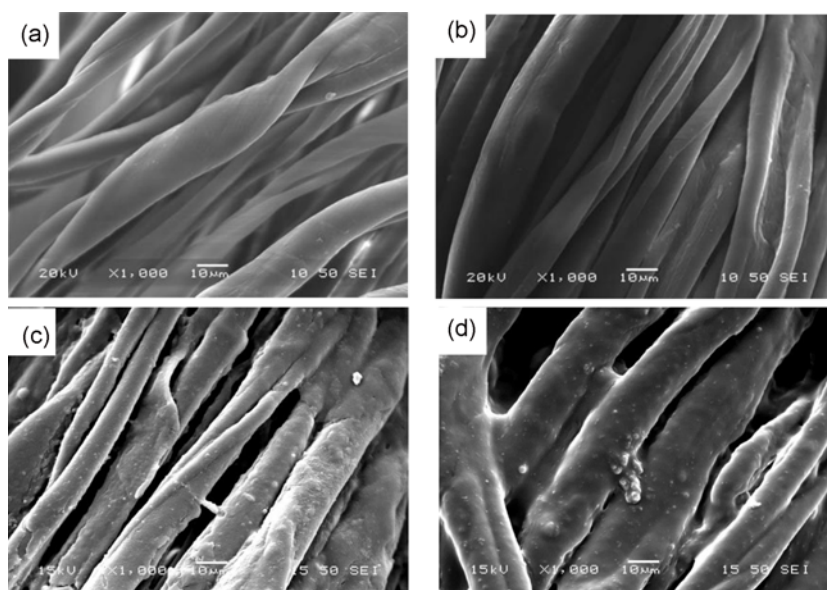


Figure 3. SEM images of FR-finished fabrics; (a) untreated, (b) DCTP 30 %, (c) DCTP 30 %+TEA 5.4 %, and (d) DCTP 30 %+TEA 5.4 %+ECH 9 %.

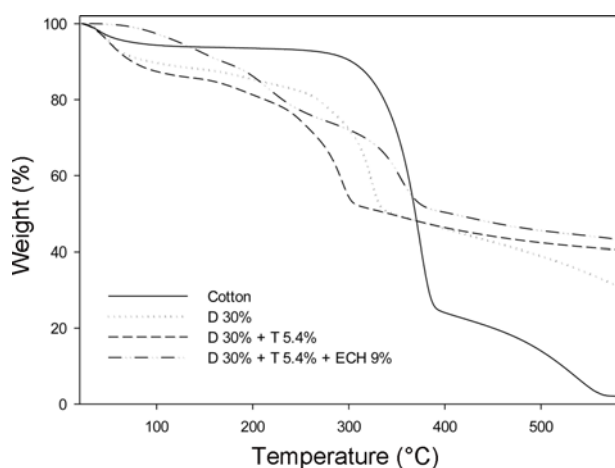


Figure 4. TGA thermodiagrams of FR-finished fabrics.

cotton (Table 3). The Nr of the FR cotton increased to 5.9 indicating nearly six-fold improvement of the flame resistance. The ECH post-treatment did increase the char yield and the residue number further to 43.0 % and 6.7, respectively. The phosphorus and nitrogen network may change the pyrolytic path of cellulose via dehydration and cross-linking. Therefore, a condensed phase mechanism can be considered for the flame retarding process, thereby reducing the overall combustion enthalpy required for the fire propagation.

Combustion Behavior of FR-Finished Fabrics

The flammability of the FR-finished fabrics was evaluated through micro-calorimetry as shown in Figure 5. The peak heat release temperature, peak heat release rate (peak HRR), and total heat release (THR) are given in Table 4. The maximum heat release of cotton occurred at 382.1 °C with HRR of 246.7 W/g resulting in THR of 12.1 kJ/g. The finished cotton fabrics with 30 % DCTP and 30 % DCTP+5.4 % TEA exhibited peak pyrolysis at 332.3 °C and 307.3 °C, respectively. The maximum HRR and THR of the FR cotton with 30 % DCTP+5.4 % TEA substantially reduced by 85 % and 83 % respectively compared with those of the untreated fabric. Char residue also increased from 2.4 % for cotton to 48.1 % for the FR-cotton treated with 30 % DCTP+5.4 % TEA. The lower emission of flammable materials and increased formation of carbonaceous char during burning can reduce overall combustion enthalpy required for fire propagation. The DCTP and TEA treatment can efficiently suppress the combustion by reducing heat release rate at earlier thermal decomposition by solid phase mechanism. In addition, the ECH crosslinking treatment for higher laundering durability did not influence the burning behavior significantly as indicated by marginal increases in THR and char residue.

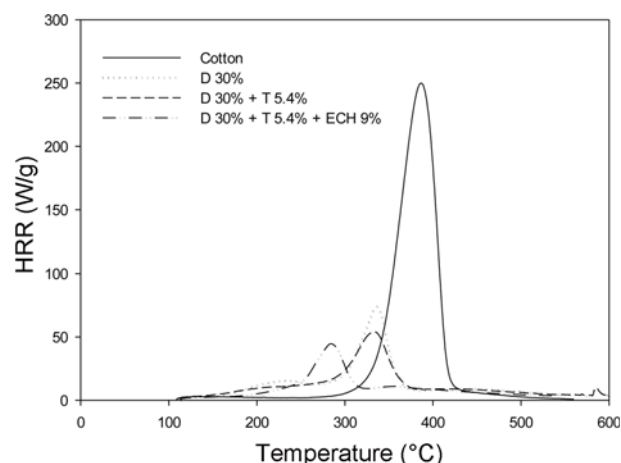


Figure 5. HRR curves of the FR-finished fabrics.

Table 4. MCC data of FR-finished fabrics

Treatment	Peak HR temperature (°C)	Peak HRR (W/g)	THR (kJ/g)	Char residue (%)
Cotton	382.1	246.7	12.1	2.4
D30+T0	332.3	63.7	5.0	40.3
D30+T5.4	307.3	37.5	2.1	48.1
D30+T5.4+ECH9	293.3	37.3	2.7	51.1

Conclusion

The TEA crosslinking of DCTP during steam curing increased the laundering washability of the FR cotton up to ten LC, while the epichlorohydrin (ECH) crosslinking of the FR cotton prolonged the washing performance up to fifteen LC, which potentially extended the durability of the self-extinguishable cotton by the formaldehyde-free DCTP finishing. The TEA and ECH can crosslink DCTP and cellulose via nucleophilic substitution and addition reactions respectively producing the highly crosslinked networks of DCTP and cellulose, which enable to withstand the repeated laundering conditions. The cotton fabric, impregnated with 5.4 wt% TEA in 10 % Na₂CO₃ solution, was optimally steam-cured at 120 °C for 10 minutes after the successive padding of 30 wt% DCTP, resulting in the synergistically enhanced flame-retarding performance up to a LOI of 39 with a SE of 2.1. Also the laundering durability of FR cotton can be significantly improved by the treatment after a padding of 9 wt% epichlorohydrin and 15 wt% Na₂CO₃ and subsequent curing at 120 °C for 3 minutes. The FR cotton fabrics decomposed at lower pyrolysis and combustion temperatures with decreased peak pyrolysis and heat release rates yielding higher contents of carbonaceous chars, suggesting a solid-phase flame-retarding mechanism.

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