

Durable Flame Retardant Finishing of PET/Cotton Blends Using a Novel PVA-Based Phosphorus-Nitrogen Polymer

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ABSTRACT: A novel polymeric flame retardant (FR) with phosphorous-nitrogen pendent groups (PVP-P-DCA) was synthesized by polyvinyl alcohol (PVA), phosphoric acid, and dicyandiamide (DCA). Its structure was characterized by FTIR, ¹H, ¹³C, ³¹P NMR, elemental analysis and TG. Poly(ethylene terephthalate) (PET)/cotton blends (T/C) was treated via pad-dry-cure process with PVP-P-DCA. The surface of FR-T/C was characterized by FTIR and SEM. The fabric performance was examined by whiteness and tensile property. The fire behavior was performed by

limited oxygen index (LOI), vertical burning test, cone calorimetry test. The durability effect, thermal stability, and flame retardancy mechanism of the treated T/C were investigated by TGA, FTIR, and SEM. The results show that PVP-P-DCA is not only an effective FR but also a good char-forming agent for the T/C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 342–353, 2011

Key words: blends; flame retardant; synthesis; finishing; synergism

INTRODUCTION

Because of having many good combination properties, the natural–synthetic fiber blends are more popular than pure natural or synthetic products. It is often possible to obtain a maximum wearing property by compensating the defects of one fiber by using another different fiber. Poly(ethylene terephthalate) (PET)/cotton blends (T/C) is just widely used as clothing and textile materials because of high strength, excellent wearing resistance, good hygroscopicity, and high air permeability.¹ In the blends, PET belongs to the category of highly flammable polymer which releases a large amount of heat when burning, and the charring residue of the cellulose component in thermolysis forms the skeleton which retains drops of the thermoplastic PET melt in the flame zone, it is well known “scaffolding effect” that creates favorable conditions for burning.²

For high inflammability and high burning rate brought by “scaffolding effect,” imparting flame retardancy to blends is a complex, essential, and crucial problem.

Up to now, many durable FRs and permanent-type FR finishing methods for T/C had been reported. For example, tetrakis-(hydroxymethyl) phosphonium chloride (THPC), tris(1-aziridinyl) phosphine oxide/sulfide, tris(2,3-dibromopropyl)phosphate, dichlorotribromophenyl phosphate, and tetrabromobisphenol-A/epichlorohydrin were all good flame retardant for T/C.^{3–7} But they were withdrawn from the market due to their strong toxicity, mutagenicity, and carcinogenicity.⁸ The phosphorus-nitrogen (P-N) FR systems, Fyrol 76, Fyroltex HP, Pyrovatex CP New, and Proban showed a good N-P synergism for T/C,^{9–12} however, these finishing methods brought a formaldehyde-released problem.¹³

Considering the flame retardancy, the durability, and the ecological-friendly processing, it is essential to find a phosphorous- and/or nitrogen-containing FR system instead of halogen-based FRs or antimony (III) oxide FRs. Besides this, it is also necessary to avoid using N/P-CH₂OH(R)-type FRs or crosslinkers, which can release formaldehyde during wearing. Our group had investigated a series of organophosphorus FRs for PET or T/C.^{14–17} Among them, a hydroxyl-functional organophosphorus FR, DHDBP, was a good FR for T/C, however, it was not yet used in practice due to bad hand-feeling and lack of ideal durability.¹⁷

Additional Supporting Information may be found in the online version of this article.

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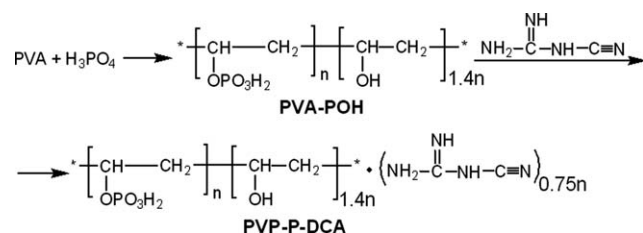


Figure 1 The synthetic route of PVP-P-DCA.

In this work, a novel PVA-based P-N polymer FR (PVP-P-DCA) was synthesized using polyvinyl alcohol (PVA), H₃PO₄, and dicyandiamide (DCA) as raw materials (Fig. 1). PVA was chosen because it was a good charring agent and had compatibility with cellulose. Beside this, orthophosphate was the best acid source,¹⁸ and DCA was a good blowing-agent in the intumescent FR system.^{19–21} As we know, if N and P elements were introduced simultaneously into the FR it can enhance the flame retardancy due to N-P synergism effect.²² Therefore, it was expected that the usage of PVA-based P-N polymer FR can endow the blends flame retardancy, durability, and good hand feeling. The PVA-based P-N polymer PVP-P-DCA was characterized by FTIR, NMR, and elemental analysis. T/C was treated via pad-dry-cure finishing and its surface was characterized by FTIR and SEM. The fire behavior of the FR T/C was studied by limited oxygen index (LOI), vertical burning test, and cone calorimetry tests. The durability effect, thermal stability, and flame retardancy mechanism were also investigated by TGA, FTIR, and SEM.

EXPERIMENTAL

Materials

The fabric used were PET/cotton blends (70 : 30 blends ratio, 190 g m⁻², twill), purchased from Sichuan Cotton Printing and Dyeing (Sichuan, China). Polyvinyl alcohol (PVA 1799) was obtained from Yunnan Yunwei (Yunnan, China). Phosphoric acid (H₃PO₄), ethanol, urea, dicyandiamide (DCA) were purchased from Kelong (Chengdu, China) and were used without purification. Used H₂O was distilled water.

Synthesis and characterization of PVP-P-DCA

PVA 1799 (50 g) and 200 mL distilled water were added into a 2-L glass flask, equipped with a stirrer, thermometer, and condenser. The mixture was stirred for 30 min. Then 100 mL H₃PO₄ (85%) was added and stirred for 30 min. When PVA was fully wetted, the mixture was stirred and heated gradually to 70°C in 30 min. While it turned to colorless transparent solution, 2 g urea was added

as a catalyst and reacted at 100°C for 120 min. The mixture added slowly into 500 mL ethanol and precipitated. Through filtrating, dissolving-precipitating for three times, and drying, the white or yellow product PVA phosphate (PVA-POH) was obtained.²³ Yield: 78%.

PVA-POH (40 g) and 50 mL distilled water were added into a 500-mL three-neck flask, equipped with a stirrer, thermometer, and condenser. The mixture was stirred for 15 min; the mixture was stirred and heated gradually to 70°C in 30 min. While it turned to transparent solution, DCA 18.0 g (0.21 mol) was added and the mixture was reacted under 100°C for 90 min until a milky white liquid was obtained. After cooled, the mixture was slowly added into 150 mL ethanol and precipitated. After dissolving-precipitating three times, the product was extracted with ethanol for 24 h in Soxhlet extractor. After drying in vacuum at 60°C for 24 h, the white product PVA-based phosphorus-nitrogen FR (PVP-P-DCA) was obtained. Yield: 85%.

The FTIR spectra of PVP-P-DCA were conducted with an FTIR spectrophotometer (Nicolet 6700, Thermo Nicolet, Waltham, MA) with a potassium bromide pellet technique. And the ¹H, ¹³C, and ³¹P NMR spectra were obtained on an NMR spectrophotometer (Varian INOVA-400, Varian, Palo Alto, CA) with hexadeuterated dimethyl sulfoxide as a solvent. The elemental composition (C and H contents) of PVP-P-DCA were analyzed by a Carlo Erba 1106 CHN elemental analyzer (Rodano, Italy). The phosphorus content (P%) of PVP-P-DCA was measured by an Optima 7300DV inductive coupled plasma emission spectrometer (PerkinElmer, Waltham, MA).

Fabric finishing and washing procedures

The different FR bath was prepared with different concentration of PVP-P-DCA and urea in distilled water at 70°C and then cooled to room temperature. pH value of the FR bath was controlled with 0.1 mol L⁻¹ H₃PO₄ or 1 mol L⁻¹ NH₃·H₂O. Twill T/C (70/30) blends were immersed in the bath (bath ratio 1 : 20) to give an ~ 100% pick-up regulated by padding. After double-dip-double-nip, fabric samples were dried at 90°C for 5 min, and then were cured at 110°C for 3 min. The treated fabric were washed at 40°C with 0.5% (w/w) sodium carbonate solution for 5 min, and finally dried at 90°C. The add-on (%) of FR was calculated from the following equation:

$$\text{add-on\%} = (w_t - w_o) / w_t \times 100\% \quad (1)$$

In Eq. (1), w_o and w_t represent the weight of T/C before and after FR finishing, respectively.

Determination of phosphorus content of the treated fabric

Approximately 3.0 g treated T/C fabric sample taken from three different parts of a specimen was cut into pieces. Then 20 mL concentrated HNO₃ was gradually added into Kjeldahl flask in which contained 0.2–0.3 g T/C pieces (accurate to 0.1 mg). The mixture was heated carefully until the yellow smoke cleared away and then was cooled slightly. About 10 mL HClO₄ was added to the mixture. The reaction mixture was then heated to 100°C to digest the pieces and to evaporate the water until 2–3 mL clear residual liquid obtained. Subsequently, the solution was fully transferred to a 100 mL flask, and was diluted to scale by the deionized water. The obtained sample was analyzed by Phospho-molybdenum Yellow Spectrophotometry method (ISO 3696-1987) to determine the phosphorus content (P%).

Determination of whiteness

Whiteness denotes the reflecting rate under the wavelength 466 nm. Whiteness determination was performed on SBDY-1 digital whiteness instrument (Shanghai Ruifeng, Shanghai, China) which was corrected with MgO standard white board (GSBA 67001), according to ISO105-J02-1997. The samples were four circular fabric pieces (6 cm diameter) overlapped together and measured one layer by layer. The whiteness of fabric was the average value of four data.

Determination of tensile property

Tensile property of fabric was measured on YG 026 type electronic textile strength machine (Nantong Sansi, Jiangsu, China) according to ISO 13934.1 94, strip width 50 mm, initial length 100 mm, pretension 2N, tensile rate 100 mm min⁻¹.

Evaluation of the flame retardancy of the finished fabric

The vertical burning test, including after-flame time, after-glow time, and char length was conducted on a CZF-2 type instrument (Jiangning Analysis Instruments Factory, Nanjing, China), according to ASTM D 6413-99. The LOI values of the samples were measured on the Oxygen Index Flammability Gauge (HC-2C, Nanjing Shangyuan Analytical Instruments, Nanjing, China) according to ASTM D 2863-97.

Thermal analysis

TGA, derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC) of PVP-P-DCA, treated, and untreated fabric were performed on

Synchronization Thermal Analysis STA 449C (Netzsch, Selb, German) at a heating rate 10°C min⁻¹. Aluminum sample pans were used. Samples (7.5 mg) were heated in the analyzer at temperatures ranging from 40 to 590°C under N₂ at a flow rate of 45 mL min⁻¹.

Measurement of surface morphology

The surface morphology of untreated and treated T/C fabric before and after washing were investigated by SEM (XL30 ESEM-TMP, Philips-FEI, Eindhoven, Netherlands) at 10 kV. The residues of untreated and treated T/C fabric obtained from the fabric after combustion were also investigated by SEM. All samples were coated with gold prior to examination.

RESULTS AND DISCUSSION

Synthesis and characterization of PVP-P-DCA

PVP-P-DCA was prepared via the reactions of PVA, phosphoric acid and DCA (Fig. 1). The hydroxyl groups of PVA were esterified with an orthophosphate at 90–110°C to form acidic mono-substituted phosphate (PVA-POH). Then the salt was formed when the acidic PVA-POH reacted with the alkaline DCA in water. The white FR PVP-P-DCA was obtained with the yield of 85.4%.

The FTIR spectrum of PVP-P-DCA was shown in Figure 2. The –OH and –NH₂ stretching vibrations appeared around 3415 and 3303 cm⁻¹, respectively. The wavelengths of 2913 and 2855 cm⁻¹ were CH₂ stretching vibration. The C≡N stretching vibration was found at 2278 cm⁻¹. Usually, the peak of –CN was sharp, however, in this study it was weak and red shifted due to the electron effect of –NH³⁺ groups which was preferred to react with the proton of PVA-POH forming salt. It was reported that the basicity order of the alkaline groups in dicyandiamide molecule is NH₂– > HN=C > –NH– > –C≡N.^{24,25} Therefore, due to the lowest basicity, –CN group would not react with PVA-POH to form salt. Only NH₂– or HN=C groups could react with PVA-POH. The wavelengths 1585 and 3191 cm⁻¹ were C=NH₂⁺ and NH₃⁺ stretching vibrations. 1689 and 1461 cm⁻¹ wave-numbers were in-plane bend vibrations of NH₂ and CH₂, respectively. P=O stretching vibration was found at 1233 cm⁻¹. The stretching vibration of C–O–P appeared at 1080 cm⁻¹. Besides this, the wavelength 951 cm⁻¹ was the characteristic absorption peak of P(V) –O.²⁶ The characteristic absorption peaks of ammonium appeared evidenced the salt-forming occurred.

In the ¹H NMR spectrum of PVP-P-DCA [Fig. 3(A)], the methylene and methine protons resonated at 1.3–1.5 (dd, *J* = 18.8 Hz, *J* = 20 Hz, 2H,

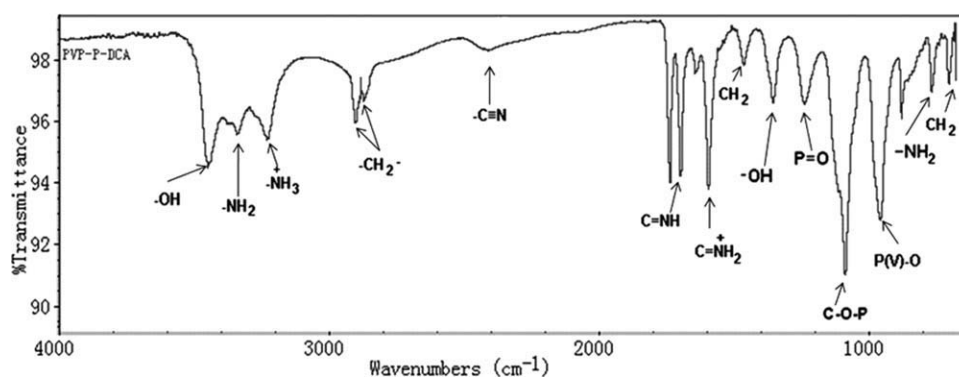


Figure 2 FTIR spectrum of PVP-P-DCA.

CH_2) and 3.8–3.9 (d, $J = 26.8$ Hz, 1H,CH), respectively. The OH chemical shift of PVP-P-DCA was found at 4.6 (s, br, 0.7H, $\text{CH}_2\text{-OH}$). The 7.1 ppm (s,1H, $-\text{NH}_2$) and 8.0 ppm (br, 0.6H, $-\text{NH}_3^+$) were assigned to NH_2 and NH_3^+ , respectively. From the ^{13}C NMR spectrum [Fig. 3(B)], we can find that the chemical shifts of carbon atom of methylene were at $\delta = 45.8\text{--}46.7$ ppm. $\delta = 64.3\text{--}68.5$ ppm assigned to methine carbon. It was noteworthy that the chemical shift of carbon atom of $\text{C}=\text{NH}$ and $\text{C}\equiv\text{N}$ were appeared at 99.8 and 156.7 ppm, respectively. Only one peak (0.32 ppm) was found in the ^{31}P NMR spectrum [Fig. 3(C)], indicated only single type phosphorus, i.e., CH-O-PO_3^{2-} , existed in PVP-P-DCA.

The values of elemental analysis (%) were shown as follows: C, 29.93%; H, 5.56%; N, 16.68% and P, 12.60%. The calculated value of O content was 35.23% ($\text{O}\% = 1\text{-C}\% \text{-H}\% \text{-P}\%$). From the results, atom ratio C : H : N : O : P was 6.3 : 13.6 : 3 : 5.4 : 1 which demonstrated that its chemical formula was $(\text{C}_2\text{H}_4\text{O})_{1.4}(\text{C}_2\text{H}_5\text{O}_4\text{P})_1(\text{C}_2\text{H}_4\text{N}_4)_{0.75}$ (shown in Fig. 1).

Thermal stability of PVP-P-DCA

TGA-DTG-DSC thermograms of PVP-P-DCA were showed in Figure 4 and the relevant thermal decomposition data were listed in Table I. From the curves, it can be seen that the degradation of PVP-P-DCA was divided into four stages. The first stage, which is also the main decomposition stage, appeared in 142–243°C. $T_{1\text{max}}$ was found at 194°C, and weight loss was 22.2%. The largest endothermic peak on DSC thermograms indicated that the decomposition of PVP-P-DCA can play a good endothermic role at beginning stage. The second decomposition stage was in 243–316°C. $T_{2\text{max}}$ was found at 289°C, and weight-loss was 21.9%. In the third stage 316–362°C, there is a small weight-loss process; however, it appeared a big endothermic peak on DSC curve. The fourth pyrolysis stage occurred above 362°C, in which $T_{4\text{max}}$ was 438°C, and weight-loss was 18.8% accompanied with three tiny endothermic peaks. At

last, the residue at 590°C was 22.8%. The results indicated that the degradation of PVP-P-DCA occurred via multi-stage, and appeared several endothermic pyrolysis stages, which may greatly enhance the concentration of incombustible gas.

Onset temperature (T_{on}) of PVP-P-DCA was 181.0°C shown in Table I. It is well known that T_{on} of effective FR must be close to or slightly lower than that of substrate polymer, namely, FR begins to decompose to play a flame-retarding role before substrate material pyrolysis. Moreover, the ideal FR acted on flame retardancy during the whole pyrolysis process of the matrix material. So PVP-P-DCA may be an efficient FR for T/C blends, because its T_{on} was lower than that of T/C blends, and its temperature range of decomposition was from 181 to 460°C similar with that of T/C blends.

Finishing process

The performance of fabric was greatly affected with the finishing condition. Therefore, the effect of the finishing bath pH values and the PVP-P-DCA concentration on the properties of treated T/C had been investigated and listed in Table II.

From Table II, we can see that under low pH value (Trial 1) the treated fabric had highest P% content and LOI value. However, the whiteness and mechanical property were reduced more than 50% compared with that of pure fabric due to the degradation of cellulose and PET under the acidic condition. While the pH value was fixed at 10 (Trial 2), the add-on, P%, whiteness, mechanical property and the flame retardancy of the fabric were all decreased. Therefore, neutral solution was the best pH value for flame retardancy finishing.

From Trials 3, 4, and 5, it can be seen that the add-ons of FR and phosphorus content (P%) were all obviously increased with the increase of PVP-P-DCA concentration. At the same time, the LOI values of the T/C fabric raised from 17 to 36. The results of vertical burning showed after-flame time

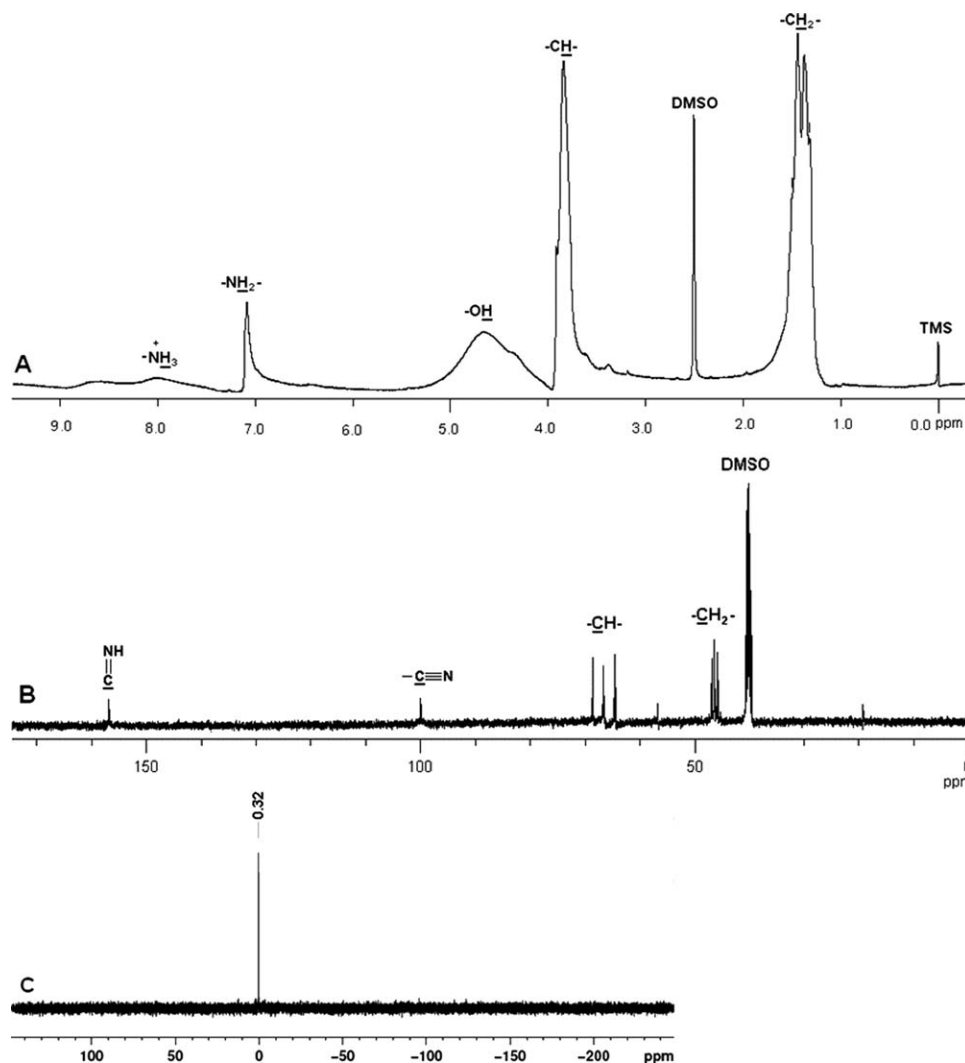


Figure 3 NMR spectra of PVP-P-DCA (A) ^1H NMR, (B) ^{13}C NMR, and (C) ^{31}P NMR.

(T_{flame}) were all less than 5 s, the maximum damage length (L_{damage}) were also less than 150 mm. When the fabric was treated by PVP-P-DCA, it did not show after-glow. But the whiteness and tensile property of the fabric was sharply deteriorated with the increase of FR concentration. Thus, the optimum concentration of FR for finishing was 200 g L^{-1} .

FTIR analysis of the finished blends

Infrared reflectance spectroscopy was an excellent analysis method to character the surface of fabric.²⁰ FTIR spectra of PVP-P-DCA, untreated and treated T/C samples were showed in Figure 5. Curve a was the characteristic absorption of PVP-P-DCA. In spectrum of virgin T/C fabric (Curve b), the major vibration absorptions peaks of PET and cotton (cellulose) can be found. For example, $3300\text{--}3600 \text{ cm}^{-1}$ was the stretching vibration of the hydroxyl groups of cellulose and PET. The stretching vibrations of CH_2 and

arC-H showed in $2860\text{--}3060 \text{ cm}^{-1}$. The stretching vibrations of C=O in arCOOC (arC is the aromatic carbon atom) at 1722 cm^{-1} and in arCOOH at 1710 cm^{-1} were very strong. The strong band at 1098 cm^{-1}

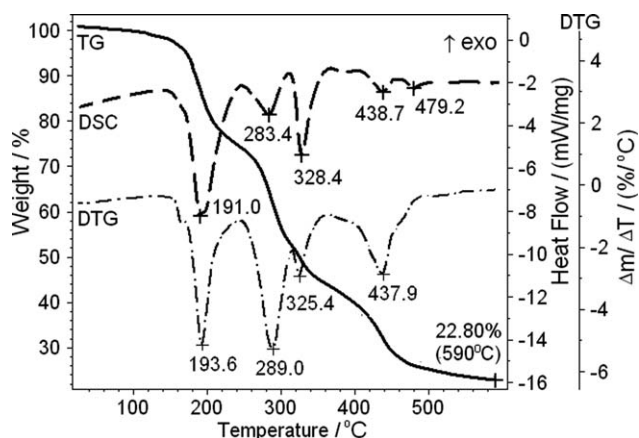


Figure 4 TGA-DTG-DSC thermograms of PVP-P-DCA.

TABLE I
Data from TGA and DTG Thermograms of PVA-POH, FR, T/C, and FR-T/C Fabrics

Samples	1st weight-loss stage				2nd weight-loss stage				Residue at 590°C (%)
	$T_{on} - T_{end}^a$ (°C)	T_{max}^b (°C)	W_{loss} (%)	R_{max}^c (%/min)	$T_{on} - T_{end}$ (°C)	T_{max} (°C)	W_{loss} (%)	R_{max} (%/min)	
PVA-POH	116–203	179	19.1	4.7	379–486	444	8.6	1.5	53.4
PVP-P-DCA ^d	181–243	194	19.5	4.8	243–316	289	21.9	5.1	22.8
T/C	301–384	359	25.9	7.2	338–448	430	49.1	11.3	24.8
FR-T/C	181–305	293	10.5	3.0	308–444	420	58.7	9.8	31.3

^a T_{on} denotes onset temperature; T_{end} denotes end temperature.

^b T_{max} denotes maximum weight-loss temperature.

^c R_{max} denotes maximum weight-loss rate.

^d The degradation of PVP-P-DCA appeared four stages, and the 1st and 2nd stages were the main decomposition stages which had been shown here.

was the stretching vibration of C—O—C in arCOOC.^{26,27} And 723 cm^{-1} was the bending vibration of CH_2 in PET. While the T/C treated with PVP-P-DCA (Curve c and d), the PVP-P-DCA characteristic absorptions peaks can be easily identified at $3415, 3303, 2278, 1689, 1585,$ and 1233 cm^{-1} , which corresponded to the stretching vibrations of OH, NH_2 , $\text{C}\equiv\text{N}$, $\text{C}=\text{NH}$, $\text{C}=\text{NH}_2^+$, and $\text{P}=\text{O}$, respectively. These bands indicated the phosphorus-nitrogen FR PVP-P-DCA had been fixed onto the surface of the blends by physical absorption.

SEM micrographs of FR-T/C

The SEM micrographs with different magnification of the treated fabric surface after washing once were shown in Figure 6. In Figure 6(A) ($100\times$), the surface of fabric was smooth and relatively neat which indicated that the adding of FR would not affect the hand feeling of fabric. From Figure 6(B) ($400\times$), it can be seen that FR was filled in between fibers. Under higher magnification [Fig. 6(C), $2000\times$] it was found that the surface of fabric became rough, and some granular species (free FR), was fixed onto the fiber by physical absorption. When the Figure 6(C)

was further magnified [Fig. 6(D), $20,000\times$], it was found that the surface of fiber was covered a laminar, uniform and compact FR. These results indicated that FRs had been attached onto fiber, which agreed with that of FTIR.

TGA of FR, virgin, and treated fabric

The TGA curves of the virgin T/C, treated T/C, and PVP-P-DCA were shown in Figure 7. The data determined from TGA curves were listed in Table I. The TGA curves of the virgin T/C and PVP-P-DCA showed that the decomposition temperature and rate of PVP-P-DCA was lower. The T_{on} and T_{max} of PVP-P-DCA were lower 120 and 160°C than those of virgin fabric, respectively. The mean weight-loss rate of FR ($R_{mean} = 2.57\%$) was a half of that of virgin T/C ($R_{mean} = 5.12\%$).

From Figure 7 and Table I, it can be seen that the T_{on} , T_{1max} , and T_{2max} of FR-T/C was lower 64 , 66 , and 10°C , respectively, than that of virgin fabric due to the decomposition of FR. The first weight-loss stage ($181\text{--}305^\circ\text{C}$) decomposed very gently, namely the total weight-loss was only 10.5% . And the maximum and mean rate of weight-loss was $3.6\%/min$

TABLE II
The Effect of Finishing Condition on Flame Retardancy and Properties of the Finished Fabrics

Trial	FR content (g L ⁻¹)	pH	Add-on (%)	P%	LOI (%)	Vertical burning test ^a			Whitness	Breaking intensity (N m ⁻¹)
						L_{damage} (mm)	T_{flame} (s)	T_{glow} (s)		
0	0	—	0	0	17.2 ± 0.1	TD ^b	NR ^c	NR	83.1 ± 3	$17,160 \pm 30$
1	200	4	19.75	2.17	31.5 ± 0.3	74 ± 3	1	0	48.4 ± 2	$13,560 \pm 40$
2	200	10	18.56	1.89	28.2 ± 0.4	139 ± 4	4	0	54.1 ± 3	$14,890 \pm 30$
3	200	7	19.48	2.09	30.4 ± 0.2	82 ± 5	2	0	62.5 ± 3	$16,120 \pm 20$
4	100	7	13.62	1.46	27.1 ± 0.3	144 ± 2	4	0	70.5 ± 2	$16,840 \pm 10$
5	300	7	23.55	2.52	36.2 ± 0.2	63 ± 4	0	0	50.9 ± 2	$15,350 \pm 30$

120°C curing 2 min, washing once.

^a L_{damage} denotes maximum damaged length; T_{flame} denotes after-flame time; T_{glow} denotes after-glow time.

^b TD denotes the case that fabrics were completely destroyed during the test.

^c NR denotes no record due to the complete destruction of the fabrics.

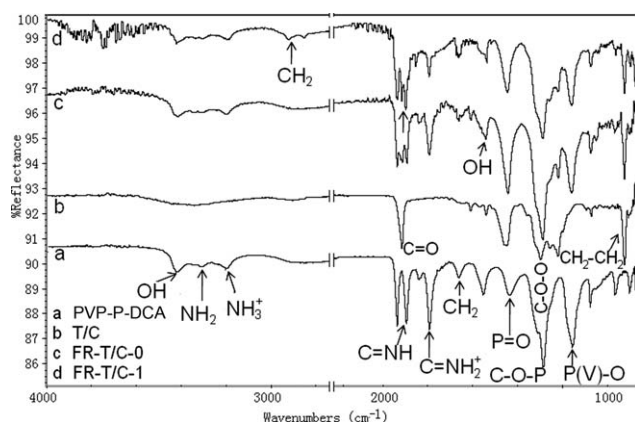


Figure 5 FTIR spectra of PVP-P-DCA (a), virgin T/C (b), FR T/C without washing (c), and FR T/C washing once (d).

and 0.9%/min, respectively. As far as virgin fabric was concerned, the total weight-loss at first stage reached 25.9%, and its maximum and average rate of weight-loss were 7.6%/min and 3.1%/min, respectively. During the second weight-loss stage of FR

finished fabric, the maximum and average rate of weight-loss decreased 1.6%/min and 4.3%/min compared to untreated fabric, respectively. Moreover, the carbon residue of FR-T/C increased 6.5% than that of virgin blends. So, the decrease of decomposition temperature and the increase of carbon residue indicated that the FR-T/C would be an effective flame retardant.²⁸

LOI and vertical burning tests

It is well known that only when the effective flame retardancy are successfully rendered to cotton component and/or PET component in blends the T/C blends can be successfully imparted fire-resistance due to the "scaffolding effect."² To evaluate FR properties of the finished blends, LOI and vertical burning test were used, and the data were given in Table II. The LOI values of the treated T/C increased with FR concentration. The LOI was 36.2 when FR content was 300 g L⁻¹ under pH = 7 after washing once, and the vertical burning test showed

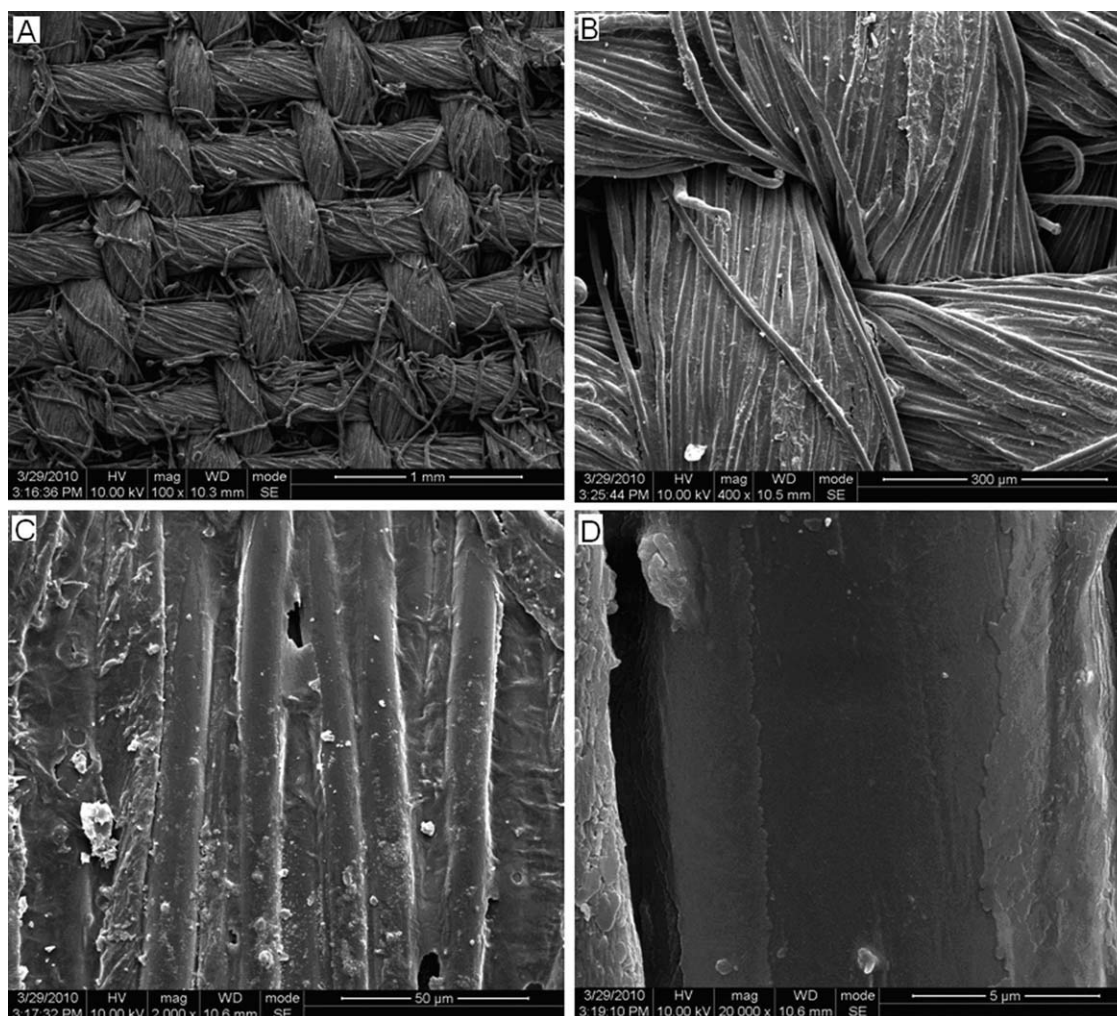


Figure 6 SEM micrographs of surface of FR-T/C fabric after washing once, (A) $\times 100$, (B) $\times 400$, (C) $\times 2000$, and (D) $\times 20,000$.

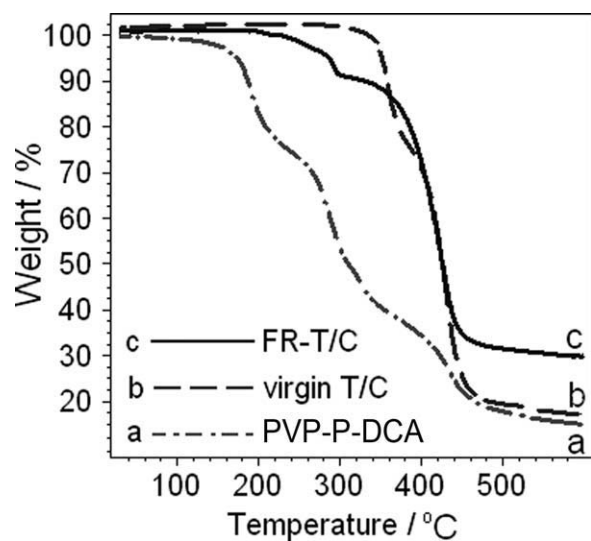


Figure 7 TGA thermographs of PVP-P-DCA (a), virgin T/C (b) and FR-T/C (c) in N_2 at heating rate of $10^\circ C \text{ min}^{-1}$.

that FR-T/C sample was promptly self-extinguished after igniting. And the maximum damaged length (L_{damage}) was only 63 mm (Table II Trial 5).

The digital photographs of FR T/C during/after the vertical burning test under the optimum conditions were showed in Figure 8. From Image A, only surface combustion can be found and the fabric was deeply carbonized rather than burned off completely. From Figure 8(B,B'), it can be seen that the fabric residue retained origin morphology of fabric in which it had no cracks and curling. The excellent charring effect of FR T/C can help imparting good flame-blocked effect, which was agreed with the TGA results.

Cone calorimetry test

Cone calorimetry test is an actual and comprehensive evaluation technique for the combustion performances of polymer materials.^{29,30} Fire hazard of materials can be evaluated by cone calorimetry data such as fire-growth degree including time to ignition (TTI) and time to flameout (TTF), the heat-hazard index including heat release rate (HRR) and total heat release (THR), toxicity-risk index including carbon monoxide production (COP) and carbon dioxide production (CO_2P). The cone calorimetry curves of FR-T/C and virgin T/C blends were shown in Figure 9 and the detailed data were listed in Table III.

From Table III it can be seen that the TTI of FR-T/C was shorter and TTF was longer than that of virgin T/C blends. This can be ascribed to fact that the FR PVP-P-DCA was decomposed before T/C blends and released some flammable gases. Simultaneously, FR played a flame-retarding role to lower the onset temperature of the blends which also made it release

some flammable gases. The heat release rate (HRR) and total heat release (THR) of FR-T/C were reduced greatly [Fig. 9(A,B)]. The HRR decreased steadily in the HRR curve of FR-T/C. The peak-HRR and THR decreased 55 and 28.8% compared with that of virgin T/C, respectively, which illustrated that the risk of heat release was greatly reduced. From Figure 9(C,D), the CO_2P curve was similar to HRR, and the total CO_2P of FR-T/C was reduced 28.8% than that of virgin T/C. The COP curve showed a letter "U" shape, which indicated that at the burning beginning and ending FR-T/C was incomplete combustion due to the char-layer covering effect. But COP of virgin T/C was increased gradually like wave-shape. The curves of CO_2P and COP of FR-fabric were different from those of virgin fabric indicated that FR greatly changed the combustion mechanism of the fabric. The results indicated that both the heat-hazard and the fire hazard were decreased. The MLR of FR-T/C was slower than that of virgin fabric and the mean-MLR decreased by about 40%. After the flameout, the char residue of FR-T/C was enhanced more than three times (shown in Table III) which correlated well with TGA data.

The digital photographs of fabric char residue after cone calorimeter test were showed in Figure 10. It can be seen from Figure 10(A), the char residue of FR-T/C maintained original morphology except for slight crimping and shrinking, but the residue of virgin T/C was like a pile of dried-cracked clay. This can be ascribed to the fact that PET component

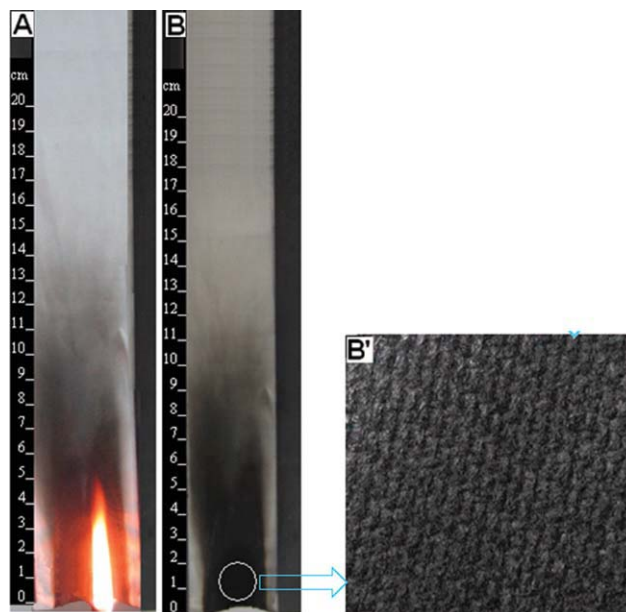


Figure 8 The digital photographs of FR T/C during/after the vertical burning test, ignited at 11s (A), after burning (B), and the fiber residue (B'). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

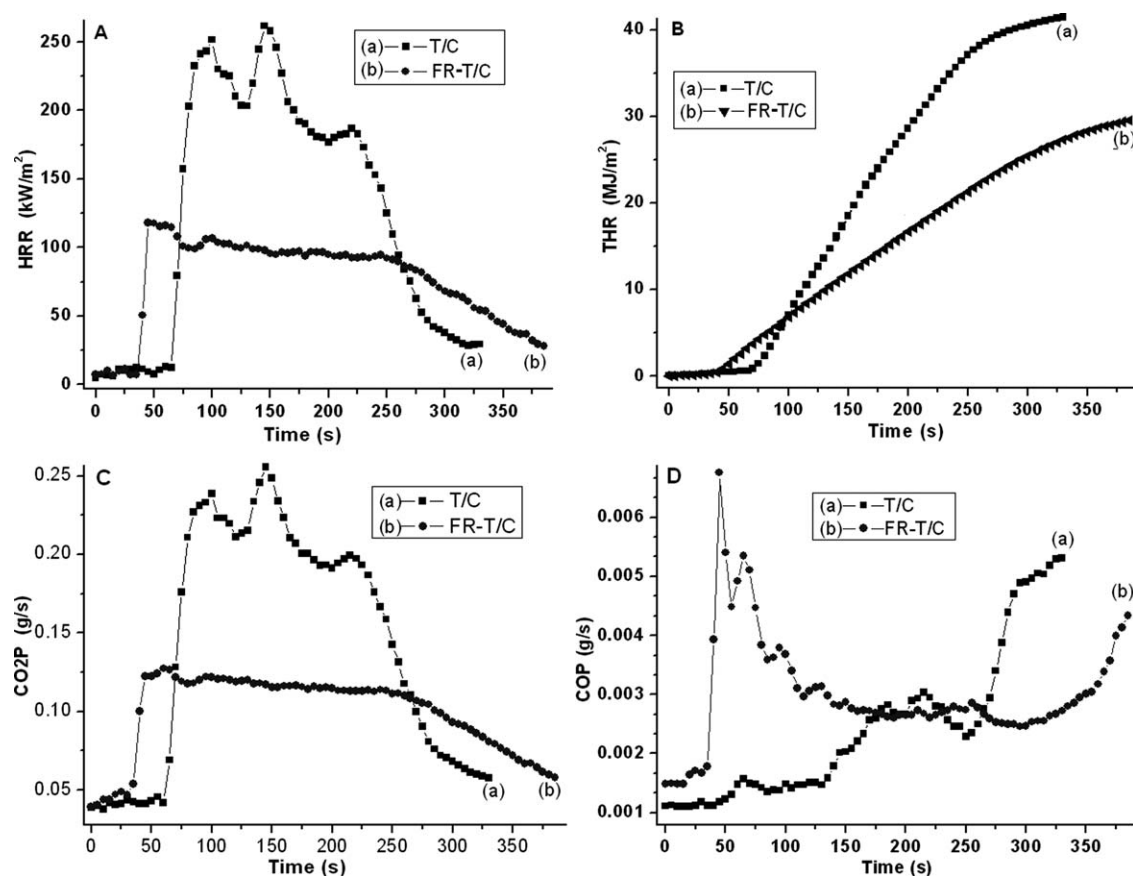


Figure 9 Heat release rate (A), total heat release (B), carbon dioxide production rate (C) and carbon monoxide production rate (D) curves of virgin T/C and FR-T/C at 35 kW m^{-2} heat flux.

melted and flowed about 255°C , and then the fabric pyrolyzed to gaseous fuel above 340°C , which escaped from the polymer melts. For the virgin fabric, it occurred obviously shrinking, melting, pyrolysis and violent burning processes, however, FR fabric showed weak melting and burning due to the fire-retarding effect of PVP-P-DCA.

FR durability of treated T/C

The wash fastness of the FR T/C was investigated by determination of P%, LOI, and vertical burning test. The samples were washed for 1, 5, and 10 times, respectively. The effect of washing cycles on the flame retardancy of T/C was listed in Table IV. It was found that the more washing times, the less LOI and P%. The LOI value of treated T/C before washing was 36.7, and after washing one and five times it was decreased to 30.4 and 27.2, respectively. When it was washed for 10 times, its LOI was almost unchanged (LOI = 26.4) and its FR retention was as high as 51.9%. The fastness may be the results of a good fixing effect of polymeric FRs. Besides this, via electrostatic interaction between the anions (OPO_3H^-) and the cation (DCA-H^+), FR mol-

ecules can be diffused into the amorphous regions of PET fibers during curing.²⁹

During the vertical burning test, the maximum damage length increased with the washing cycles. The treated fabric was no after-flame before washing due to the high adsorption of FR. And the samples can self-extinguish after washing once and five times because of the fixing of FR on the fibers though some free FR was cleared. When it was washed 10 times, however, the vertical burning tests were failed because FR on the fabric was almost cleared. The results revealed that the fixation of PVP-P-DCA on the fiber was not very sufficient.

TABLE III
The Combustion Data Determined from the Cone Calorimeter at 35 kW m^{-2} Heat Flux

Parameters	T/C	FR-T/C
Time to ignition (TTI) (s)	60	35
Time to flameout (TTF) (s)	304	382
pk-HRR (kW m^{-2})	261.8	118.0
Mean-HRR (kW m^{-2})	151.5	83.5
THR (MJ m^{-2})	41.0	29.2
Mean-MLR (g s^{-1})	0.085	0.0528
Char residue (%)	9.4	28.4

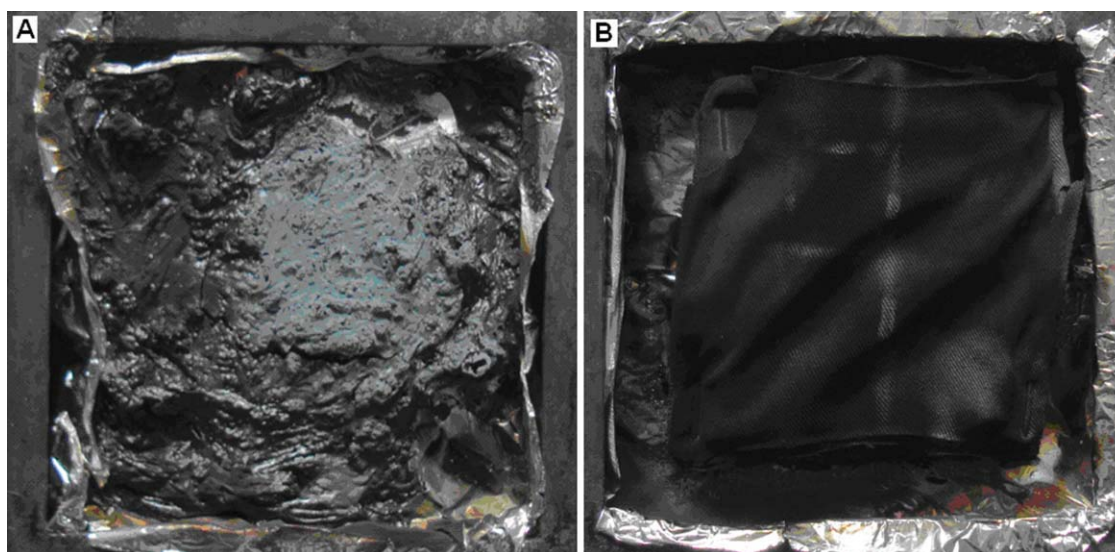


Figure 10 Digital photographs of char residue of virgin T/C (A) and FR-T/C (B) after cone calorimeter test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To further investigate the durability of FR-T/C, FTIR analysis on the surface of fabric washed for different times was performed and showed in Figure 11. In the spectrum of virgin T/C, the peaks appeared in 1722, 1098, and 723 cm^{-1} , were ascribed to C=O vibration of COOC, C—O—C vibration and CH_2 vibration, respectively. In the spectrum b (FR-T/C, without washing), the characteristic absorption peaks of PVP-P-DCA appeared at 3415, 3303, 2278, 1689, 1585, and 1233 cm^{-1} , which identified to the stretching vibrations of OH, NH_2 , $\text{C}\equiv\text{N}$, $\text{C}=\text{NH}$, $\text{C}=\text{NH}_2^+$ and $\text{P}=\text{O}$, respectively. The spectrum c, d, and e (washing 1, 5, 10 times) were very similar to b except for their characteristic peaks being lower and lower, especially, the vibration peaks of $\text{P}-\text{O}-\text{C}$ weakened greatly. After washing 10 times (spectrum e), the vibration absorption peaks of $\text{C}=\text{NH}$, $\text{C}=\text{NH}_2^+$, $\text{P}=\text{O}$, and $\text{P}-\text{O}-\text{C}$ still can be found. The results indicated that PVP-P-DCA was still fixed on the fabric. Therefore, even after washing 10 times LOI value of FR-T/C fabrics still retain 26.4.

SEM of residue of fabric

The SEM micrographs of the residual char of FR treated T/C with different magnification were shown in Figure 12. In the Figure 12(A) (100 \times), the charring residue of FR-T/C fabric maintained its original morphology, which was well agreed with the photo of FR-T/C after LOI test. It can be seen from the Figure 12(B) (400 \times), the fibers were bound together due to PET melting and there were many holes between the yarns. The high-magnification image of charring residue of FR-T/C fabric and T/C fabric [Fig. 12(C,D)] showed that char layers were a uniformly distributed sand-like and snowflake-like charring structure, respectively. The charring structure covered on the fabric can work more in the condensed phase in which it would block heat and oxygen flow and retard fabric combustion. The images further demonstrated that the FR can play an important role on the condensed phase.

All the results indicated that phosphorous-nitrogen FR, PVP-P-DCA, had a good synergistic effect,

TABLE IV
Effect of the Washing Times on the Flame Retardancy of T/C Fabric

Washing times	FR add-on (%)	P%	FR retention (%)	LOI (%)	Vertical burning test		
					Char length (mm)	After-flame time (s)	After-glow time (s)
0	28.5	3.89	—	36.7 \pm 0.1	56	NO ^a	NO
1	23.9	3.49	—	30.4 \pm 0.2	82	2	0
5	18.4	2.56	73.4	27.2 \pm 0.2	152	5	0
10	15.2	1.81	51.9	26.4 \pm 0.3	TD ^b	NR ^c	NR

^a NO denotes no record due to the self extinguishments of fabrics during the 12-s ignition time.

^b TD denotes the case that fabrics were completely destroyed during the test.

^c NR denotes no record due to the complete destruction of the fabrics.

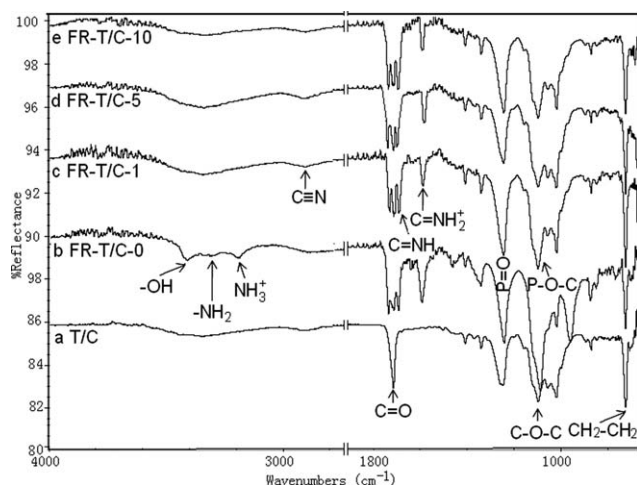


Figure 11 The FTIR spectra of virgin T/C (a), FR-T/C without washing (b), FR-T/C washing once (c), washing 5 times (d), and washing 10 times (e).

i.e., the nitrogen components prevented the fire by diluting the pyrolysis gases,^{31,32} while phosphorous components suppressed the combustion by pyrolysis residue. Therefore, FR inhibited degradation of fabric but enhanced its charring. Besides this, phosphorous-oxygen free radicals in the condensed-phase can capture hydrogen and hydroxyl radicals derived from the matrix during burning, and they were converted to phosphoric acid, metaphosphoric acid. These acid layers covered on the fabric blocked heat and oxygen flow, and retarded fabric combustion.^{33,34} So PVP-P-DCA can act on high efficiency fire-retarding for PET/cotton blends.

CONCLUSIONS

A novel polymeric FR PVP-P-DCA for T/C fabric was synthesized and characterized. Via pad-dry-curing process, T/C treated with PVP-P-DCA showed durable flame retardancy and its LOI was still up to

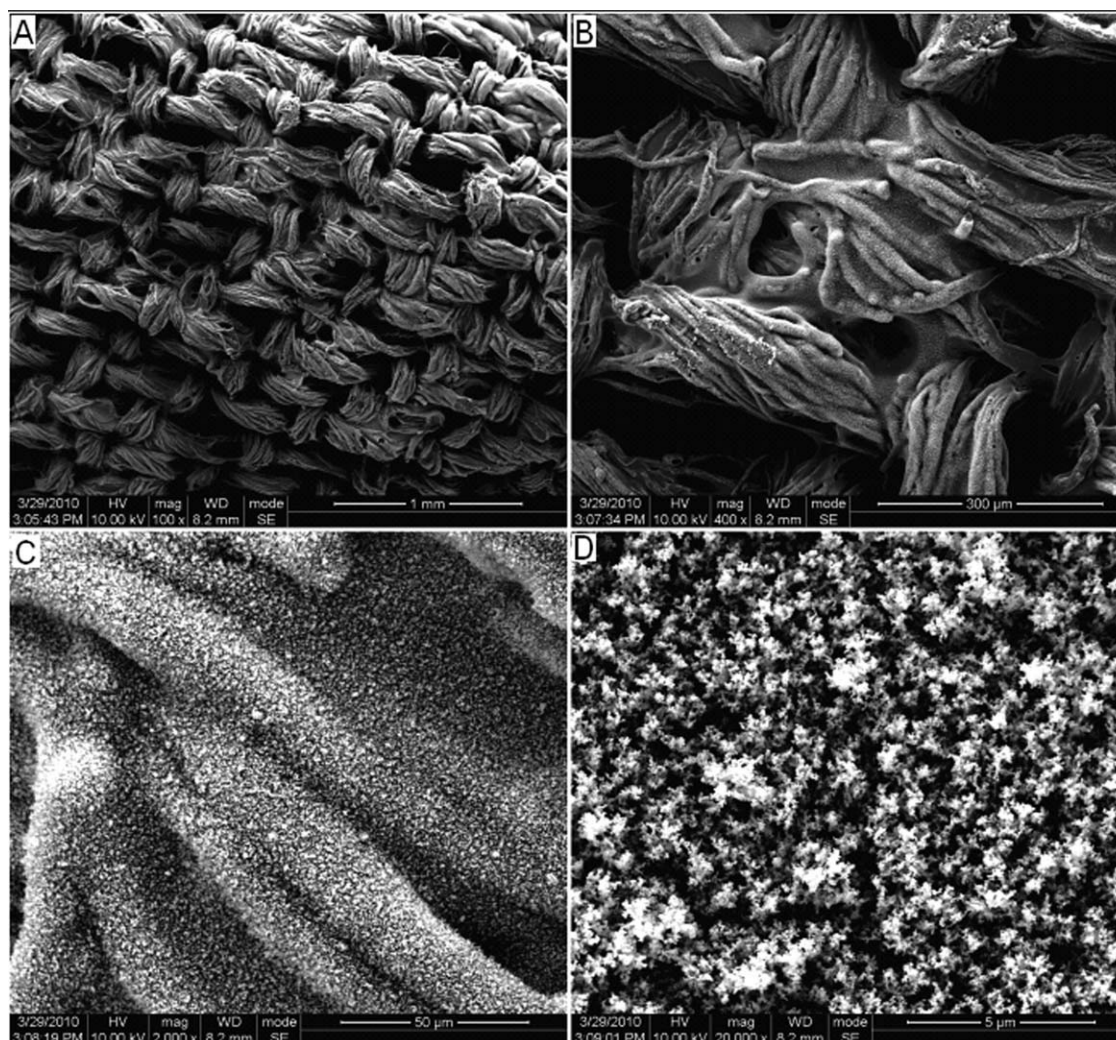


Figure 12 SEM micrographs of the residual char of T/C fabric treated with PVP-P-DAC after cone calorimeter test under different magnification, (A) $\times 100$, (B) $\times 400$, (C) $\times 2000$, and (D) $\times 20,000$.

26.4 after washing 10 times. This may be attributed to the results of the polymeric FR fixing effect, which can be diffused into the amorphous regions of PET fibers during pad-dry-curing. The FTIR and SEM results could also verify that FRs have been fixed onto the fabric. Cone calorimeter test results showed that HRR and THR of FR-T/C were reduced greatly. And the residue mass after cone test was increased 3 times comparing with that of virgin fabric. The charring residue maintained almost completely original morphology of fabric, revealing PVP-P-DCA might mainly play a fire-retarding role in the condensed-phase and a good P-N synergism.

References

1. Hwang, S. H.; Paeng, S. W.; Kim, J. Y.; Huh, W. *Polym Bull* 2003, 49, 329.
2. Aseeva, R. M.; Zaikov, E. G. *Combustion of Polymer Materials [in Russian]*; Nauka: Moscow, 1981.
3. Reeves, W. A.; Drake, G. L.; Chance, L. H.; Guthrie, J. D. *Text Res J* 1957, 27, 260.
4. Byrne, G. A.; Gardiner, D.; Holmes, F. H. *J Appl Chem* 1966, 16, 81.
5. Prival, M. J.; McCoy, E. C.; Gutter, B.; Rosenkranz, H. S. *Science* 1977, 195, 76.
6. Lee, E. S. *J Appl Polym Sci* 2002, 84, 172.
7. Kim, Y.-H.; Jang, J.; Song, K.-G.; Lee, E.-S.; Ko, S.-W. *J Appl Polym Sci* 2001, 81, 793.
8. Tesoro, G. C. *J Appl Polym Sci* 1977, 21, 1073.
9. Holme, I.; Pater, S. R. *J Soc Dye Col* 1980, 96, 224.
10. Reeves, W. A.; Marquett, Y. B. *Text Res J* 1979, 49, 163.
11. Horrocks, A. R.; Kandola, B. K.; Davies, P. J.; Zhang, S.; Padbury, S. A. *Polym Degrad Stab* 2005, 88, 3.
12. Wu, W. D.; Charles, Q. Y. *Polym Degrad Stab* 2006, 91, 2561.
13. Yang, H.; Charles, Q. Y. *Polym Degrad Stab* 2005, 88, 363.
14. Chen, D. Q.; Wang, Y. Z.; Hu, X. P.; Wang, D. Y.; Qu, M. H.; Yang, B. *Polym Degrad Stab* 2005, 88, 369.
15. Ban, D. M.; Wang, Y. Z.; Yang, B.; Zhao, G. M. *Eur Polym Mater* 2004, 40, 1909.
16. Wang, D. Y.; Ge, X. G.; Wang, Y. Z.; Wang, C.; Qu, M. H.; Zhou, Q. *Macromol Mater Eng* 2006, 291, 638.
17. Li, Q. L.; Wang, X. L.; Wang, D. Y.; Xiong, W. C.; Zhong, G. H.; Wang, Y. Z. *J Appl Polym Sci* 2010, 117, 3066.
18. Czégény, Z.; Blazso, M. *J Anal Appl Pyrolysis* 2008, 81, 218.
19. Gao, M.; Ling, B. C.; Yang, S. S.; Zhao, M. *J Anal Appl Pyrolysis* 2005, 73, 151.
20. Lecoœur, E.; Vroman, I.; Bourbigot, S.; Delobel, R. *Polym Degrad Stab* 2006, 91, 1909.
21. Gao, M.; Sun, C.; Zhu, K. *J Therm Anal Cal* 2004, 75, 221.
22. Gao, F.; Tong, L. F.; Fang, Z. P. *Polym Degrad Stab* 2006, 91, 1295.
23. Banks, M.; Ebdon, J. R.; Johnson, M. *Polymer* 1993, 34, 4547.
24. Roscoe, O. C.; Ray, A. D.; Joseph, W. H.; Nancy, E. L. *Ind Eng Chem Res* 1989, 28, 48.
25. Jones, W. J.; Orville-Thomas, W. *J Trans Faraday Soc* 1959, 55, 193.
26. Pretsch, E.; Bühlmann, P.; Affolter, C. *Structure Determination of Organic Compounds Tables of Spectral Data*, 4th ed; Springer-Verlag Berlin Heidelberg: Berlin, 2009.
27. Annakutty, K. S.; Kishore, K. *Polymer* 1988, 29, 756.
28. Tsafack, M. J.; Levalois-Grützmacher, J. *Surf Coat Technol* 2006, 200, 3503.
29. Gu, J. W.; Zhang, G. C.; Dong, S. L.; Zhang, Q. Y.; Kong, J. *Surf Coat Technol* 2007, 201, 7835.
30. Tripathy, A. R.; Farris, R. J.; MacKnight, W. J. *Polym Eng Sci* 2007, 47, 1536.
31. Uchida, E.; Iwata, H.; Ikada, Y. *Polymer* 2000, 41, 3609.
32. Grand, A. F.; Wilkie, C. A. *Fire Retardancy of Polymeric Materials*; Marcel Dekker: New York, 2000.
33. Liu, W.; Chen, D. Q.; Wang, Y. Z.; Wang, D. Y.; Qu, M. H. *Polym Degrad Stab* 2007, 92, 1046.
34. Schartela, B.; Brauna, U.; Schwarz, U.; Reinemann, S. *Polymer* 2003, 44, 6241.