A Novel Organophosphorus Flame Retardant: Synthesis and Durable Finishing of Poly(ethylene terephthalate)/Cotton Blends

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ABSTRACT: A novel, hydroxy-functional, organophosphorus flame retardant (FR), 2,2-dihydroxymethylpropane-1,3-diolylbis(hydrogen phenylphosphonate) (DHDBP), was synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, and elemental analysis. Subsequently, poly(ethylene terephthalate) (PET)/cotton (T/C; 70/30) blends were treated via pad-dry-thermosol finishing with DHDBP, citric acid, and a catalyst. Its flame retardancy, durability effect, and thermal decomposition behaviors were investigated by limited oxygen index, vertical burning test, thermogravimetric analysis, FTIR spectroscopy, and scanning electron microscopy. The results show that DHDBP was not only a reactive FR with a high efficiency but also a good char-forming agent for the T/C blends. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3066–3074, 2010

Key words: fibers; flame retardance; synthesis

INTRODUCTION

Poly(ethylene terephthalate) (PET)/cotton (T/C) blends have outstanding physical and chemical properties, including a high strength, excellent wear resistance, chemical stability, good hygroscopicity, high air permeability, and comfortable hand feeling.[1] Thus, T/C blends are widely used for home textiles and knitwear and clothing. However, because of its flammability, it is essential and crucial to impart flame retardance to T/C blends.

It is well-known that a scaffolding effect occurs in the case when T/C blends are burned; this is ascribed to the fact that the molten PET cannot flow away from the flame source.[2] Usually, fireproof fibers are obtained through one of three methods: copolymerization with a reactive flame-retardant (FR) monomer, the addition of FRs during process-ing, and the FR treatment of fabrics.[3–11] Without a doubt, the third method is an economical and practical choice. Because of the different solubility parameters and penetrability between cotton and PET, FRs are absorbed by cotton but are usually repelled by PET and vice versa. Although great efforts have been made for several decades,[12–14] no good practical solution has been developed so far.

Phosphorus is one of the most effective FR elements for oxygen-containing polymers (e.g., T/C blends), as phosphorus compounds release fewer toxic gases and less smoke during combustion compared with conventional halogen-based compounds.[4,15–19] Kim et al.[10] synthesized a halogen–phosphorus FR, dichlorotribromophenyl phosphate, and found it had good FR efficiency for T/C blends. However, it cannot be widely used because it causes severe secondary pollution. So, phosphorus-based species were recently attempted to replace halogen-containing chemicals in the textile fireproofing field. In the early period, most commercial phosphorus-containing FRs (e.g., Proban, Fyrol 76, and Pycovatex CP[20–22]) contained N—CH$_2$OR (H) or P—CH$_2$OR (H), which easily released formaldehyde when they were used. In recent years, intumescent FRs for enhancing the formation of char, phosphorus–nitrogen fire retardants with synergistic effects, and microencapsulated FRs have been widely investigated.[23–27] Wang and coworkers[7,11] synthesized an antidripping FR, poly(2-hydroxyl propylene
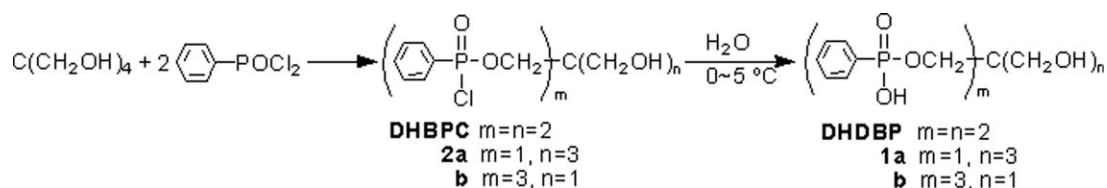
Scheme 1 Reaction route of DHDBP.

spirocyclic pentaerythritol bisphosphonate), that could impart flame retardance and dripping resistance to PET fabrics; however, it was nondurable and had an inferior hand feeling.

It is important to find a FR formula for finishing T/C blends that not only may be compatible with PET but can also be bound with cotton. In this study, a novel, halogen-free FR, 2,2-dihydroxymethylpropane-1,3-diolylbis(hydrogen phenylphosphonate) (DHDBP; Scheme 1), for T/C blends was synthesized and characterized by elemental analysis, Fourier transform infrared (FTIR) spectroscopy, ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR. We expected that the hydroxyl group of DHDBP and cotton would react with multicarboxylic acid [citric acid (CA)] via esterification during the pad-dry-thermosol finishing, which would fix DHDBP on the T/C fiber and endow it with durable flame retardancy. The combustion performance, durability, and thermal decomposition behavior of the T/C fibers (70/30) treated by DHDBP were investigated by limited oxygen index (LOI), vertical burning test, thermogravimetric analysis (TGA), FTIR, and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The fabrics used were T/C blends (70 : 30 blend ratio, 190 g/m^2) and were purchased from Jinan Zhenghao Advanced Fiber Co., Ltd. (Jinan, China). Phenylphosphonyl dichloride and pentaerythritol were obtained from Rutejin (Tianjin, China) and the First Reagent Co. (Shanghai, China), respectively. Phenylphosphonyl dichloride was distilled before use. NaOH, sodium carbonate, xylene, dioxane, ethanol, ether, CHCl$_3$, tetrahydrofuran (THF), CH$_3$OH, silica gel (400 mesh), monohydride CA, and sodium hypophosphite (NaH$_2$PO$_2 \cdot$H$_2$O) were purchased from Kelong (Chengdu, China) and were used without purification.

Synthesis and characterization of DHDBP

Pentaerythritol (13.6 g, 0.10 mol) was added to a glass flask containing 40 mL of xylene and equipped with a stirrer, thermometer, and condenser. The mixture was stirred and gradually heated. When the temperature reached 80°C, phenylphosphonyl dichloride (39.0 g, 37.9 mL, 0.20 mol) was added

drop by drop into the mixture for about 30 min. The mixture was reacted for 4 h. Then, 30 mL of dioxane was added, and the mixture was heated to 101°C. After 2 h, no HCl was released, and the reaction was considered complete. The mixture was cooled to room temperature and filtered; a main intermediate, bisubstituted 2,2-dihydroxymethylpropane-1,3-diolylbis(phenylphosphonochloridate) (DHBPC), was obtained. The intermediate was transferred to another flask with 30 mL of ice water and stirred at 0–5°C for 30 min. The suspended solution was filtered at reduced pressure. The solid was dissolved in 20 mL of ethanol; then, 40 mL of ether was added. Finally, through filtration, repeated recrystallization, and drying, the main product, DHDBP, was obtained (yield = 63.4%). The recrystallized product was analyzed by means of thin-layer chromatography. The Retention factor (Rf) values, respectively, were 0.75, 0.52 (THF/CH$_3$OH = 2/1 and 4/1), 0.25 (CHCl$_3$/THF = 3/1), and 0.55 (CHCl$_3$/THF/CH$_3$OH = 3/2/1). For every separation, only one circle spot was found; this indicated that the byproducts were removed by the repeated purification, and traces of byproducts were hardly detected by general analysis techniques.

The FTIR spectrum of DHDBP was obtained with an FTIR spectrophotometer (Nicolet 6700, Thermo Nicolet, Waltham, MA) with a potassium bromide pellet technique, and the ^{1}H-NMR, ^{13}C-NMR, and ^{31}P-NMR spectra were obtain 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 DHDBP were analyzed by a Carlo Erba 1106 CHN elemental analyzer (Rodano, Italy). The phosphorus content (P%) of DHDBP was measured by an Optima 7300DV inductive coupled plasma emission spectrometer (PerkinElmer, Waltham, MA).

Finishing of T/C blends with DHDBP

The T/C (70/30) blends were pretreated with 0.5% (w/w) NaOH and a 1% H$_2$O$_2$ water solution for 10 min and then dried at 80°C. The different FR baths were prepared in water with different concentrations of DHDBP, CA, and NaH$_2$PO$_2$. The T/C fabrics were immersed in the baths (the bath ratio was 1 : 20) to give an approximately 90% wet pickup regulated by padding. After double-dip–double-nip, the

fabrics samples were dried at 90°C for 5 min and then were cured at 165°C for 3 min. The treated fabrics were washed at 40°C with a solution of 0.5% (w/w) sodium carbonate in distilled water for 5 min and finally dried at 90°C. The add-on (%) of FR was calculated from the following equation:

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

where w_o and w_t are the weights of the T/C blends before and after FR finishing, respectively.

Determination of P% of the treated fabrics

Approximately 2.0 g of the treated T/C fabric sample taken from three different parts of the specimen was cut into pieces. Then, 10 mL of concentrated HNO_3 was gradually added to 0.3 g of T/C pieces weighed accurately, and then, 5 mL of $HClO_4$ was added to the mixture drop by drop. The reaction mixture was then heated to 100°C to digest the pieces and to evaporate the water until 2–3 mL of clear residual liquid was obtained and the T/C pieces were digested completely. Subsequently, the solution was fully transferred to a 100-mL flask and diluted to scale by deionized water. The obtained sample was analyzed by the Quinoline phosphomolybdate gravimetric method (ISO 6598-1985) to determine P%.

Evaluation of the flame retardance of the finished fabrics

The vertical burning test was conducted on a CZF-2 type instrument (Jiangning, China) according to ASTM D 6413-99. This testing method measures the vertical flame resistance of textiles in general, including afterflame time, that is, the length of time the material continues to burn after removal of the burner after a 12-s ignition time; afterglow time, that is, the length of time the material glows after the flame extinguishes; and char length, that is, the distance from the edge of the fabric that is exposed to the flame to the end of the area affected by the flame. The LOI values of the samples were measured on an oxygen index flammability gauge (HC-2C, Nanjing Shangyuan Analytical Instruments, Nanjing, China) according to ASTM D 2863-97.

Thermal analysis

TGA and derivative thermogravimetry (DTG) of DHDBP-treated and untreated fabrics were conducted on a Synchronization Thermal Analysis STA 449C (Netzsch, Selb, German) at a heating rate of 10°C/min. Aluminum sample pans were used. The samples (7.5 mg) were heated in the analyzer at temperatures ranging from 40 to 590°C under N_2 at a flow rate of 45 mL/min.
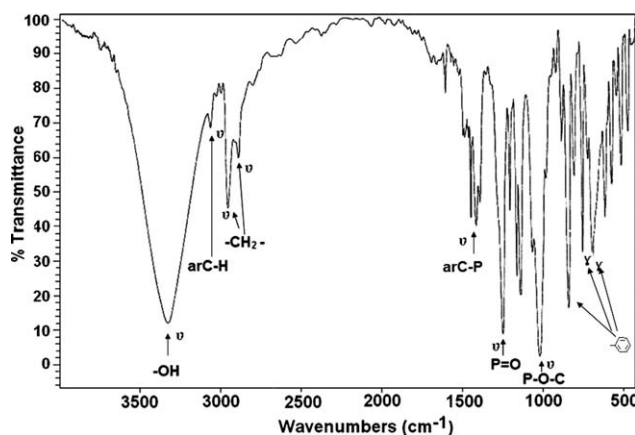
Figure 1 FTIR spectrum of DHDBP.

Measurements of the surface morphology of the treated fabrics

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

RESULTS AND DISCUSSION

Synthesis and characterization of DHDBP

DHDBP was prepared via the reaction of pentaerythritol with phenylphosphonyl dichloride (at a stoichiometry of reagents of 1 : 2), as shown in Scheme 1. Two hydroxyl groups of pentaerythritol were reacted with phenylphosphonyl dichloride through a selective reaction at 80°C. Byproducts, such as monosubstitutes and trisubstitutes (i.e., **2a** and **2b**), however, were produced. Through strict control of the stoichiometry of the reagents and the reaction temperature, side reactions were greatly reduced. The P—Cl bond of DHBPC was hydrolyzed in ice water for 30 min lest phosphate hydrolyze. The product DHDBP was purified by repeated recrystallization. The byproducts, monosubstitutes and trisubstitutes, were removed by repeated purification, and traces of the byproducts could hardly be detected by general analysis techniques, such as thin-layer chromatography.

The FTIR spectrum of DHDBP is shown in Figure 1. The —OH stretching vibration was around 3400 cm^{-1}, and the P=O stretching vibration was found at 1245 cm^{-1}. The stretching vibration of arC—O—P (arC is the aromatic carbon atom) and arC—P appeared at 1016 and 1439 cm^{-1}.[28] Also, the bands at 3052, 1593, 835, 746, and 685 cm^{-1} were the characteristic absorbing peaks of the benzene ring. In the
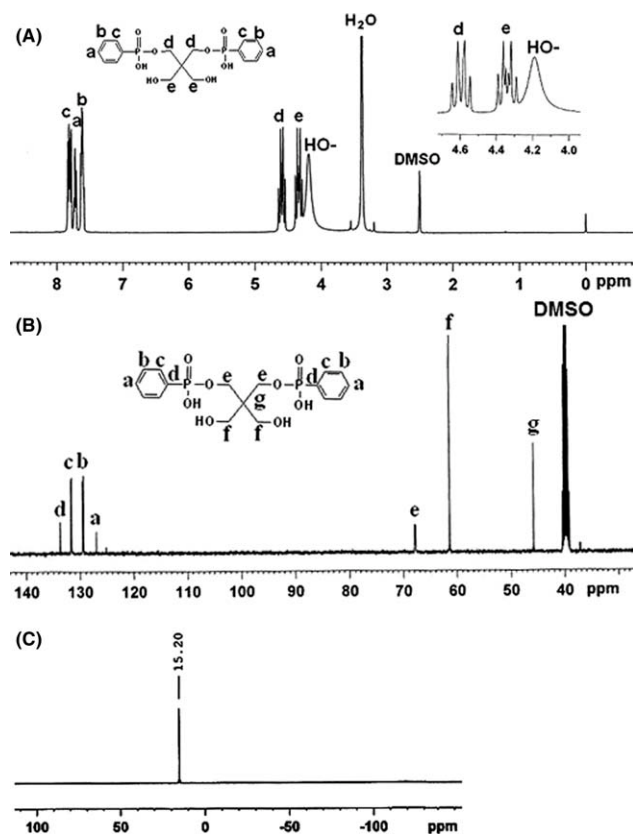
Figure 2 NMR spectra of DHDBP: (A) ^{1}H-NMR, (B) ^{13}C-NMR, and (C) ^{31}P-NMR.

^{1}H-NMR spectrum of DHDBP [Fig. 2(A)], the aromatic protons resonated at 7.8 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 4H, arC—H_o), 7.7 (t, $J = 6.8$ Hz, 2H, arC—H_p), and 7.63–7.58 (m, 4 H, arC—H_m). The chemical shifts of CH_2 and OH were found at 4.6 (dd, $J = 12.0$ Hz, $J = 12.4$ Hz, 4H, P—O—CH_2), 4.39–4.29 (m, 4H, O—CH_2), and 4.1 (s, 4H, OH). From the ^{13}C-NMR spectrum [Fig. 2(B)], we observed that the chemical shifts of the carbon atom of benzene were found at δ = 133 (arC—P), 131 (arC$_o$), 129 (arC$_m$), and 127 ppm (arC$_p$). The bands at 68 (P—O—CH_2) and 61 ppm (HO—CH_2) were assigned to the methylene carbon, and the quaternary carbon was found at 46 ppm. Only one peak (15.2 ppm) was found in the ^{31}P-NMR spectrum [Fig. 2(C)]; this indicated that only one form of phosphorous existed. The experimental values of elemental analysis (%, $C_{17}H_{18}O_6P_2$ theoretical values) were as follows: C, 48.81% (49.05%); H, 5.62% (5.33%); and P, 14.56% (14.88). The calculated value of O content was 30.66% (O% = 1 and C%–H%–P% = 30.75).

From these results, we affirmed that DHDBP was synthesized successfully.

FTIR analysis of the finished T/C with DHDBP

Figure 3 shows the FTIR spectra of the untreated and treated T/C samples. In the spectrum of the untreated T/C (70/30) fabric (curve a), the major
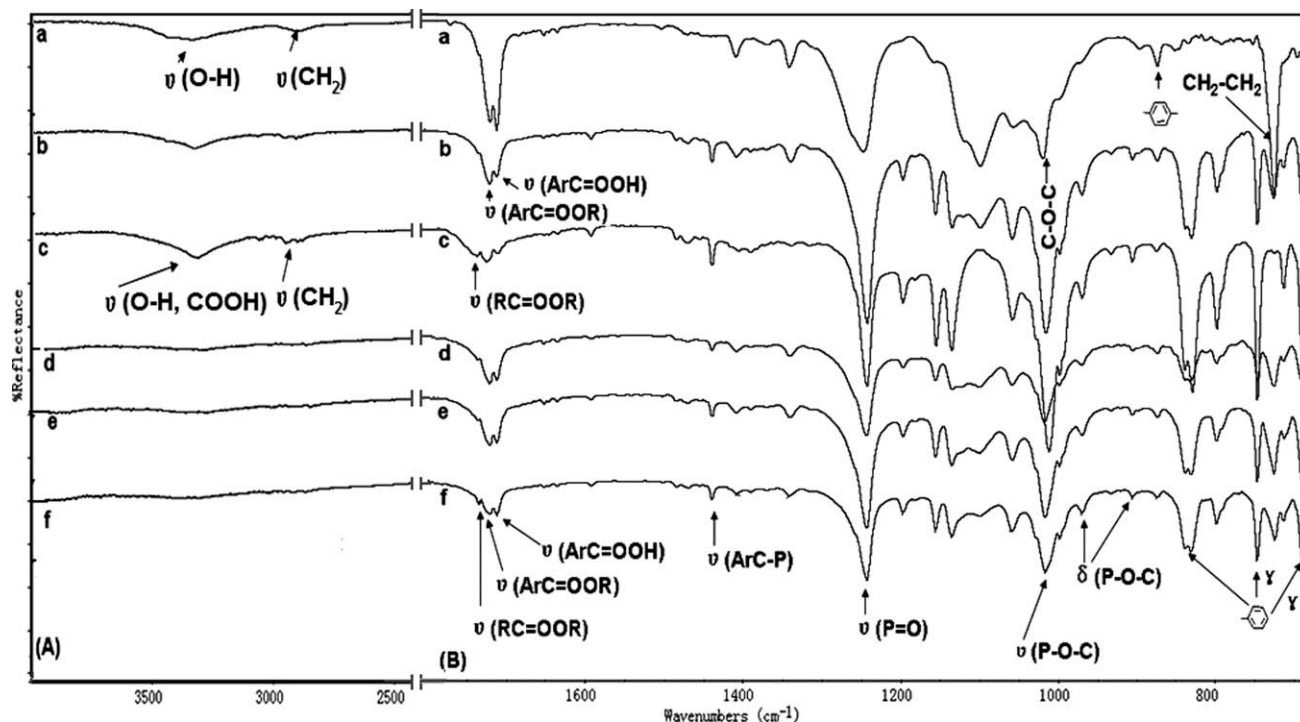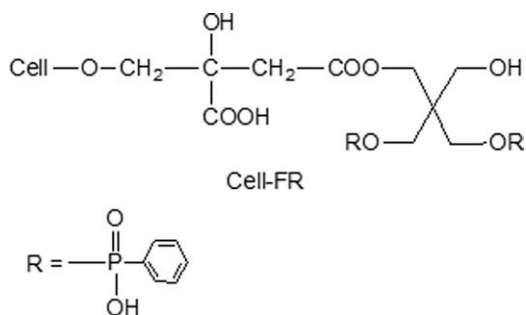

Figure 3 FTIR spectra of the T/C (70/30) fabrics: (a) not treated, (b) treated with DHDBP without CA after washing once, (c) treated with DHDBP and CA without washing, (d) with one washing, (e) with 5 washings, (f) with 10 washings, (A) wave numbers = 2450–4000 cm^{-1} and (B) wave numbers = 650–1820 cm^{-1}.

Cell-FR

$R = $ (phosphorus structure with P=O, phenyl, OH)

Scheme 2 Scheme of DHDBP or cellulose reacted with CA.

vibration absorptions peaks of PET and cotton (cellulose) were found. For example, 3300–3600 cm^{-1} was the stretching vibration of the hydroxyl groups of cellulose and PET. The stretching vibration of CH$_2$ and arC—H was at 2860–3060 cm^{-1}. The stretching vibrations of C=O in arCOOC at 1722 cm^{-1} and in arCOOH at 1710 cm^{-1} were very strong. The strong band at 1098 cm^{-1} was the stretching vibration of C—O—C in arCOOC.[28,29] The bending vibration of CH$_2$ in PET was at 723 cm^{-1}. For the T/C blends treated with DHDBP (curve b), the DHDBP characteristic IR absorptions were easily identified at 1439, 1245, 1156, and 1016 cm^{-1}, which correspond to the stretching vibrations of arC—P, P=O, C—OH, and P—O—C, respectively. These bands indicated the presence of the phosphorus-containing FR on the surface of the T/C fabric.

To endow durable flame retardancy to the T/C fabric, CA was added to the finishing bath to react with both the hydroxyl group of DHDBP and cotton in the presence of NaH$_2$PO$_2$ as a catalyst.[30] In the spectrum of the T/C fabrics treated with CA and DHDBP [Fig. 3(c)], a new absorption vibration peak appeared at 1734 cm^{-1}, corresponding to the C=O stretching of aliphatic COOC, which indicated that CA esterified with the hydroxyl groups of both cellulose and DHDBP. One possible crosslinking reaction was that one COOH group of CA esterified with the OH groups of cellulose and the other reacted with the hydroxyl groups of DHDBP, which is shown in Scheme 2.

Compared with the untreated T/C fabrics (curve a), the —COOH stretching of CA around 3500 cm^{-1} appeared more obviously in the treated T/C fabrics; this suggested that CA did not react completely. Although the reaction between cellulose, DHDBP, and CA did not proceed very well, the new absorption peak at 1734 cm^{-1} demonstrated that there were esterifications, as we expected (shown in Scheme 2); that is, two COOH groups of CA esterified with the OH groups of cellulose and DHDBP, respectively, which endowed durable flame retardance to the T/C fabrics. This was further affirmed by the spectra of the FR-treated T/C fabrics via washing for differ-

ent times [Fig. 3(d–f)]. With washing cycles (curves d, e, and f), the stretching vibrations of arC—P, P=O, and P—O—C of DHDBP became weaker and weaker, but the shape was quite similar because of some FR still preserved on the T/C fabrics. The absorption vibration peak of C=O stretching of aliphatic COOC at 1734 cm^{-1} still existed. Even with
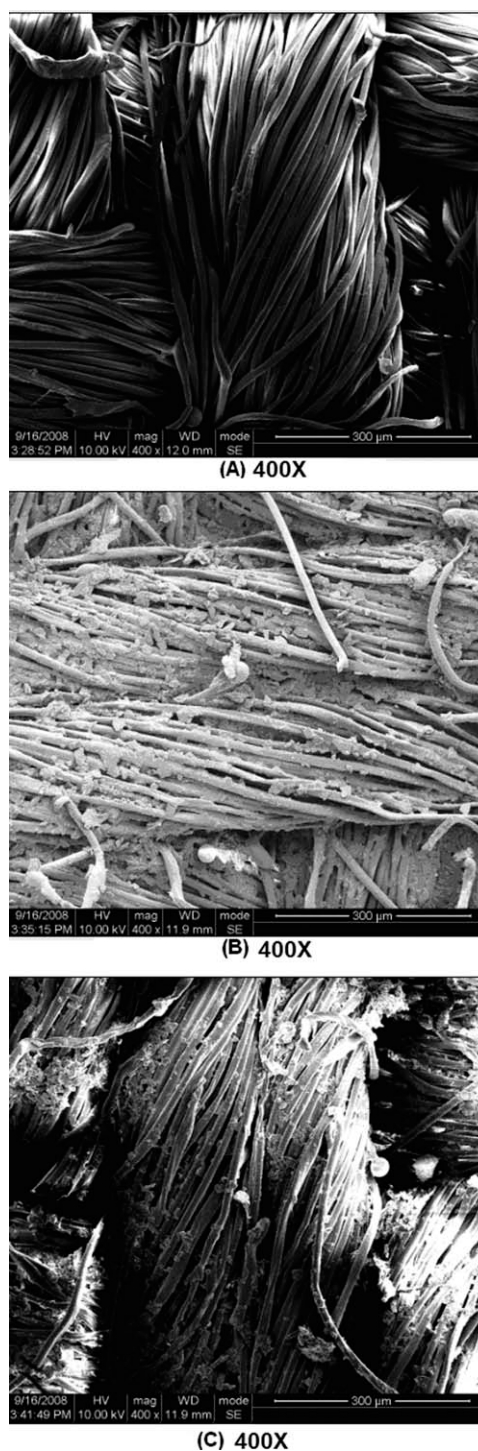

Figure 4 SEM micrographs of the surface of the (A) untreated T/C fabrics, (B) fabric treated without wash, and (C) fabric treated and washed once.

10 washings, the stretching vibration of aliphatic ester bonds were still seen on the spectrum. This indicated that DHDBP was still fixed onto the fibers.

SEM image of the treated and untreated T/C blends

As shown in the SEM photographs in Figure 4, the surface of the untreated T/C fabrics [Fig. 4(A)] was smooth and relatively neat. As far as the treated T/C fabrics [Fig. 4(B)] were concerned, the surface became rough, and many granular species packed on the fiber. After it was washed once [Fig. 4(C)], the fiber was still somewhat shaggy, although the surface was neater than that of the treated T/C fabrics without washing. This suggested that some FRs had been attached onto cotton by a chemical reaction or melted into PET through physical absorption.

TGA of DHDBP for the treated and untreated fabrics

TGA is the most favored technique for evaluating the thermal stability of various polymers.[31] The TGA and DTG curves of the treated and untreated T/C blends and DHDBP are shown in Figure 5. The data determined from the TGA and DTG curves are represented in Table I. The onset decomposition temperature (T_{on}) and the temperatures of maximum weight loss rate (T_{1max} and T_{2max}) of DHDBP were found at 285, 292, and 387°C, respectively; this indicated that DHDBP was easily decomposed. It is known that phosphorous-containing FRs can reduce cellulose and polyester inflammability, primarily by dehydration, phosphorylation, and phosphate–ester decomposition mechanisms, further forming a cross-linked network within the cellulose and PET, which can inhibit the release of volatile combustible fragments and enhance char formation.[32] Generally, the FR is expected to decompose before or near the decomposition temperature of the substrate to interfere with the burning process.[32] Because the thermal decomposition temperatures of DHDBP, that is, T_{on}, T_{1max}, and T_{2max}, were lower (62, 67, and 43°C) than those of T/C, DHDBP decomposed before the T/C blend fiber and restrained the burning process of the T/C blends.
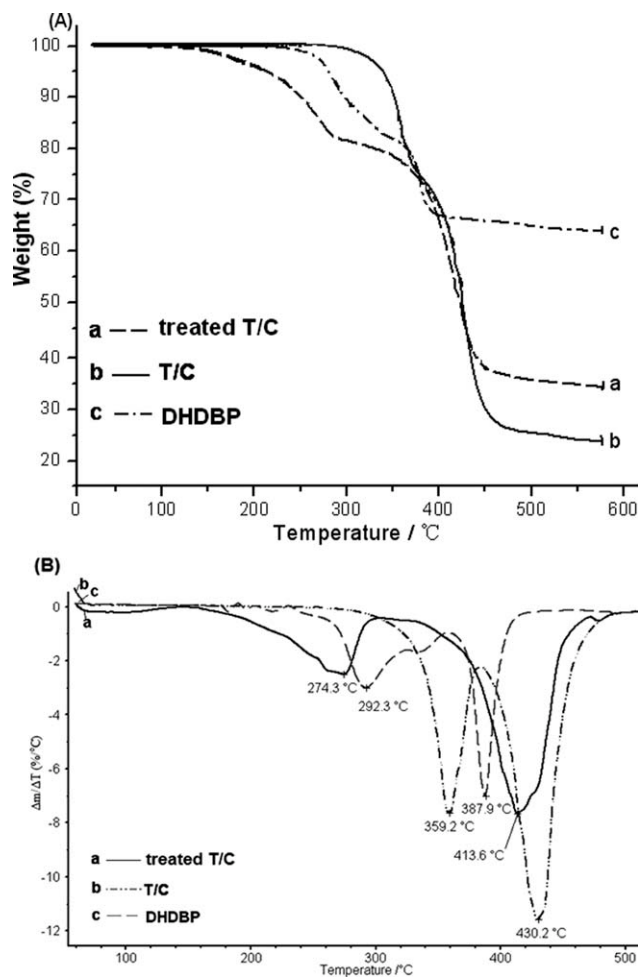

Figure 5 (A) TGA and (B) DTG of the (a) treated and (b) untreated T/C fabrics and (c) DHDBP in N_2 at heating rate of 10°C/min.

As shown in Table I, clearly, T_{on} of the treated T/C fabric was lower (113°C) than that of the untreated one. The residue of the treated T/C fabric at 585°C increased from 24.8 to 35.4%; this suggested that the addition of FRs onto the fiber may have reduced the flammability via DHDBP dehydration into char. Both the treated and untreated T/C fabrics showed two significant stages of weight loss [Fig. 5(B)]. Because of the prior decomposition of FR catalyzed the dehydration charring reaction and weakened intensity of pyrolysis of the treated T/C fabric, its two maximum weight loss temperatures (T_{max} values) all

TABLE I
Data from the TGA and DTG Thermograms of DHDBP: Treated and Untreated T/C Fabrics

Sample	FR add-on (%)	T_{on} (°C)	Weight retention (%)			T_{max} and weight loss at this stage			
			385°C	485°C	585°C	T_{1max} (°C)	Weight loss (%)	T_{2max} (°C)	Weight loss (%)
DHDBP	–	285	77.1	66.0	65.9	292	16.8	387	14.5
T/C	0	347	76.1	27.0	24.8	359	21.6	430	50.3
FR-T/C[a]	20.6	234	74.8	38.0	35.4	274	15.0	413	42.6

[a] Cured at 165°C for 3 min after one washing.

TABLE II
Flame Retardancy Results of the Finished T/C Fabrics After One Washing

Trial	Formula of the finishing bath (% w/w)			Add-on (%)	P%	LOI (%)	Vertical burning test		
	DHDBP	CA	NaH$_2$PO$_2$				Char length (cm)	Afterflame time (s)	Afterglow time (s)
0	0	0	0	0	0	17.2 ± 0.1	TD	NR	NR
1	10	0	0	3.7	0.32	21.8 ± 0.3	TD	NR	NR
2	20	0	0	4.8	0.48	22.7 ± 0.4	TD	NR	NR
3	30	0	0	5.7	0.63	23.6 ± 0.3	TD	NR	NR
4	40	0	0	6.1	0.69	23.9 ± 0.2	TD	NR	NR
5	30	6	3	14.2	1.34	25.8 ± 0.3	13.8	6.4	1.2
6	30	12	6	20.6	2.64	27.6 ± 0.2	9.8	2.3	1.0
7	30	24	12	23.0	2.75	28.4 ± 0.2	8.7	NO	NO

TD denotes that the fabrics were completely destroyed during the test. NR denotes no record because of the complete destruction of the fabric. NO denotes no record because of the self-extinguishments of fabric during the 12-s ignition time.

shifted to the lower temperature, and the residue was higher than that of untreated one. For example, when T_{1max} of the treated T/C fabric was 274°C, its weight loss was only 15.0%; however, when T_{1max} of the untreated T/C fabric was 359°C, its weight loss was 21.6%. The reduction of the decomposition temperature and the enhancement of the residue indicated that the treated fabrics had good flame retardancy.[33]

LOI and vertical burning test of the treated T/C blends

The difficulty in rendering effective flame retardancy to T/C blends was mainly due to the scaffolding effect between the cotton and PET during burning, where the molten PET component wicked onto the char of the cotton and prevented its melt dripping.[2] To evaluate the FR properties of the fabric material, the LOI values and vertical burning test results were important parameters and are given in Table II.

As shown in Table II, when the T/C fabric was treated only by DHDBP (trials 1, 2, 3, and 4), although the add-ons of FR and P% were increased with increasing DHDBP content, the LOI value of the T/C fabric was less than 24 and could not pass

the vertical burning test. Even when the concentration of DHDBP in the finishing bath was increased to 40% (w/w), the P% of the fiber could not be further enhanced, which indicated that DHDBP adsorbed on the fabric was approximately saturated.

When CA and the catalyst (NaH$_2$PO$_2$) were added to finishing bath combined with DHDBP (trials 5, 6, and 7), the add-ons and P% were enhanced sharply. The LOI values of the treated fibers were also increased greatly. For example, when the finishing bath contained 30% (w/w) DHDBP, 12% (w/w) CA, and 6% (w/w) NaH$_2$PO$_2$, the LOI value of treated T/C increased to 27.6, and the T/C could self-extinguish after 12 s of ignition; this indicated that the flame retardancy of the T/C fabric reached the best value. The excellent flame retardancy corresponded with its condensed phase retardation, which was in agreement with the TGA results.[34]

FR durability of the treated T/C blends

To investigate the washing fastness of the FR T/C fabric, it was washed 1, 5, and 10 times. The effect of washing cycles on the flame retardance of the T/C fabric is listed in Table III. With increasing number of washing cycles, the LOI and P% of the treated

TABLE III
Effect of the Washing Times on the FR of T/C Fabric

Washing time	FR add-on (%)	P%	FR retention (%)	LOI (%)	Vertical burning test		
					Char length (cm)	Afterflame time (s)	Afterglow time (s)
0	28.5	3.59	—	36.8 ± 0.1	4.6	NO	NO
1	20.6	2.64	—	27.6 ± 0.2	9.8	2.3	1.0
5	15.2	1.47	55.6	25.6 ± 0.2	TD	NR	NR
10	14.5	1.16	43.9	25.1 ± 0.3	TD	NR	NR

NO denotes no record because of the self-extinguishments of fabric during the 12-s ignition time. TD denotes that the fabrics were completely destroyed during the test. NR denotes no record because of the complete destruction of the fabric.
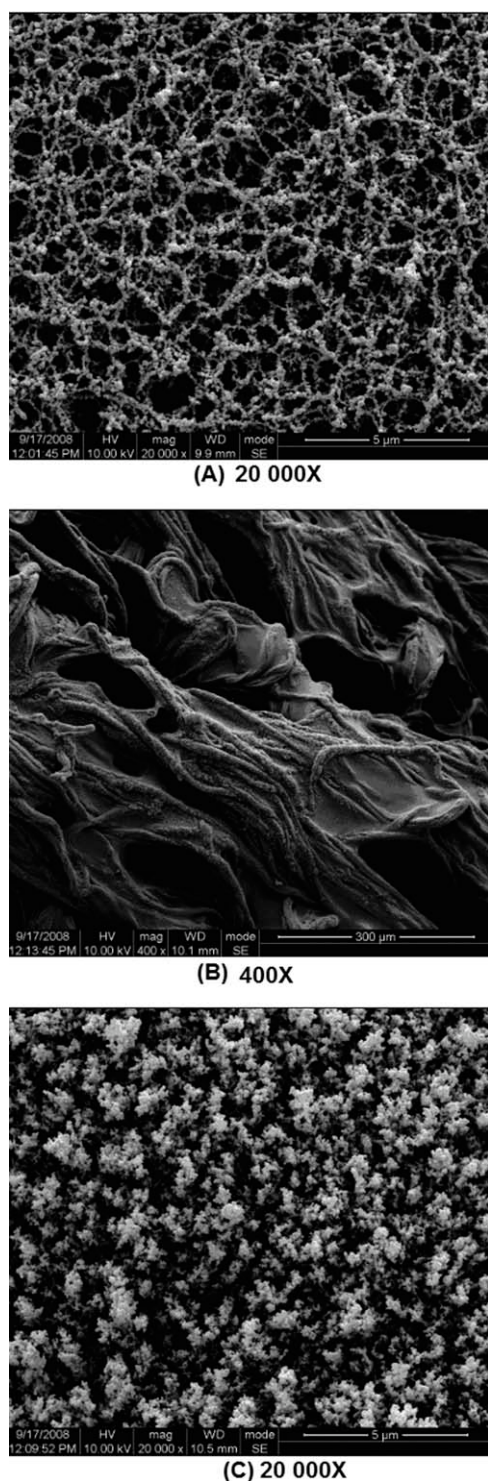
(A) 20 000X

(B) 400X

(C) 20 000X

Figure 6 SEM micrographs of the residual char of the (A) untreated and (B) treated T/C fabrics and (C) the high-magnification image of (B).

T/C decreased simultaneously. The LOI value of the treated T/C before washing was 36.8, and after washing 1 and 5 times, the values were 27.6 and 25.6, respectively. After the fabric was washed 10 times, its LOI value was almost unchanged (LOI = 25.1), and its FR retention was as high as 43.9%. This

durable flame retardancy may have been the result of the reaction between DHDBP and cellulose in the presence of CA and NaH_2PO_2, and the possible reaction pattern is shown in Scheme 2. In addition to esterification, through physical absorption during the pad-dry-thermosol finishing process, DHDBP may have diffused into the amorphous region of PET fiber, which also made it durable.

During the vertical burning test, the treated fabric was not ignited before washing because of the high adsorption of FR, and it could self-extinguish after it was washed once, in which most of the adsorption of FR had been cleared. When it was washed 5 and 10 times, however, it could not pass the vertical burning test because most of the absorbed FR on the fabric was almost cleared. The results indicate that the fixation of DHDBP on the fiber may not have been sufficient.

SEM of the residue of the untreated and treated T/C fabrics

The untreated T/C fabric was almost completely burned up in the air, and the outer surface of its residue [Fig. 6(A)] was honeycombed, which was the result of the scaffolding effect; that is, during ignition, cotton component was the initial source of fuel, which first decomposed and caught fire and subsequently burned intensely, and the PET component melted but could not flow away at about 254°C. Then, PET pyrolyzed to an additional gaseous phase fuel, which escaped from the molten fabrics and combusted, so there was left a honeycombed outer surface.[2]

However, the residue of the treated T/C fabric [Fig. 6(B)] was compact and smooth because of PET melting to cohere with the cotton, except for some gas holes on the surface. Figure 6(C), the high-magnification image of Figure 6(B), shows a uniformly distributed char structure that is obviously different from the graph in Figure 6(A). The char was discontinuous and snowflakelike as a result of the enhancing char-forming effect of FR. By forming a barrier between the flame and the underlying fiber, the observed char structure blocked the PET and cotton component by contacting the fire and inhibiting the transmission of heat.

CONCLUSIONS

A novel reactive FR, DHDBP, for T/C blend fabrics was synthesized and characterized. The T/C (70/30) fabric treated with DHDBP, CA, and NaH_2PO_2 showed durable flame retardancy, and its LOI value was still as high as 25.1 after 10 washings. This may have been due to esterification between DHDBP and cellulose with CA via a pad-dry-thermosol finishing process. The FTIR and SEM results also verified that

FR had fixed onto the fabrics. T_{on} of the treated fabric was reduced to 113°C, and the residue increased 10% compared with that of the untreated fabric. The residue morphology of the treated fabric changed from porous honeycombed to continuous snowflake-like; this indicated that DHDBP might play a flame-retarding function in the condensed phase.

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