
Preparation of Flame Retardant Cotton Fabric Using Environmental Friendly Supercritical Carbon Dioxide

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Abstract: Due to its environmentally benign character, supercritical carbon dioxide (scCO₂) is considered in green chemistry, as a substitute for organic solvents in chemical reactions. In this paper, an innovative approach for preparation of flame retardant cotton fabric was obtained by utilizing supercritical carbon dioxide with co-solvent. A novel phosphorus-nitrogen containing piperazine derivative, tetraethyl piperazine-1,4-diyl diphosphonate (pdp) and a sulfur-nitrogen containing derivative, tetramethyl piperazine-1,4-diyl diphosphonothioate (pdpt) were synthesized, and their chemical structures were confirmed by nuclear magnetic resonance (¹H and ¹³C NMR) and elemental analysis. pdp and pdpt were then used to treat cotton fabric processed in scCO₂. Thermogravimetric analysis (TGA), vertical flame test (ASTM D6413-08), and limiting oxygen index (LOI, ASTM D2863-09) were performed on the treated cotton fabrics, and showed promising results. When the treated fabrics were tested using the vertical flame, we observed that the ignited fabrics self extinguished and left behind a streak of char. Treated higher add-on fabrics were neither consumed by flame, nor produced glowing ambers upon self extinguishing. The results from cotton fabrics treated with new phosphorus-nitrogen containing piperazine derivatives demonstrated a higher LOI value as well as higher char yields due to the effectiveness of phosphorus and nitrogen as a flame retardant for cotton fabrics. Furthermore, SEM was employed to characterize the chemical structure on the treated fabrics as well as the surface morphology of char areas of treated and untreated fabrics.

Keywords: Cotton Fabric, Flame Retardant, Supercritical Carbon Dioxide, Flame Test

1. Introduction

Consumption of cotton is encouraged in a variety of consumer markets because cotton is abundant, low in cost, appealing to consumers, and is a versatile starting material for new product development. However, cotton is readily attacked by flame, microbes, and insects, and requires chemical modification for resiliency. In this paper, we will focus on making cotton fabrics resistant to attack by flame.

Phosphorus-containing compounds for flame retardants are widely used in the textile industry to make cotton textiles flame resistant [1]. Phosphorus-containing flame retardant compounds have been chemically reacted with cotton, producing products with an ether cross linker between the

phosphorus compound and the cellulosic material. In condense phase, the phosphorus containing functional groups are converted by thermal decomposition to phosphoric acid, forming a protective char. Char development and intumescences provide low flammability to cotton textiles [2, 3]. Nitrogen-containing flame retardants in combination with phosphorus compounds have multifunctional advantages: 1) low toxicity during combustion, 2) high efficiency measured by cone calorimeter, and 3) low smoke development in fire accidents [4]. Some nitrogen containing compounds such as urea, dicyandiamide, and melamine will accelerate phosphorylation of cellulose through formation of a

phosphorus-nitrogen intermediate, and thus synergize the flame retardant action of phosphorus [5, 6].

Supercritical fluids (SCFs) are widely applied as a media to process biopolymers and synthetic polymers. They provide an alternative technique to modify natural cellulose [7]. SCFs are non-toxic, inexpensive, environmentally benign, non-flammable, and are known for their high diffusion in organic matter. Furthermore, SCFs can eliminate or reduce the use of organic solvents and water when dyeing or impregnating hydrophobic or hydrophilic compounds into cotton textiles [8, 9]. A commonly used SCF is supercritical carbon dioxide (scCO₂), which has been used for extractions, impregnations, drying, and dyeing fabrics or polymers [10, 11]. Current scCO₂ impregnation studies have not obtained when cotton fabric is treated with molecules having no reactive functional groups such as the flame retardants reported in this study. Herein, we investigate the use of scCO₂ to impregnate flame retardants into cotton fabric.

A novel phosphorus-nitrogen containing piperazine derivatives, tetraethyl piperazine-1,4-diylldiphosphonate (pdp) and a sulfur-nitrogen containing derivative, tetramethyl piperazine-1,4-diylldiphosphonothioate (pdpt) were synthesized, and their structures were characterized by proton and carbon-13 nuclear magnetic resonance (NMR). Degradation of untreated and treated fabrics was studied by thermogravimetric analysis (TGA) in nitrogen and air atmospheres to determine char content upon degradation at 600°C. ASTM D2863-09 protocol [12] was used to determine the limiting oxygen index (LOI) values of fabrics to quantify the amount of oxygen in nitrogen needed to burn them. Finally, the flammability of fabrics was assessed by the vertical flame test (ASTM D6413-08) [13] to demonstrate that efficient flame resistance can be provided by new P-N containing monomers treated on cotton fabrics. Herein we report and discuss these results.

2. Experimental

2.1. Materials

Reactions were conducted under dry nitrogen atmosphere. Piperazine, diethyl chlorophosphate, dimethyl chloro thiophosphate, potassium carbonate, and commercially available solvents were obtained from Aldrich and used as received. Twill fabric, 258g/m² (Testfabrics Inc., Style-423) was bleached and mercerized. The innovative reaction was conducted under carbon dioxide atmospheric conditions and carbon dioxide with siphon tube was purchased from Airgas Co.

2.2. Synthesis of Tetraethyl

Piperazine-1,4-Diylldiphosphonate (pdp)

In a 500 ml three-neck flask, piperazine (5.0g, 0.058mol) and acetonitrile (150ml) were mixed and stirred. After stirring for 30 min, potassium carbonate (10.0g) was added, and the mixture was stirred for 30 min. Diethylchlorophosphate (21.0g, 0.122mol) in acetonitrile

(130ml) was then added dropwise via an additional funnel and contents were stirred for 14hr under nitrogen. Subsequently, deionized water (200ml) was added and extracted with methylene chloride (100ml x 3). The aqueous layer was extracted, and the organic layer combined, dried over magnesium sulfate, and filtered through sintered glass. The removal of the solvent gave light yellow oil as pdp (18.8g, 91.0% yield with no purification needed). ¹H-NMR (400 MHz, CDCl₃) δ-ppm: 1.33 (t, 12H, -OCH₂CH₃), 3.12 (t, 8H, -CH₂CH₂-), 4.05 (q, 8H, -OCH₂CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ-ppm: 16.3, 44.7, 62.5.

2.3. Synthesis of Tetramethyl

Piperazine-1,4-Diylldiphosphonothioate (pdpt)

In a 500 ml three-neck flask, piperazine (5.0g, 0.058mol, 1 eq.) and acetonitrile (150ml) were mixed and stirred. After stirring for 30 min, potassium carbonate (10.0g) was added, and the mixture was stirred for 30 min. Dimethylchlorothiophosphate (19.6g, 0.122mol, 2.1 eq.) in acetonitrile (130ml) was then added dropwise via an additional funnel at 0°C and contents were stirred for 14hr under nitrogen (time for equilibration from 0°C to room temperature was not determined). Subsequently, mixture was filtered and filtrate was dried over magnesium sulfate, and filtered through sintered glass. The removal of the filtrate solvent gave white powder as pdpt (18.5g, 95.4% yield with no purification needed). ¹H-NMR (400 MHz, CDCl₃) δ-ppm: 3.22 (t, 8H, -CH₂CH₂-), 3.65 (d, 12H, -OCH₃). ¹³C-NMR (100 MHz, CDCl₃) δ-ppm: 45.5, 53.6.

2.4. High Pressure Supercritical Carbon Dioxide (scCO₂)

Reactor Procedure

The supercritical reactor consisted of ultra high purity carbon dioxide, a series II Prime/Purge pump, and a high pressure series temperature control reactor (Figure 1). The cotton fabrics were immersed in 50% aqueous isopropanol solutions containing various percentages of flame retardant, pdp and pdpt, passed through a laboratory padder (10psi). The fabric was then wrapped around a metal wire cage, which prevents the fabric from being entangled with the stirrer, and placed into the scCO₂ reactor. They were stirred in scCO₂ in a 2L vessel, heating up to 90°C. Treating in scCO₂ was carried out at 90°C for 2 hours under 1800-2000 psi pressure. Fabric samples were then dried at 100°C for 5 min and cured at 160°C for 4 min.

2.5. Measurements

2.5.1. Nuclear Magnetic Resonance Spectrum

NMR spectra were recorded on Varian 400 MHz instrument using CDCl₃ as solvent. ¹H and ¹³C NMR are given in δ relative to TMS.

2.5.2. Thermal Analysis

The pdp, pdpt, untreated control and treated fabric were evaluated by thermogravimetric analysis for the thermal stability (TA Instruments, Q500). Each sample (5-7 mg) was

examined under continuous nitrogen flow atmosphere at a heating rate of 10°C/min from room temperature to 600°C.

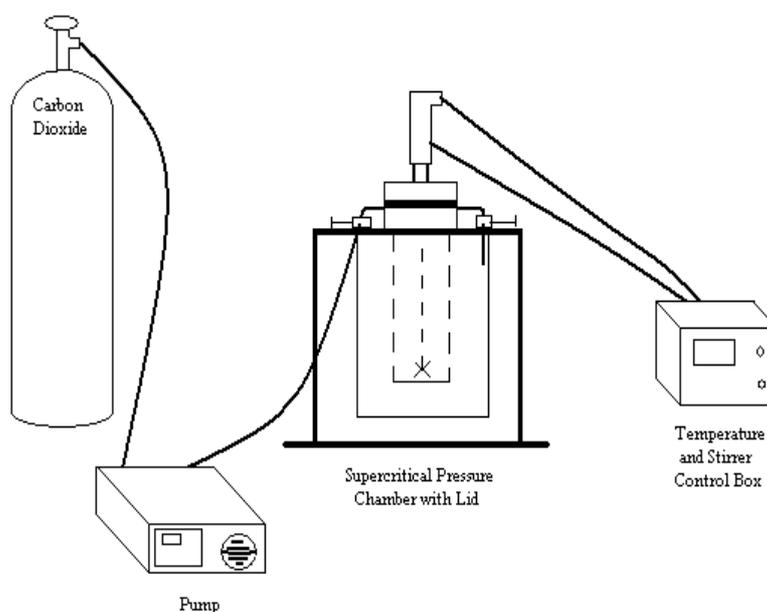


Figure 1. Picture and diagram for the supercritical reactor.

2.5.3. Flame Testing (Limiting Oxygen Index - LOI, and Vertical Flame Testing)

LOI was performed according to ASTM D2863-13 using a Dynisco Polymer Test Limiting Oxygen Index chamber. Treated fabrics (13 x 6 cm) were conditioned at 21°C with 65% RH for 48 h prior to use. The average LOI values of four consecutive measurements were reported [12]. Vertical flame tests were conducted on vertical flammability model VC-2 instrument (Govmark Inc.) with strips of fabrics (30×7.6 cm) according to ASTM D-6413-08 [13].

2.5.4. Scanning Electron Microscope

Scanning electron microscope (SEM) images were taken

using Philips XL 30 ESEM with a magnification of 1500X. Samples were coated with gold for analysis purposes.

3. Results and Discussion

3.1. Synthesis and Structural Characterization of PDP and PDPT

Pdp and pdpt were prepared in excellent yields of 91% and 95%, respectively, and all starting materials were available at low cost. No purification was required at the end of the reaction, and therefore made the synthesis very accessible. Pdp dissolved readily in water but pdpt failed to dissolve. Moreover, pdpt isn't soluble in many organic solvents such

as methanol (MeOH), ethanol (EtOH), isopropanol (*i*-PrOH), hexane, ethyl acetate (EtOAc) and dimethylsulfoxide (DMSO). Pdpt is partially soluble in acetone, ethyl ether, tetrahydrofuran (THF) and acetonitrile (CH₃CN), and it is completely soluble in chloroform (CHCl₃) and dichloromethane (CH₂Cl₂). Like pdp, pdpt is very stable at room temperature over a long period of time (more than two years for pdpt and one and half years for pdp). The chemical

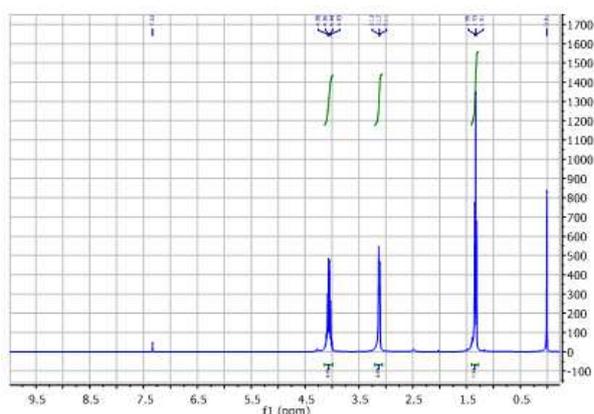
structure of pdpt was studied by NMR, and its data are listed in Table 1 and Figure 2 together with pdp data for comparison. From Table 1, it is clear that sulfur influences the chemical shift and splitting pattern of proton and carbon peaks. In ¹³C NMR, a triplet pattern and a doublet are observed for two carbons of pdpt while three doublets are seen for all three carbons of pdp.

Table 1. NMR data of pdp and pdpt.

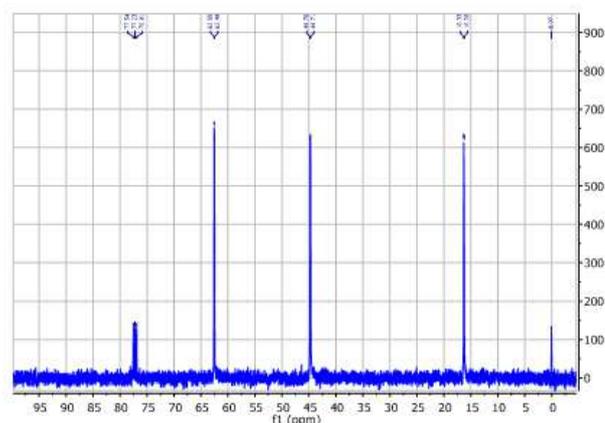
Structure	pdp		pdpt	
	¹ H δ-ppm	¹³ C δ-ppm	¹ H δ-ppm	¹³ C δ-ppm
Spin systems	¹ H δ-ppm	¹³ C δ-ppm	¹ H δ-ppm	¹³ C δ-ppm
a	1.33	16.3	3.65	53.6
b	4.05	44.7	3.22	45.5
c	3.12	62.5	-	-

(a) pdp

Proton NMR

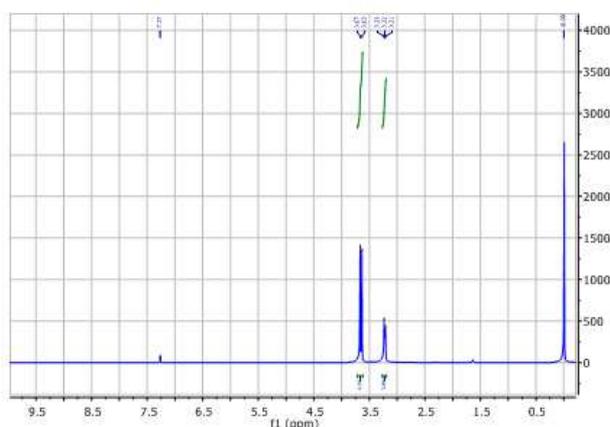


Carbon 13 NMR



pdpt

Proton NMR



Carbon 13 NMR

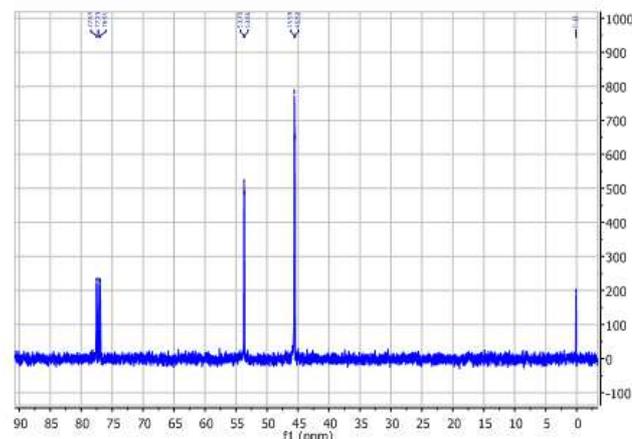


Figure 2. ¹H and ¹³C NMR spectra of (a) pdp (top) and (b) pdpt (bottom).

3.2. Fabric Treatment

Cotton twill fabrics were treated with pdp and pdpt using impregnation solution method. After application, drying, and curing, the treated samples appeared white. The add-on values of 5.6, 7.0, and 14.7 wt% of pdp and 11.2, 14.2, and 17.0wt% of pdpt were obtained.

3.3. Thermal Properties

Figure 3 and Figure 4 show graphs for onset of degradation and % char at 600°C by TGA for compounds, pdp and pdpt, and for untreated and treated cotton samples, and the thermal degradation data were obtained in nitrogen atmosphere. Also, Table 2 shows summaries of values for % add-on, degradation onset (°C), and char content at 600°C.

The onset of degradation of the two chemicals takes place at 178°C, pdpt, and 189°C, pdp, and that of the treated fabrics initiates roughly at 280°C, pdpt, and 270°C, pdp, the flame retardants lower the onset point of the bulk material as compared to the control. Thermal degradation curves of treated fabrics normally comprise of at least two stages: the first is the degradation of the flame retardants, the chemicals, and the second is the degradation of main materials, the fabrics. Depending on concentration of the flame retardants on the fabrics, the first stage may or may not be obvious. It is well known that phosphorus additives reduce the onset temperature for the second stage of treated cellulose by 50°C - 150°C [15, 16].

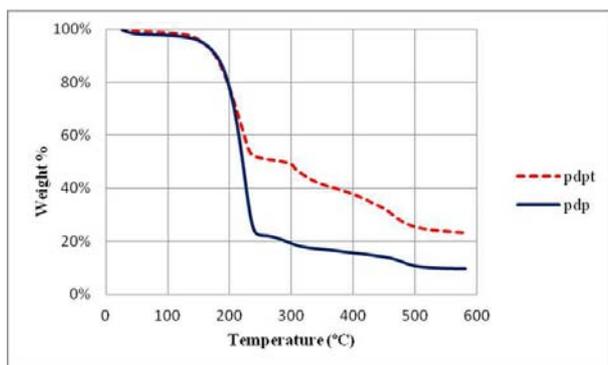
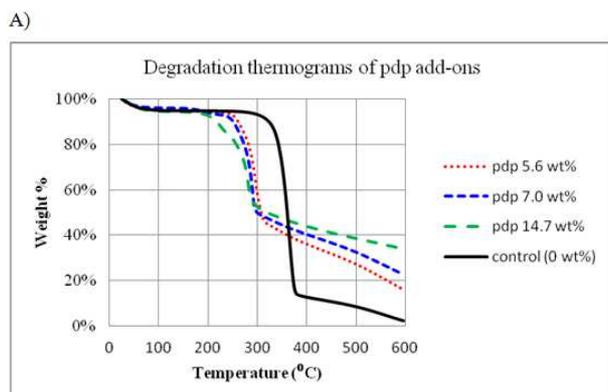


Figure 3. Thermogravimetric Analysis graphs for pdp and pdpt. Top curve (red dot line): degradation thermogram of pdp. Bottom curve (blue solid line): degradation thermogram of pdpt.



B)

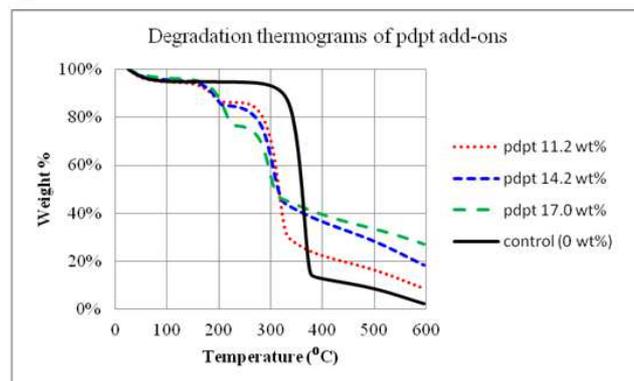


Figure 4. Thermogravimetric curves of untreated control fabric and treated fabrics with pdp (A) and pdpt (B).

With regard to the control, the TGA curve shows the mass loss starting at 300°C, then displaying a turning point at 320°C, which is where the rate of its mass loss reaches its maximum. It then continues losing more weight until it reaches 85% weight loss close to 600°C. During this process, cotton produces volatiles including combustible and non-combustible species, at around 350°C. At a higher temperature, the degradation generates a smouldering phenomenon, leading to a slower mass loss [17].

While the onset temperature for the second stage of all pdp fabrics ranges from 260°C - 280°C following the pattern, it occurs later from 278°C - 300°C for all pdpt fabrics. Pdpt fabrics have a second stage onset temperature close to the onset temperature of the control.

Although both types of fabric achieve add-on values close to each other, their char residues are significantly different. As seen in Figure 4, the mass loss of all treated fabrics is much lower than that of the control. Again, phosphorus flame retardants promote char generation, and therefore, flame resistance in the treated fabrics. While pdp provides much less char residue than pdpt, its treated fabrics have a much higher char yield when compared with pdpt fabrics. An explanation was sought for the fact that pdp was better as a flame retardant than pdpt. In the molecular structure of pdp and pdpt, two effective flame retardant elements P and N are present. However, these two structures differ from each other in two aspects: the number of carbons in phosphorus moiety and the atoms to which the phosphorus are being attached.

Being one of the key elements for flame retardant property in polymeric systems [18, 19], sulfur is supposed to enhance the flame retardancy in pdpt fabrics; as a result, pdpt fabrics are expected to yield higher char residue than the pdp fabrics. While an extra carbon in phosphorus moiety in pdpt may not be the main contributor to the difference in the formation of the char as seen in other derivatives [15], it is likely that when applied onto cotton fabric the sulfur influences the thermal decomposition of pdpt, which could reduce sulfur's synergistic effectiveness in the process of forming char.

Table 2. Char content determination by TGA at 600°C in Nitrogen atmosphere.

Sample add-on (%)		Onset of degradation (°C)	Char% yield at 600°C
Control	0	333.1	2.3
pdp		188.6, 271.9, 456.7	9.7
pdp w/fabric	5.6	276.3	16.2
	7.0	275.2	22.8
	14.7	268.6	33.7
pdpt		178.2, 300.6, 452.1	23.4
pdpt w/fabric	11.2	171.1, 295.9	8.8
	14.2	175.9, 281.8	18.5
	17.0	190.5, 279.9	27.3

3.4. Flame Retardant Properties of Treated Fabric

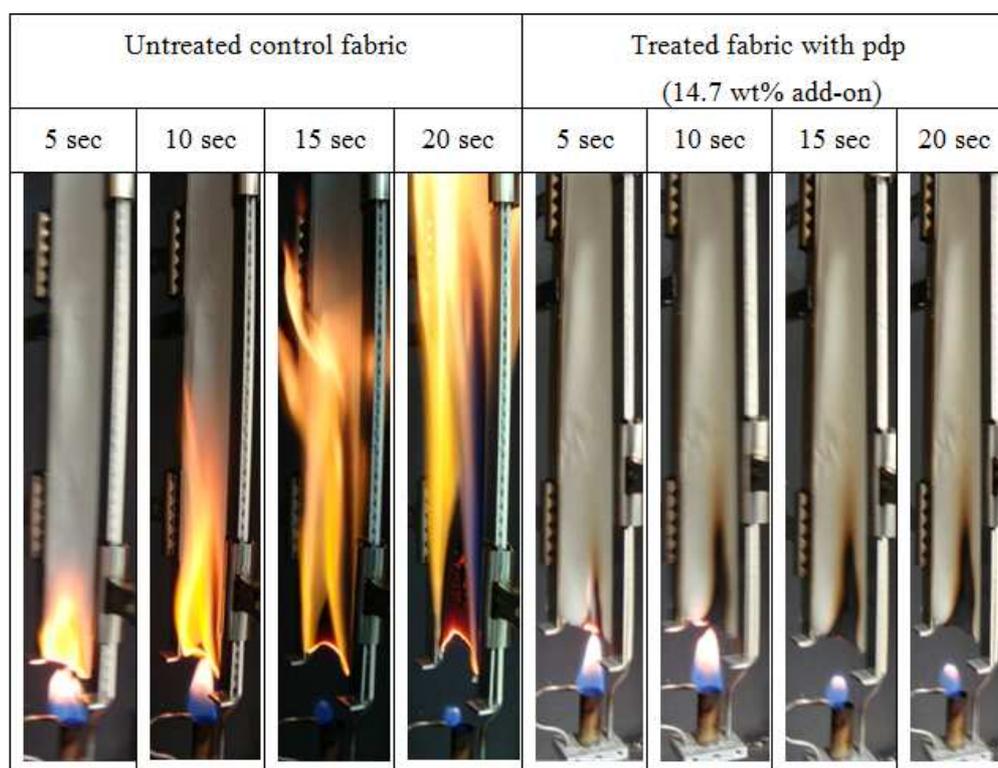


Figure 5. Picture of control untreated twill fabric (left) and treated twill fabric (14.7 wt% add-on, right) during vertical flammability test by ASTM D-6413-11 method.

Limiting oxygen index (LOI) values denote the minimum amount of oxygen needed to sustain a candle-like flame when a sample is burned in an atmosphere of oxygen and nitrogen. Textiles are considered to be flammable when LOI values are below 21% oxygen in nitrogen and are considered to be flame-retardant when LOI values fall in the range of 26-28%. At these LOI values, flame retarded test fabric samples are expected to pass open flame tests in either the horizontal or vertical direction [20, 21]. Passing an open flame test means that the ignited test sample self extinguished following a very short after-flame time, did not glow after the flame extinguished by itself, and showed a char length that did not equal the length of the test sample. LOI values of untreated fabrics are between 17 and 19% oxygen in nitrogen. LOI data for treated fabrics are ranged between 23.6% and 29.8%. Cotton fabrics treated with pdp

provided LOI values of 24.5, 26.5, and 29.8% when add-on values were 5.6, 7.0, and 14.7%. With the pdpt, LOI values of 23.6, 24.0, and 24.8% were realized when add-on values were 11.2, 14.2, and 17.0%, respectively.

Convinced that pdp and pdpt will afford flame resistance to fabrics of different constructions, we tested the treated fabrics by the vertical flame test ASTM D6413-08 and observed gratifying results (Figure 5 and Table 3). Figure 5 contains the images taken during the flammability tests and Table 3 summarizes the test results for the control and highest add-on treated samples. Following 12-second exposure to flame, there was no occurrence of afterglow burning upon the removal of the flame, as well as no melting or dripping during the burning of all pdp and pdpt samples. Char lengths were 8.5 cm for 14.7 wt% of pdp and 9.5 cm for 14.2 wt% of pdpt cotton twill fabrics.

Table 3. Vertical flame test of untreated and treated fabrics by ASTM D6413-08.

	Untreated fabric	pdp treated fabric	pdpt treated fabric
Wt% add-on	0	14.7	14.2
After-flame time (s)	28.8, 24.8	0	0
After-glow time (s)	103.2, 108.5	0	0
Char length (cm)	n/a	8.5	9.5

3.5. Morphologies of the Treated Fabric

SEM micrographs in Figure 6 show the microstructures of the control, 14.7 wt% add-on pdp and 14.2 wt% add-on pdpt. The surface of the control in (a) appears to be smooth and flat while the surfaces in (c) and (e) show the binding of the chemicals. In (d) and (f), the chemicals provide a good flame shield for the underlying material by forming a frothy and swollen outer layer. This protective layer helps keep the material from being destroyed by further burning. The occurrence of the blisters (nodules) can be due to the

entrapment of the decomposition gas between the coating of pdp or pdpt and the twill surface. These blisters continue forming throughout the rest of the treated area (d and f). Some of them become bigger because of the continuing heat causing the expansion of gas; that increases the internal pressure in the blisters and causes an explosion to release the built-up gas as seen in (d and f). Comparing (b) with (d) and (f), it is obvious that the surface of the control is destroyed completely since it doesn't have any protective layer. As a result, the burned control (b) produces a char that is very loose and threadlike.

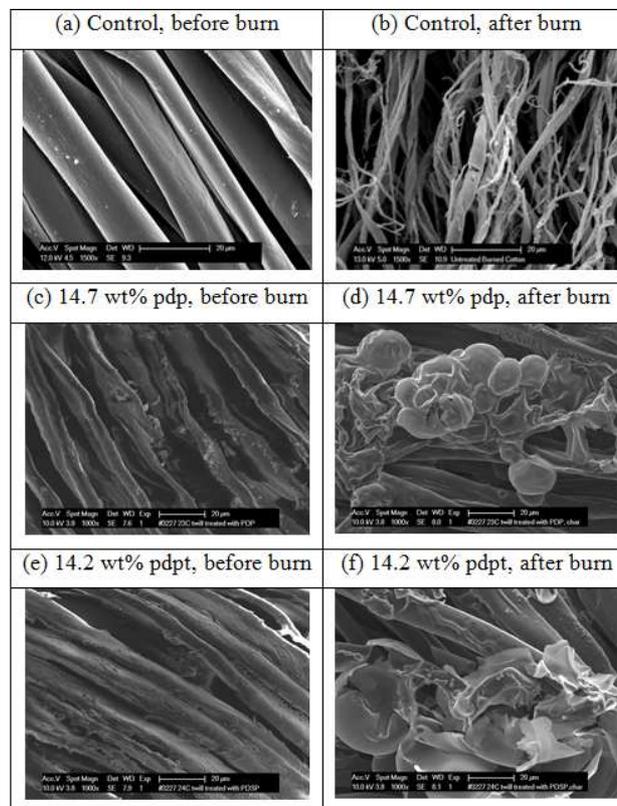


Figure 6. SEM micrographs of different regions of untreated control, 14.7wt% add-on pdp and 14.2 wt% add-on pdpt; before and after burn (a),(b) for control, before and after burn (c),(d) for 14.7wt% pdp, and before and after burn (e),(f) for 14.2wt% pdpt.

4. Conclusion

New phosphorus-nitrogen containing piperazine derivative, tetraethyl piperazine-1,4-diylidiphosphonate (pdp) and sulfur-nitrogen containing tetramethyl piperazine-1,4-diylidiphosphonothioate (pdpt) were successfully prepared. The main differences in the structure of pdp and pdpt were that sulfur replaced oxygen and one carbon was reduced in phosphorus moiety. Tests performed on TGA showed that char yield for pdp treated fabric samples is higher than that of pdpt samples, and pdp samples provided lower onset of degradation than pdpt ones. Fabrics treated with pdp and pdpt passed the vertical flammability test starting at the all levels of add-on%. Pdp treated fabric samples had higher LOI values when compared with pdpt samples at similar add-on levels. SEM micrographs indicated treated fabrics could form a protective layer, which prevented the fabric from being burned completely. Both pdp and pdpt formed a layer wrapping around the cotton fibers to protect them from being destroyed by heat and flame. The inferior action of pdpt could be attributed to the ability to degrade into more gas products arising from the sulfur atom attached to the phosphorus in phosphorus moiety. In conclusion, both piperazine derivatives are promising flame retardants for applications to cotton textiles. Further investigation to understand their flame retardant mechanism is underway.

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