# THE MECHANISM OF ACTION OF PIPERAZINE-PHOSPHONATES DERIVATIVES IN COTTON FABRIC Thach-Mien D. Nguyen, SeChin Chang Brian Condon USDA-ARS Southern Regional Research Center (SRRC) New Orleans, LA

## <u>Abstract</u>

Piperazine-phosphonates additives are known to be very effective flame retardants on different polymeric systems, especially cotton cellulose. In order to understand their mechanism of action, we carried out the investigation of their thermal behavior on cotton fabric by, first, employing the attenuated total reflection infrared (ATR-IR) spectroscopy to characterize the treated fabrics; second, we used the thermogravimetric analysis-fourier transform infrared (TGA-FTIR) to study the evolved gases produced thermally; and finally, we utilized the pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) to detect the species formed during pyrolysis. The experiment's results showed some distinctive details in the thermal degradation of the fabric when applied with these additives.

## **Introduction**

Although the piperazine-phosphonates system technology has been well developed and widely available, one can hardly find any serious work done to study their mode of action. It is only until recently that we can find in textile and non-textile literatures some serious experiments and their results on the thermal characterization for piperazine-phosphonates on cellulose acetate and thermal decomposition and interaction with other compound for non-flame retardant piperazine derivatives (Gaan et al., 2011; Husain et al., 2009; Naik et al., 2008). In this research, we prepared *Diethyl 4-methyl piperazin-1-ylphosphoramidate* (**D**) and *Tetraethyl piperazine-1,4-diyldiphosphoramidate* (**T**) and then engrafted them on cotton fabric. To gain insights into their thermal degradation, the ATR-IR, TGA-FTIR and Py-GC/MS techniques were used to study the control and treated cotton fabrics.

#### **Materials and Methods**

The chemicals used in the experiments were purchased from Aldrich and were used in their original forms except tetrahydrofuran (THF) and acetonitrile (CH<sub>3</sub>CN). These solvents were dried using the Solvent Purification System from Innovative Technology. All reactions were conducted under nitrogen and were monitored by silica gel 60  $F_{254}$  thin layer chromatography (TLC) from EMD. Cotton fabric from 100% cotton cellulose was obtained as twill fabric with the weight of 258 g/m<sup>2</sup> (from Testfabrics, Inc., Style 423). This fabric was desized (starches removed), bleached and was cleared of all resins and finishes.

First, the preparation of **D** and **T** was carried out (Scheme 1) (Nguyen et al., 2012; Nguyen et al., 2014). Once obtained, they were characterized by the NMR Varian 400 MHz spectrometer using CDCl<sub>3</sub> as a solvent. In the NMR data, the <sup>13</sup>C and <sup>1</sup>H chemical shifts are relative to SiMe<sub>4</sub> and <sup>31</sup>P chemical shift to external 85% H<sub>3</sub>PO<sub>4</sub>. Next, both were engrafted on the mercerized cotton twill samples. As the results of this treatment, the following concentrations which are called add-on levels were achieved 18 and 19 wt % for **D** and **T**, respectively. Finally, the control and treated fabrics **D-18** and **T-19** were studied using different analytical techniques ATR-IR, TGA-FTIR and py-GC/MS. In addition, py-GC/MS was also used to study **D** and **T** chemicals.

#### Scheme 1 Synthesis of D and T



# **Results and Discussion**

# ATR-IR

**D-18** and **T-19** do have something in common: they both have the peak characteristics of P=O and O-P-O at around  $1240 - 1228 \text{ cm}^{-1}$  and  $820 - 790 \text{ cm}^{-1}$ , respectively (Shagidullin et al., 1990). The signature peak at 972 cm<sup>-1</sup> is found for **T-19**, which corresponds to the asymmetric vibration of P-N-C group in which the alkyl is not CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> (Shagidullin et al., 1990). At lower frequency, P-N absorption for **T-19** is shown at 772 cm<sup>-1</sup>; this may be due to the attachment of two alkyl groups at N end (Bellamy, 1975). In the range  $820 - 790 \text{ cm}^{-1}$ , O-P-O peak of **D-18** becomes broad and less intense; this may be ascribed to the perturbation from -N-(C)<sub>2</sub> group attached to the NH which links to P (Chittenden and Thomas, 1966). Based on these data, both chemicals remain intact during the treatment process for the fabrics.

# TGA-FTIR

All three profiles share several common features, such as hydrocarbon OH (~ 3300 - 3000 cm<sup>-1</sup>); hydrocarbon CH<sub>2</sub>, CH<sub>3</sub> (~ 3014 – 2600 cm<sup>-1</sup>); CO<sub>2</sub> (~ 2360 - 2310 and 710 cm<sup>-1</sup>); CO (~ 2185 - 2100 cm<sup>-1</sup>); and water vapor (~ 4000 – 3500 and 1800 - 1500 cm<sup>-1</sup>) (Shen and Gu, 2009; Wang et al., 2007). When comparing the evolution profiles for **D**-**18** and **T-19**, it is noticeable that they do possess two similar characteristics: C-O of EtOH (1271, ~ 1040 – 970 cm<sup>-1</sup>) and P-O-C<sub>2</sub>H<sub>5</sub> (730 – 690 cm<sup>-1</sup>) (Garrigues et al., 1997; Shagidullin et al., 1990).

Besides these common features, **D-18** and **T-19** reveal their differences in other signature peaks. Around  $1774 - 1695 \text{ cm}^{-1}$ , **D-18** contains the absorption for P(=O)-OH (Bellamy, 1975). Moreover, this region extends further down to  $1633 \text{ cm}^{-1}$ . In many phosphoramidates and similar materials, P-NH<sub>2</sub> exhibits its deformation absorption in the region  $1650 - 1550 \text{ cm}^{-1}$  (Shagidullin et al., 1990). There are two separate peaks in the overall range  $1186 - 990 \text{ cm}^{-1}$  for **D-18**, which are identified as being in some way related to the CH<sub>2</sub> and/or C-O-H deformation similar to those of the untreated fabric (Shen and Gu, 2009; Wang et al., 2007). While P-N and NH<sub>2</sub> absorptions are seen for **D-18** at ~ 993 – 900 and 823 cm<sup>-1</sup>, P-O-P asymmetric vibration appears for **T-19** at around  $1040 - 1000 \text{ cm}^{-1}$  (Shagidullin et al., 1990). Furthermore, the characteristic absorption for H<sub>2</sub>C=CH<sub>2</sub> from 940 – 900 cm<sup>-1</sup> is detected for **T-19** (Kaljuvee and Kuusik, 2006). During the thermal decomposition, the gases released from the untreated fabric are mainly the products of the reduction of cellulose molecule, the appearance of free radicals, oxidation, dehydration, decarboxylation, and decomposition of cellulose to tarry pyrolyzate-containing levoglucosan, which vaporizes and then decomposes at later time or higher temperature.

# Py-GC/MS

The chromatogram of the untreated fabric comprises of several different species such as aldehydes, ketones, furans, furfural and nucleoglucosan which are similar to those reported in literature (Zhu et al., 2004). When cotton fabric is treated with phosphorus, nitrogen and/or halogen containing FRs, the numbers of gas products are reduced (Nakanishi et al., 2000). In treated fabrics, triethyl phosphate, tetraethyl pyrophosphate and 1-methyl piperazine were detected. There still remain a number of unknown compounds which could not be recognized by the MS library in each chromatogram. In addition to the common species, 2-cyclopentanedione, 3-methyl (or may be methyl cyclopentenolone) and tetraethyl pyrophosphate are detected for **T-19** while 1-methylpiperazine and 4H-pyran-4-one, 3,5-dihydroxy-2-methyl are seen for **D-18**. Among these four compounds, 2-cyclopentanedione, 3-methyl (or may be methyl cyclopentenolone) and 4H-pyran-4-one, 3,5-dihydroxy-2-methyl come from the secondary decomposition of anhydrous sugars (Shen and Gu, 2009) while tetraethyl pyrophosphate and 1-methylpiperazine are the products of the decomposition of **T-19** and **D-18**, respectively.

Py-GC/MS studies on **T** and **D** provide more insights into their own breakdown. Besides triethyl phosphate which is common pyrolysis product for both chemicals, tetraethyl pyrophosphate which was seen in **T-19** was detected again for **T**. Overall, the results from pyrolysis for **T** and **D** show some piperazine and nitrogen containing derivatives. As the results, the appearance of the piperazine and nitrogen containing derivatives likely comes from the secondary pyrolysis of the piperazine moiety; the latter may have dissociated from the mother compounds during the first stage of the decomposition.

# Possible mechanisms for thermal decomposition of T and D

Data from the TGA-FTIR and py-GC/MS reveal that  $\mathbf{D}$  and  $\mathbf{T}$  may decompose by hydrolysis or elimination to release ethanol, phosphate esters, ethylene and the acidic derivatives which may catalyze the formation of char (scheme 2). In the case of  $\mathbf{D}$ , besides the formation of the acidic intermediate, phosphoramidate and ethanol, the

hydrolysis may also result in the cleavage of N-N bond to release the piperazine derivative. It is reported that piperazine-NH containing compound can cleave at N-N bond to release a piperazine species (Naik et al., 2008). The newly formed piperazine derivative is further broken down to nitrogen containing derivatives.

Scheme 2 Proposed mode of action of **D** and **T** 



#### **Summary**

The results showed that a) most main products are enhanced when the residence time is increased; b) the control generates more gas products that all come out at later time; c) most evolved gases from the control are flammable substances which are products of the depolymerization of cotton cellulose; d) both treated fabrics release ethanol, phosphate esters, acidic intermediates, with or without ethylene and nitrogen derivatives and maybe some products from cotton cellulose; f) more activities are observed for **D-18** than **T-19**.

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