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Effect of phosphorus flame retardants on thermo-oxidative decomposition of cotton

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Abstract

The effect of six organophosphorus compounds, including Pyrovatex CP (PCP), diammonium phosphate (DAP), phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP) and triallyl phosphoric triamide (TPT) on the flame retardancy of cotton cellulose was studied. PCP, PA, and DAP are more efficient compared with the other three compounds in improving the limiting oxygen index (LOI) of cotton. The effectiveness of these compounds was investigated using scanning electron microscope (SEM) images of char formed after LOI tests, char content, activation energy of decomposition and heat of combustion data. SEM images showed that DAP, PCP and PA chars maintain the surface morphology during the burning process, which might be due to the formation of a protective layer or crosslinking effect. PA, PCP, and DAP treated fabrics have a higher activation energy of decomposition, higher char content and lower heat of combustion.

Keywords: Phosphorus based flame retardants; Activation energy of decomposition; Heat of combustion; LOI

1. Introduction

Phosphorus based flame retardants (FRs) act in condensed phase mode on cotton cellulose where the phosphorus compounds affect thermal decomposition of the substrates. During the thermal decomposition most phosphorus FRs could form phosphoric and polyphosphoric acids which could dehydrate cellulose and accelerate the formation of char [1]. It is generally believed that most phosphorus FRs react by this mechanism but the efficacy of these phosphorus FRs varies to a great extent. Recent ban of halogen based FRs [2,3] and toxicity issue related to existing formaldehyde based FRs [4,5] has made the research for new FRs even more important. However, current studies in this group have shown that certain phosphorus structures are very effective than others at similar levels of phosphorus content on the fabric [6]. We searched the literature and found no clear explanation to address this phenomenon, which stimulated this effort of study.

To explore flame retardant mechanisms of phosphorus compounds six different phosphorus reagents such as Pyrovatex CP [*N*-methylol-3-(dimethylphosphono)propionamide] (PCP), diammonium phosphate (DAP), phosphoric acid (PA), tributyl phosphate (TBP), triallyl phosphate (TAP) and triallyl phosphoric triamide (TPT) were employed in treatment of cotton fabrics. These phosphorus compounds were chosen because they are either effective flame retardants (PCP, PA, DAP) or potential flame retardants possessing reactivity with cellulose under radical or other chemical conditions. For example, both TAP and TPT contain allyl groups that can be grafted onto cellulose using radical polymerization process. Cotton fabrics treated with similar levels of phosphorus content were tested for limiting oxygen index (LOI) as an indicator of flame retardancy of the treated product. It was found that PCP, PA and DAP treated fabrics with similar levels of phosphorus content had higher LOI values as compared to other FRs. We tried to explain the effectiveness of FRs using techniques such as Scanning Electron Microscope (SEM) images,

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thermograms (Themogravimetric Analyzer, TGA) and heat of combustion from calorimeter. The decomposition activation energy of the treated fabrics was also calculated. Results indicated that DAP, PCP and PA formed more chars and the chars were in different surface morphology from that of the fabrics treated by other three agents during the burning process. DAP, PCP and PA treated fabrics also exhibited higher activation energy of decomposition, higher char content and lower heat of combustion than the other samples.

2. Experimental

2.1. Materials

Cotton fabrics (#400) were purchased from Test Fabrics Inc. (West Pittston, PA). *N*-Methylol-3-(dimethylphosphono)-propionamide or Pyrovatex CP (PCP) was supplied by CIBA Specialty Chemicals Corporation, North Carolina, USA, triallyl phosphate (TAP) was purchased from TCI, America. Diammonium phosphate (DAP), phosphoric acid (PA), tributyl phosphate (TBP) were purchased from EM Science, USA, and triallyl phosphoric triamide (TPT) was prepared according to a method described in literature [6]. The structure of TPT was confirmed by nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy.

2.2. Sample preparation

Cotton fabrics were treated with the FRs at different concentrations and padded through a laboratory padder to control a wet pick up of 100% on the fabrics. PCP, DAP, PA are freely soluble in water and hence were applied from aqueous solutions. TAP, TPT, TBP are almost insoluble in water and thus were applied in acetone onto the fabrics. Pick-up rate is defined as the percentage of weight increase per dry weight of the fabric. To achieve a particular level of phosphorus content the fabrics were treated with FR solutions as shown in Table 1. The treated fabrics were then dried at 80 °C for 5–10 min and conditioned under standard conditions (65% relative humidity and 21 °C) for 24 h. The amounts of phosphorus on the fabric were calculated based on the dry weight gained by the dry fabric (predicted %P) and elemental analysis of treated fabrics (actual phosphorus content % P). The phosphorus content on treated fabrics was measured at the DANR analytical laboratory at the University of California, Davis.

2.3. Measurements

Limiting oxygen index (LOI) values of the fabrics were measured according to ASTM standard method D2863-00. A JD-14 oxygen index tester (MKM Machine Tool Company) was used to determine the volumes of O_2 and N_2 required for ignition and the onset of burning. LOI values were calculated according to the following equation.

$$\mathrm{LOI}\,(\%) = [O_2]/([O_2] + [N_2]).$$

Table 1
Treatment of cotton fabrics with different phosphorus compounds

Flame retardant	Concentration of FR in padding bath (wt%)	Predicted %P values based on padding	Actual %P based on elemental analysis
PCP	6.8	1	1.01
	13.6	2	1.90
	27.2	4	3.86
DAP	4.5	1	1.05
	9.0	2	2.07
	18	4	4.01
PA (85%)	3.8	1	0.96
	7.6	2	1.97
	14.2	4	3.91
TPT	6.9	1	1.21
	13.8	2	1.87
	27.6	4	3.92
TBP	8.6	1	0.93
	17.2	2	1.89
	34.4	4	3.89
TAP	7.0	1	0.98
	14.0	2	2.10
	28.0	4	3.80

The chars (residues) obtained after the LOI tests were collected, and surface morphologies of the chars after LOI tests (only fabrics containing 2% and 4% P) were analyzed using a Scanning Electron Microscope (SEM), Philips XL30TMP (FEICO/Philips, Hillsboro, OR, USA).

Thermal gravimetric analyses (TGA) were carried out under air atmosphere at a heating rate of 5–40 °C/min using a TGA-50 thermal analyzer (Shimadzu Corporation). For kinetic studies heating rates of 5, 10, 20, and 40 °C/min under air were used to collect data. The activation energy of decomposition was calculated using a Kissinger method. Heat of combustion for treated fabrics was determined using ASTM D-240 method using an adiabatic bomb calorimeter. In our experiment we used a Parr 1341 Plain Jacket Calorimeter fitted with 1108 Oxygen Combustion Bomb (Parr Instrument Company, USA). For TGA and combustion analysis the treated samples were ball milled to powder and employed in the tests.

3. Results and discussion

3.1. Flammability of treated fabrics

Table 2 shows LOI values of cotton fabrics treated with six different phosphorus compounds at various phosphorus (P) contents. The LOI of untreated cotton fabric was 18.5. With increase of phosphorus contents the LOI values increase for all FR treated fabrics. There was a greater increase in LOI values from the samples treated by DAP, PA and PCP compared to those that were treated by TBP, TAP and TPT, respectively. The DAP treated samples showed the highest LOI values among all samples at the same phosphorus content. It is understandable to have phosphoric acid and diammonium