CELLULOSE CHEMISTRY AND TECHNOLOGY

THE SUPERIORITY OF RED PHOSPHORUS OVER POLYMETAPHOSPHATE AS FLAME-RETARDANTS ON CELLULOSIC SUBSTRATES

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Red phosphorus and sodium polymetaphosphate, observed as efficient flame-retardants for cotton fabric, have been selected for a comparative study, in quantities evidenced as effective in the author's previously published papers. The vertical flame spread test method, applied for the evaluation of flame-retardancy, was observed to introduce the optimum loading for achieving flame-retardancy, the outcomes illustrating the superiority of red phosphorus over sodium polymetaphosphate. Thermogravimetric explanations agreed with the data of the vertical flame spread test, which might be beneficial for a better understanding of the action of red phosphorus *versus* sodium polymetaphosphate, in terms of flame-retardancy. It is deduced that the efficiency of flame-retardants depends on their structure, as well as on their physico-chemical characteristics.

Keywords: cotton fabric, flame-retardancy, red phosphorus, sodium polymetaphosphate

INTRODUCTION

Nowadays, the need to discover new ways for extinguishing blazing fires and to slow down or prevent the ignition and propagation of fires became a central topic on the agenda of most countries. Toxic gases and the generated smoke polluting the atmosphere are among the other hazards caused by fires, related to the combustibility of materials such as wood, textiles, paper, plastics, etc. With a view to reducing or even extinguishing combustion, flame-retardants (FRs) are applied during or after the manufacturing of such materials, thus modifying the pyrolysis reaction of polymers or the oxidation reaction involved in combustion during heating, decomposition, ignition or flame spreading. The use of flame-retardants in consumer products saved many lives from fires.[1] The familiar additives applied as flame-retardants are inorganic, such as phosphates, halogenated substances, borates, dicyano-diamide, etc.[2-4]

Phosphorous compounds are one of the most important groups of chemicals applied as flame-retardants. It is well known that phosphorous salts do an excellent job in flame retardation. It should be noted that red phosphorus is a flammable solid by itself, readily combustible, but without spontaneous ignition, although it may be also fired by an ignition source, heat, friction, static electrical spark, oxidizing agents, or by a physical impact. Red phosphorus may re-ignite even after the fire is extinguished. The auto-ignition temperature for red phosphorus is 260 °C (500 °F). When red phosphorus burns, phosphorous (V) oxide is produced. The phosphorous (V) oxide absorbs the water vapors from the air, producing corrosive phosphoric acid.[5] The toxic side effects of phosphorus-based flame-retardants are still under debate, since, although they may save lives, they produce noxious fumes during fire.[6]

It has been accepted that phosphorous compounds reduce the formation of flammable carbon containing volatiles, by increasing the conversion of polymeric materials to a char residue during pyrolysis.[7]

The other chemical described in this article is sodium polymetaphosphate, whose structure justifies its inferior ability to impart flame-retardancy. Since it has a polymeric structure, it evidences a high molecular mass (12000-18000) and up to 200 PO_4 units in the chain. Though mainly made up of long chains, it contains up to 10% ring metaphosphate and some crosslinked material.[8] Therefore, it is assumed that its efficiency in imparting flame-retardancy declines, due to the involvement of phosphates in its polymeric chain. The vertical flame spread test method for the estimation of fabric's combustibility, proposed by the author as Mostashari's Flammability Tester (Fig. 1), proves that this polymeric compound illustrates only a low tendency towards imparting flame-retardancy.[9]

On the contrary, a spectacular flame-retardancy is to be anticipated when using red phosphorus. Consequently, the objective of this study is to compare the effectiveness of red phosphorus and sodium polymetaphosphate used as flame-retardants, by the vertical flame spread test and also by thermogravimetry, to provide a better understanding of the advantages of red phosphorus.

EXPERIMENTAL

Materials (Sample preparation)

All specimens, of "plain" construction, with a density of 144 g/m^2, unfinished 100% pure cotton fabric, were laundered and dried. The fabrics (22 cm by 8 cm strips) were cut along the weft direction and pre-washed in hot distilled water. The samples were then dried horizontally at 110 ºC for 30 min in the oven, cooled in a desiccator and weighed with an analytical balance.

With the exception of the first set, *i.e.* the 100% pure cotton samples, all the other sets of specimens were impregnated with suitable concentrations of additives, at 20-22 ºC. The applications were made on the fabrics by squeeze-rolling and horizontal drying in an oven at 110 ºC for 30 min, after which the fabrics were cooled in a desiccator and re-weighed with analytical precision. Prior to the vertical flammability test, the specimens were kept over night under standard conditions: the temperature ranging between 20-22 ºC and relative humidity – between 65-67%.

Methods (Flammability test)

To characterize flammability, a vertical flame spread test method, Mostashari's Flammability Tester, inspired by the procedure described in DOC FF 3-7,[10] has been designed (Figs. 1-2). A description of the flammability test is comprehensively provided in previously published studies.[11-26]

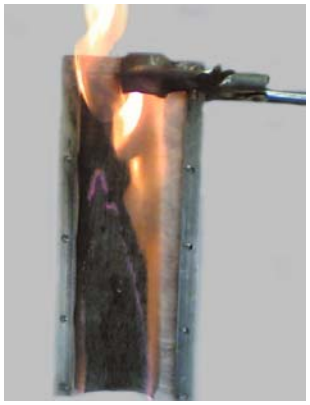

Figure 1: Mostashari's Flammability Tester shortly before the end of the experiment with a low addition of red phosphorus

Figure 2: Mostashari's Flammability Tester during the test with a low addition of sodium polymetaphosphate

Thermogravimetry

Thermogravimetric analysis (TGA) was carried out on a TGA V5.1A Dupont Thermal Analyzer. In the experiment, a pulverized pure cotton fabric, *i.e.* additive-treated cotton fabric, at an optimum addition for imparting flame-retardancy, was used. All specimens were heated from 20 to 600 ºC, in the atmosphere, at a heating rate of 10 ºC/min.

RESULTS AND DISCUSSION

In recent years, the author investigated the effect of sodium polymetaphosphate,[9] as well as that of red phosphorus,[22] in imparting flame-retardancy to fabrics. The optimum add-on percentage values of these chemicals, reproduced according to tables from previous articles, are given together with their new comparative TGA curves, for a better understanding of the superiority of red phosphorus over sodium polymetaphosphate in imparting flame-retardancy. In fact, the present study reveals the excellent capacity of red phosphorus to impart flame-retardancy, compared to sodium polymetaphosphate.

The optimum additive contents characterizing the treating solution formulae are given in Table 1. It should be mentioned that untreated cotton fabric required 30 s to burn completely, however no flame spread could be detected when optimum tabulated additions were applied.

Generally, phosphorous compounds possess high flame-retardation efficiency. When burning, the phosphorus-based flame-retardants form foamed cellular crusts as barriers between the flame and the underlying polymeric materials, which results in the prolongation of the burning time or in the extinguishment of fire. It has also been reported that phosphorus-containing flame-retardants may operate in two ways, namely:[27]

(a) by interrupting the exothermic process and thus suppressing combustion by capturing free radicals;

(b) by increasing the char yield by means of redirecting the chemical reactions generating carbon residue rather than CO or CO_2, and by the formation of a surface layer on the protective char.

The action mode of phosphorous compounds has also been discussed.[28-30] Jolles and Jolles[28] stated that, on heating, phosphorous compounds form phosphoric acid, which covers the polymer surface as a stable coating material, thus transforming it into a carbonaceous residue. However, Tohka and Zevenhoven[29] suggested the same pathway, occurring in the solid phase, through thermal decomposition, converting the phosphorous compounds into phosphorous acid, which extracts water from the pyrolysing substrate, transforming it into char. Meanwhile, Troitzsch[30] stated that phosphorous compounds are particularly effective in high oxy-content materials, such as cellulose and oxygen-containing plastics, the reactions occurring in the condensed phase and at a high oxy-content, extracting water from the pyrolysing substrate. More exactly, the phosphoric acid or phosphorous (V) oxide forms esters and dehydrates the oxygen-containing polymers, thus causing charring.[30]

As to sodium polymetaphosphate, made up mainly of long chains, it contains up to 10% ring metaphosphates and some cross-linked material.[8]

In fact, although sodium polymetaphosphate has a complex chemical structure, the formula $Na_6P_6O_{18}$ is generally ascribed[31] to it. Despite the presence of phosphate in its polymeric structure, its efficiency in imparting flame-retardancy declines, due to the involvement of phosphorus in its polymeric construction, together with other elements so that, indeed, its flame-retarding ability is confined and rather hidden as to the effect of red phosphorus. Actually, this compound evidenced a tendency towards flame-retardancy, *i.e.* a high amount (around 36.78%) of this salt is needed to impart flame-retardancy to the cotton substrate (Table 1). On the contrary, high flame-retardancy was attained when using a much lower content of red phosphorus, *i.e.* only a 3.95% addition of this chemical was sufficient to show its flame-retardancy on the cotton substrate, meaning spectacular flame-retardancy attained with a much lower content of chemical. Since phosphorus has not been mixed with other elements in the structure of red phosphorus, its action is quite free and vigorous.

Comparative TG curves of untreated and red phosphorus-treated cotton fabric, as well as those of cotton fabric treated by the optimum additions of sodium polymetaphosphate, are shown in Figure 3, which illustrates that the weight loss for the pure cotton fabric began at around 350 ºC, while for the fabrics supported with red phosphorus and/or sodium polymetaphosphate, the weight loss started at a considerably lower temperature zone, following the sequence:

Red phosphorus < sodium polymetaphosphate < untreated cotton fabric

Indeed, thermal analysis data (the TG curves in Fig. 3) demonstrate that these chemicals catalyze the dehydration process of the cellulosic substrate. Quite noticeably, according to the chemical theory, the role of certain flame and glow retardants is to promote pyrolysis products, when the polymer is subjected to thermal degradation. Ideally, the carbon present in cellulose could be confined to the solid phase during thermal decomposition, after which degradation could be achieved as a result of the catalytic dehydration shown below:

$$(C_6H_{10}O_5)_X \longrightarrow 6xC + 5XH_2O$$

Generally, the dehydration of the cellulosic substrate is catalyzed under the action of dehydrating agents, such as acidic or neutral species that form Lewis acids at high temperatures, *i.e.* they function exclusively when heated, being stable at normal temperature.[32] Note that the complete dehydration of cellulose accounts for around 60% of the weight loss, at around 350 ºC, in the presence of air,[33] while the weight loss for specimens treated at a temperature $t < 350$ ºC exceeds this limit.

Table 1
The effect of red phosphorous- and sodium polymetaphosphate-supported cotton fabric at an optimum addition for flame-retardancy

Set	Material	Treating solution formulae	Optimum additive content, wt%	Char length, cm
A	Sodium polymetaphosphate	0.45	36.78	0.2
B	Red phosphorus	0.40	3.95	1.5
C	Untreated cotton fabric	-	-	-

Each experiment was repeated five times and the results averaged.
Note: For flame-retarded (FR) samples, the char length was ≤ 2.0 cm

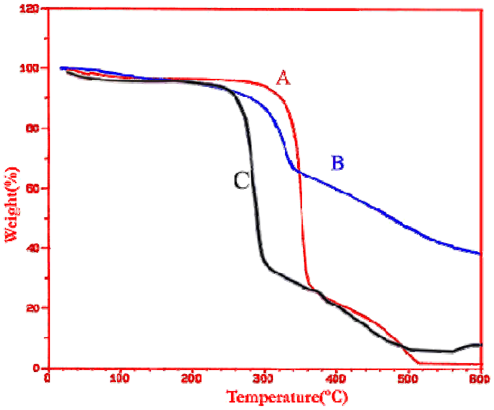

Figure 3: Comparative TG curves for A – pure cotton fabric, B – sodium polymetaphosphate-treated cotton fabric, and C – red phosphorus-treated cotton fabric, at an optimum addition to impart flame-retardancy

Indeed, red phosphorus-supported cotton fabric has been profoundly well-catalyzed and the dehydration of carbohydrates occurred more significantly as compared to sodium polymetaphosphate-supported cotton fabric and/or untreated substrate. Hereupon, higher amounts of water could be released over a temperature range below 350 ºC, which correlates well with the superior flame-retardancy of red phosphorus. It is worth mentioning that the liberation of an additional amount of water, compared to sodium polymetaphosphate-supported cotton fabric and/or untreated cotton substrate might lead to flame dilution and the reduction of its temperature, thus assuring the superiority of red phosphorus in flame retardation.

CONCLUSIONS

When red phosphorus and/or sodium polymetaphosphate were used on the cotton fabric, the TG spectra were lower in comparison with the normal pyrolysis of the pure cotton substrate. That is, the treatments caused a well-timed, lower temperature range of their thermal degradation zone, as compared to that for the untreated cotton substrate. Indeed, the treated substrates displayed a weight loss priority around 300 ºC, as compared to the untreated one, where it occurred around 350 ºC. Moreover, the catalytic action of these additives could be illustrated *via* the excessive weight of the residues in their TG spectra. That is, the formation of solid char rather than the generation of flammable volatile pyrolysis products could be seen in the TG spectra. This means that the treatments assured the pyrolysis of the cellulosic substrate for producing more char in comparison with the untreated fabric. Therefore, the production of flammable volatiles could be confined, and solid phase and water vapor were yielded, which supports the chemical theory explaining flame-retardancy. Furthermore, thermogravimetric results agree with those of the vertical flame spread test. Ultimately, it seems that red phosphorus has vigorously catalyzed the combustion process of the substrate, enhancing the oxidation of the carbon residue, plausibly by the activation of atmospheric oxygen. However, sodium polymetaphosphate has not, demonstrating only a slight tendency towards such phenomena. In fact, these sequences could be also seen in the comparative TG spectra, such a behavior being assigned to its multiple physico-chemical characteristics, due to the polymeric chain involvement. Indeed, the efficiency of this polymeric (complex) phosphorus-containing chemical is much lower than that of red phosphorus! These deductions could imply that the efficiency of the flame-retardants depends on the structural nature, as well as on the physico-chemical characteristics of the additives.

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