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TG studies of synergism between red phosphorus (RP)–calcium chloride used in flame-retardancy for a cotton fabric favorable to green chemistry

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Abstract The combined effect between calcium chloride and red phosphorus (RP) on the flame-retardancy of a cotton fabric (woven construction massing 152 g/m^2) has been studied in this work. The laundered bone-dried massed samples were impregnated with suitable concentrations of individual aqueous red phosphorus suspensions and/or calcium chloride solutions and some bunches were impregnated with appropriate admixed solutions of the both chemicals. An acceptable synergistic effect was then experienced by using an admixed bath containing 0.20 F red phosphorus and 0.20 M calcium chloride for impartation of flame-retardancy to a cotton fabric. By using a vertical flame spread test the optimum mass of the mixture needed to donate flame-retardancy was obtained to be about 5.88 g anhydrous additives per 100 g dry fabric. Thermogravimetry (TG/DTG) results concerning untreated and treated cotton fabrics at the optimum addition were obtained and their curves were compared and commented, fortifying the flame spread tests outcomes. It can be deduced that the applied treatment functioned as a catalyst at the combustion's temperature of the polymeric substrate and, thermosensibilized the combustion process. This synergism is in favor of green chemistry as well as the economical and industrial view points.

Keywords Calcium chloride · Flame-retardancy · Green chemistry · Red phosphorus · Synergism · Thermogravimetry

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Introduction

Cotton, the most commonly used textile fiber, is also highly combustible. So its flame-retardancy finishing and garments made by this fiber becomes necessary to improve human safety under many circumstances. Nowadays most of the efforts in this area have been focused on reducing cotton's flammability [1].

Flame-retardants are chemicals that can be applied to materials such as: fabrics, set pieces, props and costumes etc. to inhibit their ability to burn. Note that these products are not called flame-proofed (although industries still prefer to call them that way). In fact, it is impossible to prevent a flammable material from burning if enough heat is applied to it. Nevertheless, a flame-retardant material will keep the fire from a burning source for more than a few seconds, thus reducing the chance of flame spreading [2].

Halogen fire-retardant systems usually are used for this purpose, however, in spite to show high efficiency; these systems give nasty combustion products which possess a number of negative characteristics, such as corrosiveness, toxicity, etc. Nevertheless several halogen-free fire-retardant additives are still commercially available, acting with a number of mechanisms depending on their chemical structure [3].

On the other hand nowadays much current attention has been paid to phosphorus compounds, as it is known that they are quite effective in flame protection of materials [4].

Moreover synergistic studies between chemicals are also one of the most beneficial and interesting subjects on flame-retardation; in fact combining fire-retardant additives could be more effective than using them individually. Formulations of at least two fire-retardants may have synergistic, and/or antagonistic effects. Actually an additional effect is the sum of the effects of the mixed

components taken independently. Synergism means that the observed effect is greater than individual efficiency of each additive, on the contrary antagonism stands for their adversely effectiveness [5].

The aim of this work is to study the flame-retardancy improvement, concerning calcium chloride in a mixture with red phosphorus, so that their binary influence as effective flame-retardants for a cotton fabric could be achieved.

Experimental section

Materials (sample preparation)

All fabrics were woven (plain) construction massing 152 g/m^2, unfinished 100% cotton fabric, laundered and dried. The samples were then cut along the warp direction in 8 × 22 cm strips and pre-washed in hot distilled water. They were then dried horizontally at 110 °C for 30 min in an oven, cooled in a desiccator and massed with an analytical precision. This method has also been developed and introduced in the previous publications of the corresponding author including in this journal [6–16].

With the exception of the first set, all other sets of fabrics were impregnated independently at 20–22 °C, dipped and stirred for 10 min with suitable concentrations of red phosphorus and/or calcium chloride or their combinations. They were then squeeze rolled and dried horizontally in an oven at 110 °C for 30 min, afterwards, they were cooled in a desiccator, re-massed with an analytical precision. The treated fabrics were then kept overnight under laboratory's conditions before carrying out the vertical flammability test, so that their humidity regained during this period. The laboratory's environment was in average temperature ranged between 20 and 22 °C and the relative humidity (RH) ranged between 65 and 67%.

Method of evaluation

Flammability test

The vertical flame spread test method by impression of the procedure described in DOC FF 3-71 [17] was employed to assess the flammability of the fabrics. It has been designed and named as Mostashari's Flammability Tester (Fig. 1). This method was also accepted for publication in the corresponding author's previous articles [6–16].

Thermogravimetry

Thermogravimertey was put in practice with a TGA V5.1A Dupont 2000 thermal analyzer. This apparatus was used to measure the mass loss during thermal degradation. To fulfill thermal analysis, a pulverized untreated cotton fabric, and treated fabrics at optimum additions were put in practice. All specimens were heated from 20 to 500 °C in air at a heating rate of 10 °C/min.

Fig. 1 Mostashari's Flammability Tester with a partly burned fabric at the end of the failure of combustion

For a better understanding about the synergistic effect of calcium chloride with red phosphorus, the thermogravimetric analyses and the appropriate synergism at the optimum addition to achieve flame-retardancy were also accomplished.

Results and discussion

The experimental results are listed synoptically in Table 1. The vertical flame spread tests were carefully carried-out to measure the burning times in sec in column 6. Char lengths are shown in column 7. The states of the samples after the accomplishment of the tests are given in column 8, CB means completely burned, PB for partly burned, and FR stands for flame-retarded. The burning rates in cm/s could be calculated by dividing the length of the burned fabrics by their burning times are illustrated in column 9.

It can be deduced from the experimental results of the fifth column that the efficient quantity of red phosphorus as a flame-retardant expressed in g per 100 g dried fabric is about 3.95%. This figure for supported fabrics by calcium chloride has also been obtained as 6.66%. These data were obtained by applications of 0.4 F and 0.35 M bath solutions of red phosphorus and calcium chloride respectively. Moreover the results of the fifth column illustrate the combination of 0.20 F red phosphorus and 0.20 M calcium chloride solutions donated about 5.88% loading of the mass into the specimens. This addition is around the efficient amount of impartation of flame-retardancy for a cotton fabric. The tabulated results show that inadequate quantities of red

Table 1 Synergistic effect of deposited "red phosphorus (RP)–calcium chloride" on the flame-retardancy imparted to cotton fabric (woven 152 g/m^2)

Set no.[a]	Treating solution P (formalities)	Treating solution $CaCl_2$ (molarities)	Treating solution (admixed bath) P–$CaCl_2$ respective (formalities and/or molarities)	Percent add-on drying at 110 °C and massing	Burning time (s)	Char length (cm)	State of the fabric[b]	Burning rate (cm/s)
1	Untreated	–	–	_	27	–	CB	0.81
2	0.30	–	–	2.30	16.30	–	CB	1.35
3	0.35	–	–	3.00	4	3.6	PB	0.90
4	0.40	–	–	3.95	–	1.5	FR	–
5	–	0.30	–	4.53	15.70	–	CB	1.40
6	–	0.33	–	5.70	8	7.3	PB	0.91
7	–	0.35	–	6.66	1	1.4	FR	–
8	–	–	0.15–0.15	3.71	25	–	CB	0.88
9	–	–	0.18–0.18	5.51	5	3.4	PB	0.68
10	–	–	0.20–0.20	5.88	1	1.5	FR	–

For flame-retarded (FR) samples char length ≤2.0 cm

[a] Average of five tests for each set of samples

[b] CB stands for completely burned, PB for partly burned, and FR stands for flame retarded

phosphorus and/or calcium chloride decrease the burning times and therefore increase the burning rates, which agrees with the general trend reported by Reeves and Hammons [18].

That is: under the optimum limit addition of these add-ons, a tendency to decrease in the burning time and the increase in the burning rate could be observed. Indeed the latest-mentioned investigators distinguished that the inefficient quantities of certain flame-retardants accelerate the burning process of cotton fabric [18]. Hereupon by deposition of insufficient quantities of some flame-retardants, the imperfect rapid burning deformation could occur and a decrease in burning time and an increase in the burning rate is the outcome. Plausibly this is due to the relative rigidity donated to the substrate by the use of some additives such as the afore-mentioned add-ones. It is likely that the feedback of heat into the bulk's surface could make it susceptible to participate in a rapid, uncompleted surface combustion. However if adequate amount of the above-mentioned addition are deposited onto the cotton fabric, the presence of generated combustion dust conducts away the heat from the cellulosic substrate at a comparable rate, which the heat is being supplied by the flame, so the flame-retardancy could be enhanced.

TG/DTG curves concerning untreated cotton fabric (1.7697 mg) and treated fabrics with optimum addition of calcium chloride (2.4705 mg) and supported fabric by red phosphorus (2.0108 mg) and their synergism (2.2314 mg) were obtained (Figs. 2, 3, 4, 5, 6).

For red phosphorus supported fabric the major mass loses was around 290 °C (Fig. 3); note that the combustion temperature of pure cotton substrate is about 350 °C

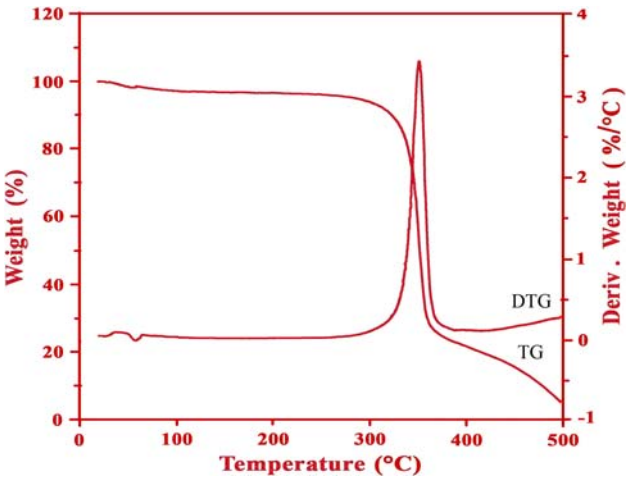

Fig. 2 TG/DTG of untreated (UT) cotton fabric

(Fig. 2). For fabric treated with calcium chloride this temperature was about 300 °C (Fig. 4). The TG/DTG curves concerning synergistic effect of the treated sample illustrated a significant mass loss occurred rather smoothly below the thermal degradation zone of pure cellulose that is around 310 °C (Fig. 5). Ultimately the comparative TG curves illustrate the enhancement of mass losing occurring either for individual additives at their optimum addition or their synergism combination with regard to pure cotton fabric (Fig. 6). So it can be deduced that the applied treatment functioned as a catalyst at the combustion's temperature of the polymeric substrate and, thermosensibilized the combustion process. This action is discussed in the Chemical Action Theory. According to this theory the

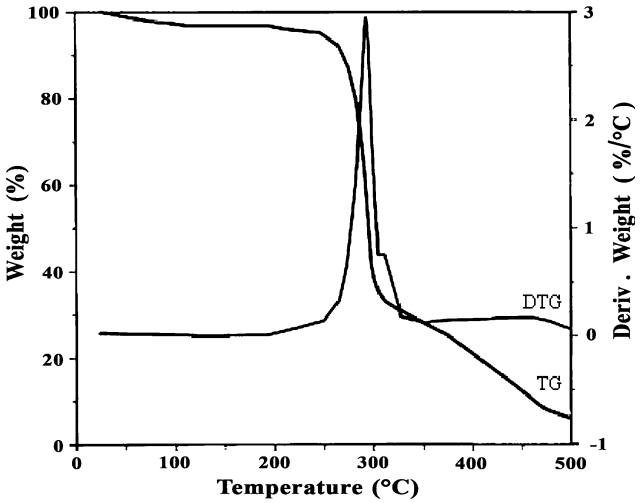

Fig. 3 TG/DTG of FR cotton fabric treated by the optimum addition of RP to achieve flame-retardancy

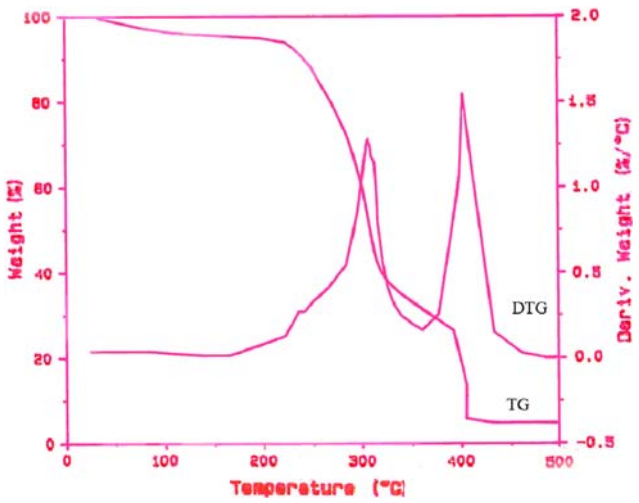

Fig. 5 TG/DTG of FR cotton fabric treated by the synergism of $CaCl_2$-RP at optimum addition to achieve flame-retardancy

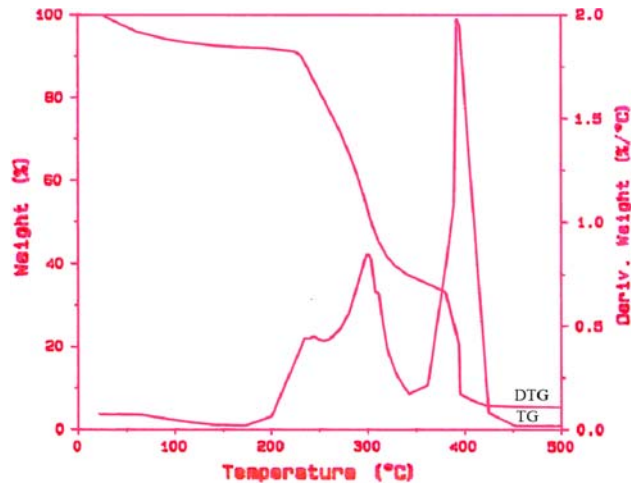

Fig. 4 TG/DTG of FR cotton fabric treated by the optimum addition of $CaCl_2$ to achieve flame-retardancy

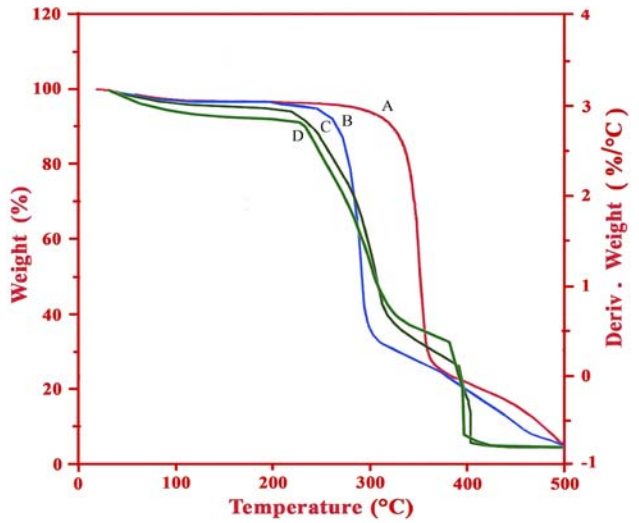

Fig. 6 TG comparative curves. (A) TG spectra of untreated cotton fabric. (B) TG spectra of FR cotton fabric by the RP, at optimum addition. (C) TG spectra of FR cotton fabric by the $CaCl_2$, at optimum addition. (D) TG spectra of FR cotton fabric by the synergism of RP/$CaCl_2$, at optimum additions

action of certain flame and glow retardants is to promote the pyrolysis products when the polymer is subjected to thermal degradation. Ideally the carbon present in cellulose could be forced to the solid phase during the thermal decomposition, and then the degradation could be pushed through a catalytic dehydration shown below [19]:

$$(C_6H_{10}O_5)_x \rightarrow 6xC + 5xH_2O$$

It is mentionable that halogenated flame-retardants act in the vapor phase. That is; they actually interfere with the chemistry of the flame's propagation. Chlorine and bromine covalent bond containing chemicals are both effective in this role [20]. These materials introduce halogens into the combustible matrix and during combustion various halide species are released including hydrohalides that react via free-radicals and highly reactive combustion products, thereby reducing combustion reactions [21].

$$^{\bullet}OH + HX \rightarrow H_2O + {}^{\bullet}X$$

$$^{\bullet}H + {}^{\bullet}X \rightarrow HX$$

$$RH + {}^{\bullet}X \rightarrow HX + {}^{\bullet}R$$

It is worthy to mention that; the use of halogenated additives in polymers despite having a number of technical advantages in applications, has also some drawbacks, e.g. they tend to produce environmental and health problems due to the evolution of nasty corrosive and obscuring smoke during combustion, which caused a great concern in Europe. Therefore non-halogenated systems are becoming

of interest. Hence as an alternative, much effort has been done to use phosphorus-based compounds to be substitutes for halogenated additives [22].

It is mentionable that phosphorus compounds mainly influence the reactions taking place in the solid phase. By thermal decomposition the flame-retardant is converted to phosphorus acid which in the condensed phase extracts water from the pyrolysing substrate, causing it to char. Meanwhile, some phosphorus compounds may act, similar to halogens, in the gas phase as well. That is; they act by a radical trap mechanism [23].

The phosphorous containing additives can also catalysis the clipping of the polymer chains, thereby reducing the molecular mass.

Red phosphorous is an example of a retardant, acting by chemical action mechanism. The non-oxidative pyrolysis of the polymer could be retarded by phosphorous, which acts by scavenging the free radicals formed during the thermal degradation of the polymer. They act similar to halogenated flame-retardants but only in the condensed phase [24].

Conclusion

Red phosphorus is a flammable solid, nevertheless if applied into polymers and/or in the synergism serves as a flame-retardant. In this work the synergism of red phosphorus (0.20 F) and calcium chloride (0.20 M) caused 5.88% dry loading into a cotton fabric and demonstrated a desirable performance of flame-retardancy. It is a reasonable addition in aggregate. This seems due to their collaboration to promote the formation of non-volatile char residues and less flammable gases, when the treated polymer is subjected to thermal decomposition. By thermogravimetric analyses it can be deduced that the applied treatment functioned as a catalyst at the combustion's temperature zone of the polymeric substrate and, thermosensibilized the combustion process.

Although each of these chemicals subject to be used individually may lead environmental problems by generating great quantities of nasty toxic and corrosive fumes during combustion, so restricting their applications. Nevertheless the use of a decreased amount of the combined additives to achieve a desirable performance of flame-retardancy is in compliance with the green chemistry's view points as well as the economical and industrial advantages. Moreover the low addition of this combination may also be beneficial to avoid destructive physical characteristics, such as poor-handle etc. which could affect the physical and mechanical properties, where applied onto the substrate.

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