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THERMOGRAVIMETRY STUDIES OF COTTON FABRIC'S FLAME-RETARDANCY BY MEANS OF SYNERGISM OF LITHIUM BROMIDE AND ANTIMONY TRIOXIDE

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The synergism of lithium bromide and antimony trioxide on the flame-retardancy of a cotton fabric (woven, plain 150 g m^2) has been investigated in this study. The impregnations of cotton fabric with suitable individual additives and/or their appropriate admixed formulation were carried out. The flammability test has also been fulfilled using described procedure, in the earlier published articles. Their outcomes comply with thermogravimetry's data. Moreover the latest mentioned outcomes support the catalytic effect of this synergism. Explanation of the data could be in favor of existing flame-retardation's theories. Ultimately this synergism is in compliance with the green chemistry and economical viewpoints.

Keywords: *antimony trioxide, chemical action theory, condensed phase retardation, flame-retardancy, free radical theory, lithium bromide, synergism, thermogravimetry*

Introduction

In recent years, polymeric composites are widely used in the production of new engineering materials. It is perceived as the reflection of technological development. Meanwhile the polymeric composites are promising, due to their economically versatile applicability and good mechanical properties. They are used in many applications, such as housing materials, transport and electrical engineering. Due to the increasing demands on polymers, the development of safe and environmental friend flame-retarded polymers has gained great importance nowadays. Many types of flame-retardants are added to polymers to reduce their flammability. Flame-retardants are defined as chemicals that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing down or inhibiting them [1].

When used individually, they are effective in improving some, but not all of the physical properties of the virgin polymers [2]. Many types of flame-retardants are used in consumer products. They are mainly phosphorus, antimony, aluminum and boron-containing compounds, chlorides and bromides [1].

Combining fire-retardant additives can provide more effective results than using them individually. Formulations with at least two fire-retardants may have synergistic, and/or antagonistic effects. An additive effect is the sum of the effects of the two components taken independently. Synergism means that the observed effect is greater than additive, while an antagonistic effect is less than an additive [2].

In the flame-retardation study, many systems such as phosphorus-nitrogen, halogen-antimony, metallic hydroxide, red phosphorus (RP) have been found to have synergistic effects [3].

The aim of this investigation is to study the flame-retardant efficiency of lithium bromide's synergism with antimony trioxide by using the vertical flame spread test. Moreover the thermogravimetry's curves, i.e. their (TG/DTG) data have been obtained, compared and commented.

Experimental

Materials

All fabrics were woven (plain) construction weighing 150 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 Mostashari *et al*. [4–12].

It is mentionable that with the exception of the first set; all other sets of fabrics were impregnated independently at 20–22°C, by dipping and stirring for 10 min into the suitable concentrations of antimony trioxide and/or lithium bromide or their combinations. They were then squeeze rolled and dried horizontally in an oven at 110°C for 30 min, afterwards, they were

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Fig. 1 Mostashari's flammability tester with a flame-retarded fabric after the end of the flammability test

cooled in a desiccator, re-massed with an analytical precision. The treated fabrics were 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%. The above-mentioned method has also been described in the previous investigations and also in the accepted articles in this Journal [4–12].

Methods

Flammability tester

A vertical flame spread test method following the procedure described in DOC FF 3-71 [13] was employed to determine the flammability of the fabrics. It has been designed and named as Mostashari's flammability tester (Fig. 1). The description of this tester has also been described in previous published articles including in this Journal [4–12].

Thermogravimetry

This technique, measures the mass changes of a specimen as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Hence for a better understanding about the role of synergism of lithium bromide together with antimony trioxide on the flame-retardancy donated to cotton fabric, the thermogravimetry of pure cotton, and the treated one with lithium bromide, antimony trioxide as well as their synergism at optimum addition for flame-retardancy were accomplished.

TG curves obtained for each specimen with a TGA V5.1A Dupont 2000 Thermal Analyzer. This apparatus was used to determine the mass loss during thermal decomposition. To fulfill thermogravimetry, a pulverized pure cotton fabric, and the treated fabric with the additives at optimum additions were put in practice. All samples were heated from 20 to 500°C in air at a heating rate of 10°C min^{-1}.

Results and discussion

The experimental results are listed in Table 1. By using our vertical flammability tester the optimum efficient content of additives applied as flame-retardants into the cotton fabric are summarized to ascertain the burning characteristics of the specimens. In column 6 burning times are given.

The burning rates in cm s^{-1}, calculated by means of dividing the length of the burned samples by their burning times, are shown in column 7. Char lengths are illustrated in column 8. The states of the samples after the fulfillment of the vertical flame spread test are given in column 9, CB stands for completely burned and FR means completely burned.

Table 1 Synergistic effect of deposited 'antimony trioxide-lithium bromide' on the flame-retardancy imparted to cotton fabric (woven 150 g m^{-2})

Set* No.	Treating solution Sb_2O_3 (formalities)	Treating solution LiBr (molarities)	Treating solution (admixed bath) Sb_2O_3– LiBr respective (formalities and/or molarities)	Percent add-on drying at 110°C and weighing	Burning time/s Sd**	Burning rate/ cm s^{-1}	Char length/ cm	State of the fabric***
1	untreated	–	–	–	27±1.10	0.81	–	CB
2	0.16	–	–	8.89	28.3±1.21	0.78	–	CB
3	0.17	–	–	16.03	–	–	2.0	FR
4	–	0.10	–	2.71	14.3[#]±1.86	1.54	–	CB
5	–	0.15	–	3.85	–	–	0.8	FR
6	–	–	0.025–0.013	2.15	10[#]±1.97	2.20	–	CB
7	–	–	0.050–0.025	6.81	1±1.99	–	1.0	FR

*Average of 5 tests for each set of samples; **Sd stands for standard deviation; ***CB stands for completely burned and FR stands for flame-retarded; [#]Longitudinal (on the surface) burning. Note: for flame retarded (FR) samples char length ≤2.0 cm

It can be attributed from the tabulated results in the fifth column that the efficient amount of antimony trioxide as a flame-retardant expressed in g per 100 g cotton fabric is about 16.03%. This figure for lithium bromide supported fabric has also been determined as 3.85%. However the results of fourth and fifth columns show that the combination of 0.05 formal antimony trioxide and 0.025 molar lithium bromide donated around 6.81% mass loading to the samples. This addition is around the optimum quantity for impartation of flame-retardancy to the cotton fabric. TG/DTG curves concerning untreated cotton fabric (1.0768 mg) and treated fabrics with optimum addition of lithium bromide (1.6060 mg) and its synergism with antimony trioxide (2.8133 mg) were obtained (Figs 2–6).

For lithium bromide treated fabric the mass loss occurred mainly at temperature around 260°C. For antimony trioxide supported fabric this temperature was around 350°C. However for their synergism, the major mass loss obtained at around 290°C.

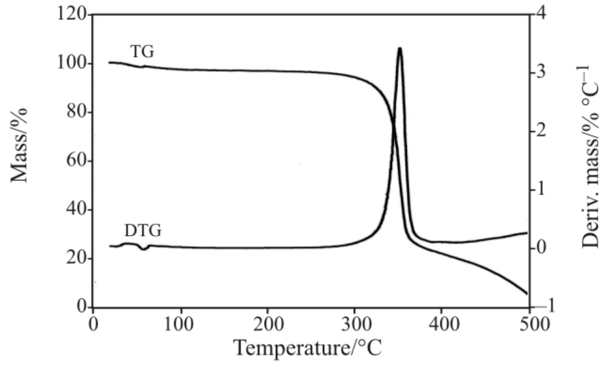

Fig. 2 TG/DTG of untreated (UT) cotton fabric

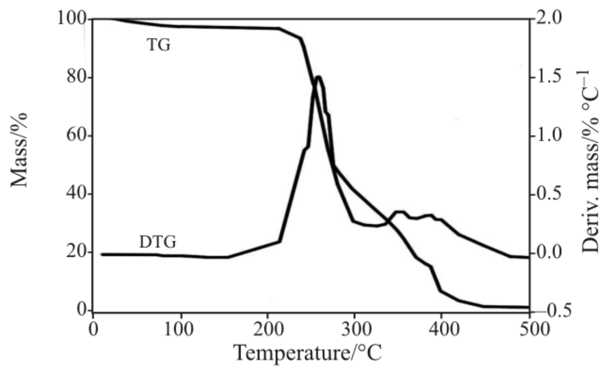

Fig. 3 TG/DTG of flame-retarded cotton fabric treated at the optimum addition of LiBr to achieve flame-retardancy

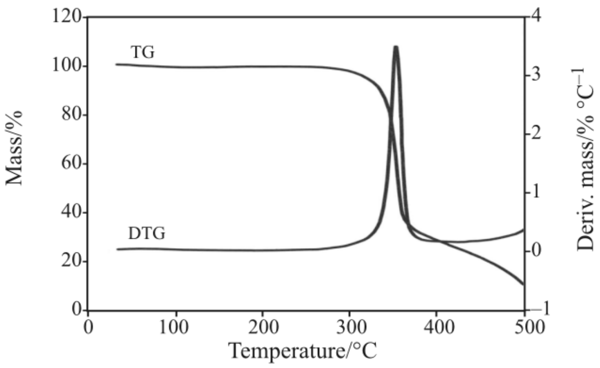

Fig. 4 TG/DTG of flame-retarded cotton fabric treated at the optimum addition of Sb_2O_3 to achieve flame-retardancy

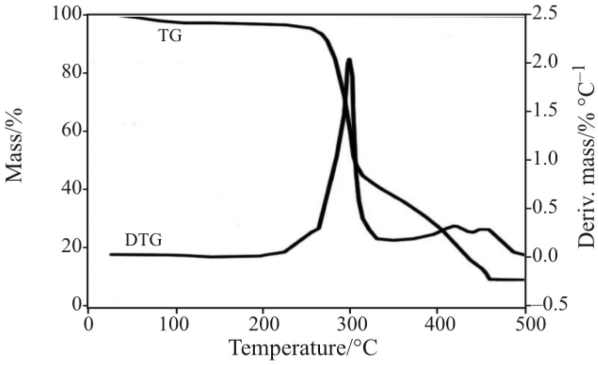

Fig. 5 TG/DTG of flame-retarded cotton fabric treated at the synergism of LiBr–Sb_2O_3 at optimum addition to achieve flame-retardancy

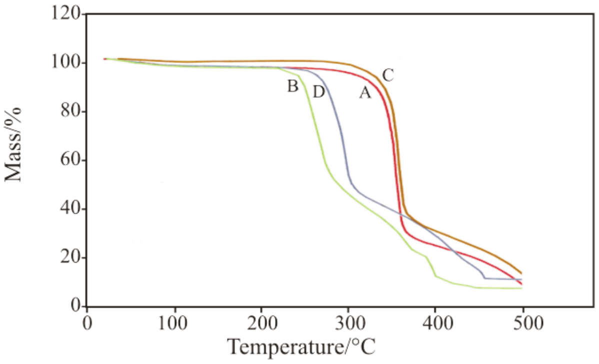

Fig. 6 TG comparative curves: A – TG spectra of untreated cotton fabric. B – TG spectra of FR cotton fabric by the lithium bromide, at the optimum addition. C – TG spectra of FR cotton fabric by the antimony trioxide, at the optimum addition. D – TG spectra of FR cotton fabric by the synergism of lithium bromide/antimony trioxide, at the optimum addition

Note that the combustion temperature of cotton substrate is about 350°C. This trend in the relative mass loss is due to cellulose dehydration. It seems to be in favor of the outcomes of our flame spread test summarized in Table 1. Curve A, in Fig. 6 illustrates that in the case of untreated cotton fabric, the mass loss in the air occurred after 100°C, at a relative slow rate, up to 300°C. Above this temperature, the rate of mass loss increases steeply up to 370°C, when the maximum mass loss attains 74%. Once more, the rate of mass loss slows down between 370 and 500°C, the total mass loss at this temperature being of 98%, which may be explained through oxidative char formation. However for treated specimens smooth mass losses could be seen. Indeed thermal stability of treated samples strongly affected their flammability. The combustibility's results at Table 1 support this suggestion. This synergism with an overall is in favor of environmental view points as well as the economical benefits, since low addition of its combination is needed. The synergistic effect of the treated sample illustrated a significant mass loss rather smoothly below the degradation zone of cellulose (Figs 5 and 6). The plausible mechanism of their flame-retardancy seems to be in favor of free radical theory proofing the catalytic effect of this synergism [14].

It is stated that both antimony and lithium components have been used independently to improve the flame-retardancy of cellulosic materials without the assistance from other halogen containing compounds i.e. they could act as catalysts. Apparently they alter the thermal degradation pathways of the substrate via condensed phase mechanism in such a manner that higher amounts of non-volatile char residues and less flammable gases could be generated during the thermal decomposition of the substrate [15]. Nevertheless antimony oxides and antimonates could somehow be converted to volatile species when applied with halogen compounds. It is usually accomplished by releasing of halogen acids at the combustion temperature's zone. That is: halogen acids react with the antimony-containing materials to form antimony trihalide and/or antimony halide oxide.

These materials act in the substrate both at condensed phase and in the flame zone to suppress the flame propagation. These are in compliance with condensed phase retardation as well as chemical action theory [14, 16, 17].

In the condensed phase, they enhance the char formation. Char acts as a physical barrier towards the flame and inhibits the volatilization of flammable volatiles. In fact, in the flame zone, antimony halides and halide oxides, generated in sufficient volume, could provide inert gases, as a blanket over the substrate, thus excluding oxygen and preventing flame spread is the resultant.

These compounds alter the chemical reactions occurring at fire temperatures in the combustion zone; hence they reduce the ease of ignition at which oxygen can combine with the flammable volatile products. It is also suggested that antimony oxychloride or trichloride reduce the rate at which the halogen leaves the flame zone [18], thus increasing the probability of reaction with the reactive species. It is likely that antimony trichloride evolves heavy vapors, which form a protective layer over the condensed phase, stop oxygen attacking and thus choke the flame. It is also assumed that the liquid and solid of antimony trichloride particles evolved in the gas phase reduce the energy content of the flames by wall or surface effects [16, 18, 19]. That is: they show the effect of dust or wall in the combustion zone of cellulose as described in the wall effect theory [19]. According to this theory 'if a high enough concentration of dust is present in the air, no flame can propagate'. This action is claimed due to the absorption and dissipation of heat by the inert dust, causing a lowering of temperature, which is named as dust or wall effect [16, 19].

The addition of antimony trioxide allows the formation of volatile antimony species (antimony halides or antimony oxyhalide) capable to interrupt the combustion process by inhibiting $H^{\bullet}$ radicals via a series of reactions proposed below [20]:

$$Sb_2O_3+6HX\leftrightarrows 2SbX_3+3H_2O$$
$$SbX_3+H^{\bullet}\leftrightarrows SbX_2+HX$$
$$SbX_2+H^{\bullet}\leftrightarrows SbX+HX$$
$$SbX+H^{\bullet}\leftrightarrows Sb+HX$$
$$Sb+O^{\bullet}\leftrightarrows SbO^{\bullet}$$
$$SbO^{\bullet}+H^{\bullet}\leftrightarrows SbOH$$
$$SbOH+H^{\bullet}\leftrightarrows SbO^{\bullet}+H_2$$

Antimony trioxide on its own has been reported to act a catalyst for carbon oxidation; in fact it has an inhibiting effect on char oxidation when used with other inorganic fillers. However, a chemical explanation for this unexpected effect was not given in the literature [15].

It is worthy to mention that halogen-containing compounds such as lithium bromide when used independently could act as flame-retardants in compliance with the free-radical theory [14, 17]. They could be involved to remove high-energy $^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O^{\bullet}$ and the like radicals generated during the burning process by the suppression via their chlorine or bromine compounds when used as flame-retardants; the reaction is represented below [16, 17]:

$$RX+{}^{\bullet}H\rightarrow HX+R^{\bullet}\ (X=\mathrm{Cl,\ Br})$$

It is noticeable that $R^{\bullet}$ is a less active radical than $^{\bullet}H$. It is also mentionable that halogenated flame-retardants absorb a significant amount of energy during the propagation of fire, so they play an important role in stopping the chain reaction of the combustion process.

As it was mentioned hereinbefore, HX also acts as a catalyst [21]. Consequently the influence of synergism concerning antimony trioxide's accompaniment with lithium bromide could also illustrate a suitable performance to impart flame-retardancy for a cotton fabric. It is noticeable that nowadays the study concerning synergism of elements and/or their related components to achieve flame-retardancy has gained a great interest. Among them the synergism of phosphorus-halogen, nitrogen-phosphorus, etc., has been exemplified in the scientific literature [21–26]. In consequence; it is then attribatable that, while the additive effect is the sum of the individual actions, the effect of synergism is higher than this sum [27]. Note that: our experimental proved a suitable synergism. Ultimately using less halogenated flame-retardant by this synergism and alike could help to protect the environment from potentially hazardous side effects of halogenated gases generated during combustion, so these types of synergism could be recommended.

Apart from this synergism which is in favor of environmental viewpoints it has also economical benefits, since low addition of antimony trioxide as well as a diminished amount of lithium bromide was required.

Conclusions

The synergism of antimony trioxide and lithium bromide into the cotton fabric to impart flame-retardancy demonstrated a favorable performance. This is due to their collaboration to promote the formation of non-volatile char residues and less flammable gases, when the polymeric substrate is subjected to thermal decomposition. Therefore free-radical theory ascribed in the chemical action theory as well as 'condensed phase retardation' may be involved to justify this accompaniment. Thermogravimetry experiments supported the suggestion concerning catalytic effect of this synergism. The low addition of this combination may also be beneficial to avoid destructive characteristics donated into the substrate, which could affect its physical and mechanical properties, such as poor-handle, etc., where applied into the substrate. Ultimately the use of a decreased amount of the combined additives to achieve the same performance of flame-retardancy is in compliance with the green chemistry's viewpoints as well as the economical advantages. That is: potential hazards to the environment concerning halogenated gases generated during combustion could be limited.

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References

1 U. Atikler, H. Demir, F. Tokatlı, F. Tıhmınlıoğlu, D. Balköse and S. Ülkü, Polym. Degrad. Stab., 91 (2006) 1563.
2 E. Kandare, G. Chigwada, D. Wang, C. A. Wilkie and M. H. Jeanne, Polym. Stab., 91 (2006) 1209.
3 Du. Longchao, Q. Baojun and X. Zhenjin, Polym. Stab., 91 (2006) 995.
4 S. M. Mostashari, M. A. Zanjanchi and O. Baghi, Combustion, Explosion Shock Waves, 41 (2005) 426.
5 S. M. Mostashari and O. Baghi, J. Appl. Fire Sci., 12 (2003–2004) 203.
6 S. M. Mostashari and Y. K. Nia, J. Therm. Anal. Cal., 92 (2008) 489.
7 S. M. Mostashari, Y. K. Nia and F. Fayyaz, J. Therm. Anal. Cal., 91 (2008) 237.
8 S. M. Mostashari and S. Z. Mostashari, J. Therm. Anal. Cal., 91 (2007) 437.
9 S. M. Mostashari and A. Farkhondeh, Asian J. Chem., 17 (2005) 2803.
10 S. M. Mostashari and S. Z. Mostashari, Asian J.Chem., 17 (2005) 2331.
11 S. M. Mostashari, H. Haddadi and Z. Hashempoor, Asian J. Chem., 18 (2006) 2388.
12 S. M. Mostashari, Y. K. Nia and S. Baie, J. Chem, 25 (2007) 926.
13 U. S. Department of Commerce Standard for Flammability of Childrens Sleepware (DOC. FF 3-71), Federal Register, 36, No. 146, July 19 (1971).
14 J. H. Troitzsch, Chimica Oggi–Chemistry Today, 16 (1998) 10, 14.
15 F. J. W. J. Labuschagne, W. W. Focke and J. C. Mentz, SA Patent (No. 2001/4876) assigned to University of Pretoria entitled: 'Intumescent Flame Retardants', (2002).
16 S. M. Mostashari, 'The Production of Flame-Retarded Acetate Rayon', M.Phil. Thesis, University of Leeds, (1978) pp. 11–12.
17 M. Kenser and W. De Vos, J. Chem. Edu., 78 (2001) 41.
18 G. J. Van Esch, 'Flame-Retardants environmental health criteria 192', (1997).
19 Z. E. Jolles and G. I. Jolles, Plastics Polym., 40 (1972) 319.
20 http://www.specialchem4polymers.com/tc/Flame-Retardants/index.aspx?id=9305
21 J. Troitzsch, International Plastics Flammability Handbook: Principles-Regulations-testing and Approval, Hanser Munich (1990).
22 G. C. Tesoro, S. B. Sello and J. J. Willard, Textile Res. J., 38 (1968) 245.
23 W. A. Reeves, R. M. Perkins, H. Piccolo and G. L. Drake, Textile Res. J., 40 (1970) 223.
24 G. C. Tesoro, S. B. Sello and J. J. Willard, Textile Res. J., 39 (1989)180.
25 H. Demir, E. Arkış, D. Balköse and S. Ülkü, Polym. Degrad. Stab., 89 (2005) 478.
26 S. M. Mostashari, R. Amirrahamet and A. Farkhondeh, Asian J. Chem., 18 (2006) 2391.
27 A. Tohka and R. Zevenhoven, Processing Wastes and Waste-Derived Fuels Containing Brominated Flame-retardants, Helsinki University of Technology Department of Mechanical Engineering Espoo, (2001) 11–12.

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