THERMOGRAVIMETRIC INVESTIGATION

ON THE FLAME-RETARDANCY OF LITHIUM BROMIDE

ADDED TO COTTON FABRIC

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The present paper discusses the results obtained from the investigation on the effect that lithium bromide, as non-durable finish, exerts on the flammability of 100% cotton fabric (plain, 150 g/m^2). The bone-dried weighed fabrics were impregnated with suitable concentrations of lithium bromide, through squeeze-rolling and drying. The samples were then cooled in a desiccator and reweighed with analytical precision. By using our *vertical flame spread tester*, the optimum add-on value for imparting flame-retardancy to cotton fabric was determined to be around 3.85 g lithium bromide per 100 g fabric. The thermogravimetric (TG/DTG) results obtained for both untreated and salt-supported cotton fabrics, at an optimum addition, were evaluated and their curves were compared and commented. The results obtained comply with condensed phase retardation, chemical action theory and gas dilution theory.

Keywords: chemical action theory, condensed phase retardation, flame-retardancy, gas dilution theory, lithium bromide, thermogravimetry

INTRODUCTION

In recent years, polymeric composites have been widely used for the production of new engineering materials, which is perceived as the reflection of technological developments. Meanwhile, polymeric composites are promising, due to their economically versatile applicability and good mechanical properties, which recommends them for their numerous applications, such as in housing materials, transport and electrical engineering. Due to the increasing demand for polymers, the development of safe and environmentally friendly flame-retarded polymers has gained great importance. In fact, many types of flame-retardants are added to polymers to reduce their flammability.[1]

A flame-retardant system is a compound or composition added to materials to increase their resistance to combustion. Some flame-retardants forming acids during combustion are halogen-containing materials, which act through gas-phase, free-radical inhibition, etc. Other groups of retardants produce many non-combustible gases and dilute the amount of fuel or oxygen supplied to the fire, *i.e.* they function *via* gas dilution.

The enhancement in the formation of solid residues on the surface of the burning material is another way to reduce flame spreading. Also, some flame-retardants reduce the rate of heat release during combustion, by affecting the heat transfer pathway to the polymer substrate. Another group of flame-retardants form a foaming char on the surface of the combusting material, *i.e.* they contribute to intumescence.[2]

The present study investigates the effect that lithium bromide, deposited as non-durable finish, has on the flame-retardancy imparted to cotton fabric.

EXPERIMENTAL

Materials and method

All samples were plain (woven) constructions of unfinished 100% cotton fabric, weighing 150 g/m², laundered and dried, cut as 8×22 cm strips along the warp direction and pre-washed in hot distilled water. The fabrics were then dried horizontally in an oven at 110 ºC for 30 min, cooled in a desiccator and then weighed with analytical precision, as mentioned in previous articles.[3-15]

Bath treatment

With the exception of the first set, all other samples were immersed into an individual bath of 100 mL lithium bromide solution of suitable concentrations, at a temperature of 20-22 °C, for 5 min, after which they were squeeze-rolled and dried horizontally in an oven, at 110 °C, for 30 min.

Further on, they were cooled in a desiccator and reweighed on an analytical balance. The treated fabrics were then conditioned overnight under laboratory conditions, prior to the fulfillment of the vertical flammability test, so that their humidity was regained during this period. The laboratory conditions involved the temperature range of 20-22 °C and the relative humidity (RH) between 65 and 67%.

Flammability test

The vertical flame spread test method (Mostashari's Flammability Tester) described in DOC FF 3-71 was employed to determine the flammability of the fabric.[3-16]

Thermogravimetry

A thermogram was obtained for each specimen on a TGA V5.1A Dupont 2000 Thermal Analyzer, used to determine the mass loss during thermal degradation. To this end, pulverized untreated cotton fabric and fabric treated with lithium bromide were used.

All samples were heated from 20 to 500 ºC in air, at a heating rate of 10 ºC/min, which permitted a better understanding of the role of lithium bromide on the flame-retardancy imparted to the cotton fabric. Hence, the thermogravimetric analysis of both pure cotton and cotton treated with this salt as a flame-retardant, at an optimum addition, was accomplished.

RESULTS AND DISCUSSION

The experimental results obtained are summarized in Table 1. The applied moles are shown in column 4. Vertical flame spread tests were carefully accomplished to ascertain the relation between addition values and burning time values (given in seconds – column 5). Char lengths (in cm) are listed in column 6 and the burning rates are calculated by dividing the length of the burned fabrics by their burning time value (in seconds – column 7). Column 8 shows the state of the specimens upon the completion of the tests: CB stands for completely burned and FR – for flame-retarded. The tabulated results show that inadequate quantities of lithium bromide applied as a flame-retardant decreased the burning time values and hence increased the burning rate, which agrees with the results obtained by Reeves and Hammons.[17] Otherwise said, below the optimum limit of the add-ons, a decrease in the burning time and hence an increase in the burning rate resulted. The just mentioned investigators observed that inefficient amounts of certain flame-retardants accelerate the burning process of cotton fabric,[17] *i.e.*, by the deposition of insufficient amounts of some flame-retardants, imperfect rapid burning deformation occurs, a decrease in the burning time and an increase in the burning rate thus resulting. Plausibly, this might be due to the relative rigidity given to the substrate by the use of some additives, such as the above-mentioned add-on. It is likely that heat feedback into the bulk surface made it susceptible to participate to a rapid, incomplete surface burning. However, if adequate amounts of the above-mentioned add-on are deposited on the cotton fabric, the heat from the cellulosic substrate can be absorbed by the flame-retardant at a comparable rate, supplied by the flame, so that flame-retardancy is achieved.

It can be deduced from the experimental results of the third column that the most efficient addition of lithium bromide for imparting flame-retardancy to dried cotton fabric is of about 3.85%.

Halogen-containing flame retardants started to be applied since the 1970s, while in the 1980s their use considerably increased. Halogen-based flame retardants operate in the vapor phase. On heating, they decompose and form halogen radicals, which interfere with the oxidation of volatile fuels. In the gas phase, they react with the oxygen and hydrogen radicals, thus reducing their concentration and hence extinguishing fire.[2]

Table 1
Effect of lithium bromide on the flame-retardancy of cotton fabric (plain, 150 g/m^2)

| Set* No	LiBr treating solution (molarities)	Percent (add-on) after drying at 110 ˚C and weighing	Applied moles	Burning time (s)	Char length (cm)	Burning rate (cm/s)	State of the fabric**
1	Untreated	_	_	27	_	0.81	CB
2	0.10	2.71	0.03	14.3	_	1.54	CB
3	0.15	3.85	0.04	_	1.4	_	FR
4***	0.20	4.84	0.06	_	0.8	_	FR

* The table shows the average values of five replicates; ** CB – completely burned and FR – flame-retarded;*** Confirmation tests when applying excessive quantities of lithium bromide; Note: For flame retarded (FR) samples, the char length was ≤ 2.0 cm

Noticeably, the action of halogen-containing compounds as flame-retardants agrees with the free radical chain mechanism,[18] manifested in the gas phase, during combustion. Possibly, it assumes the formation of high-energy ˙OH, ˙H, ˙O˙ and similar radicals, formed during combustion, which can support the burning process, so that their removal or conversion may help to suppress the flame. To achieve this goal, these active radicals should be converted to less active ones. Actually, this suppression is believed to occur via chlorine or bromine compounds used as flame-retardants:

$$RX + ˙H \rightarrow HX + R˙ \qquad (X= Cl \text{ or } Br)$$

Interestingly, R˙ is a less active radical than ˙H.

Mention should be also made of the fact that halogenated flame-retardants absorb a significant amount of energy, thus cooling the combustion zone. Furthermore, the bonds between carbon-halogen will homolytically break and the free halogen atoms formed by this process will react with the polymer's hydrogen atoms, generating hydrogen halide molecules. Such molecules play some role in stopping the chain reaction produced during the propagation of combustion or fire. They may, for instance, inhibit or deactivate the ˙OH radicals:

$$˙OH + HX \rightarrow H_2O + ˙X$$
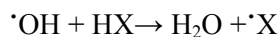
Further on, the newly generated free halogen radicals regenerate HX by capturing the free hydrogen radical present in the gaseous phase, or by reacting with the polymer's body:

$$˙H + ˙X \rightarrow HX$$
$$RH + ˙X \rightarrow HX + R˙$$
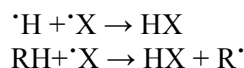
Other different reactions proposed in the specialty literature[19] are based on withdrawing the energy from the combustion–propagation zone or from the burning region via the heavy halogen atoms. Thus, HX ultimately acts as a negative catalyst. After all, the hydrogen halides as non-flammable gases could also form non-combustible protective layers interfering with the reach of air oxygen, thus stopping combustion.

Generally, the stability of bromine in a typical flame-retardant molecule means that it can provide the highest activity as flame-retardant, on being also highly cost-effective. The choice of flame-retardant systems for particular applications will depend on how the material decomposes in fire, as well as on the required physical properties. Once they act inside the flame, Brominated Flame-Retardants (BFRs) can be applied in any type of application; indeed, their utilization in some plastics may possibly be the only choice.

The fact that BFRs are particularly efficient on addition level basis means that they may frequently have less impact on the physical properties of a plastic than other systems. There is also a wide range of available BFRs, permitting the selection of the optimum product, to balance the cost with the physical properties, temperature resistance, processing and all other characteristics, particularly important for the final applications.[20]

The TG/DTG curves of both untreated cotton fabric and cotton treated with an optimum amount of lithium bromide are plotted in Figures 1-3,

respectively. For pure cotton fabrics, the major mass loss occurs at around 350 ºC (Fig. 1). However, for fabrics treated with lithium bromide, at an optimum addition, thermal degradation occurred around 260 ºC (Fig. 2).

Ultimately, the comparison of the TG curves illustrates that a significant mass loss occurred rather smoothly below the degradation zone of

pure cellulose (Fig. 3). TG/DTG data analysis permits to deduce the catalytic dehydration of the substrate by means of lithium bromide, since the thermal degradation of the salt-treated cellulose occurred at a well-blow temperature zone with regard to the degradation zone of the untreated cotton fabric. Hence, the chemical action theory describing its action could be justified.
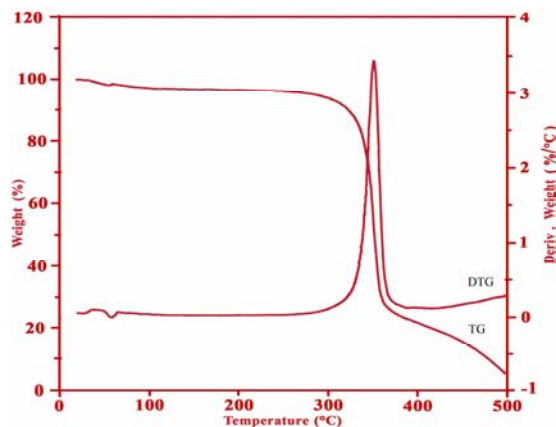

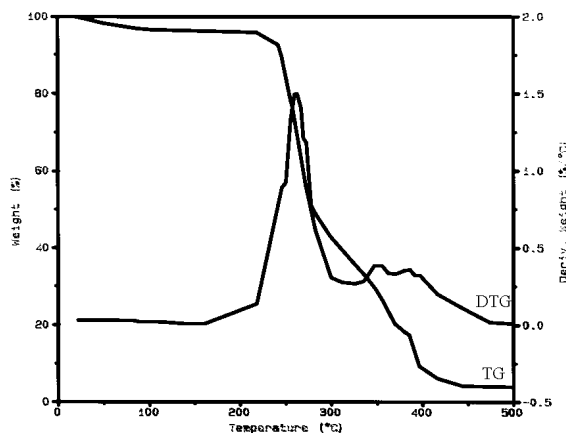Figure 1: TG/DTG of untreated (UT) cotton fabric

Figure 2: TG/DTG of flame-retarded cotton fabric treated by an optimum addition of LiBr to achieve flame-retardancy
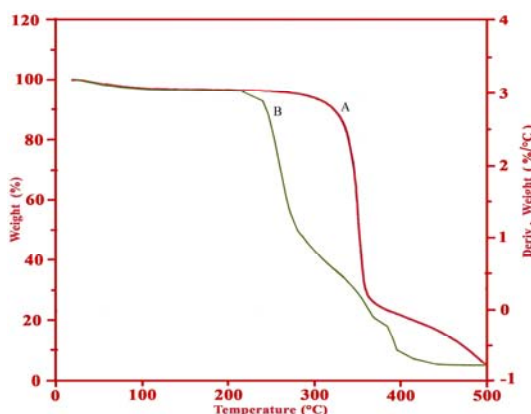

Figure 3: Combined curves: A – TG spectrum of UT cotton fabric (normal pyrolysis); B – TG spectrum of FR cotton fabric treated with lithium bromide (enhanced pyrolysis)

According to the theory stated by Troitzsch,[21] the flame-proofing action of some chemicals is due to an enhanced formation of solid char, mainly carbon residue, during thermal decomposition, that is, the carbon content present in the polymer has been confined to the solid phase, so that the generation of water vapors from

the substrate, instead of volatile pyrolysis products, is enhanced.

In other words, the combustion pathway could be catalyzed by using dehydrating agents such as acidic or neutral species, possibly including the afore-mentioned salt, at high temperatures.

CONCLUSIONS

As a halogen-containing compound deposited on the cotton fabric, lithium bromide demonstrated a desirable flame-retardancy, its action being assigned to the liberation of free bromine radicals during the combustion of the substrate. These radicals could be converted into hydrogen bromide in the combustion zone of the polymer. It should be also remarked that the generated gases act as a blanket, preventing the access of air oxygen and making the burning process very difficult. Therefore, due to the dilution of the flammable volatiles generated during combustion, the flame is snuffed out.

Also, it is worth mentioning that, as a water-soluble species, this salt cannot be used to flame-retard garments. However, the results obtained could be useful for some other commercial purposes, as in plastics and polymer applications, etc.

Ultimately, lithium bromide, necessary only in low amounts for granting good flame-retardancy, meets the requirements of green chemistry and presents some economic advantages.

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