Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 2, 535–540

TG COMPARISON BETWEEN THE EFFICIENCY OF DEPOSITED AMMONIUM BROMIDE AND AMMONIUM CHLORIDE ON THE FLAME-RETARDANCY IMPARTED TO COTTON FABRIC

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This study investigates the effect of ammonium bromide and/or ammonium chloride as nondurable finishes on the flammability of 100% cotton fabric, (woven construction, weighing 144 g m^{-2}). The laundered bone-dried, weighed fabrics were impregnated with suitable concentrations of aqueous ammonium bromide and/or ammonium chloride solutions by means of squeeze rolls and dried at 110°C for 30 min. Afterwards they were cooled in a desiccator, re-weighed with an analytical precision and kept under ordinary conditions before the fulfillment of the vertical flame test. The optimum add-on values to impart flame retardancy expressed in g anhydrous ammonium bromide and ammonium chloride per 100 g fabrics were individually obtained to be about 3.5–3.89 and 17.31–17.99%, respectively.

Thermogravimetric analysis (TG/DTG) of pure cotton and the salts treated fabrics were fulfilled and their curves were compared and commented. The results obtained comply with free radical theory, and also proved the superiority of ammonium bromide for the impartation of flame-retardancy in regard to ammonium chloride.

Keywords: *ammonium bromide, ammonium chloride flame-retardancy, flammability, free radical theory*

Introduction

Flame-retardants are added to polymers, fibres and paper in order to protect the final product from burning or at least to obtain a flame retarding effect [1]. Flame-retardants should inhibit or even suppress the combustion process. Depending on their nature, flame-retardants can act chemically and or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, that is: they may intercept heating, decomposition, ignition or flame spread [2]. The field of flame-retardancy of polymers has greatly developed and expanded during the last 20 years. The expansion includes both the number of new systems invented and developed, as well as many new kinds of products being flame-retarded or requiring flame-retardancy treatment. There has been highly remarkable increase in the number of scientists and engineers engaged in the development of flame-retardation technologies [3].

Delaying the propagation of a fire, a few minutes might save lives by giving people enough time to get out of the fire's zone.

Modern safety standards require self-extinguishing capability of a product when the material is exposed to the most common sources of fire found in its normal surroundings [4].

Hence flame-retardants are becoming an increasing global source of artificial and persistent chemicals nowadays. The most widely used additive type flame-retardants are inorganic components. Among them halogenated compounds and phosphorous compounds, boric acid, ammonium phosphates and borates, ammonium sulfate and chloride, zinc chloride and borate, antimony oxide, sodium borate and dicyanodiamide have also been applied as flame retardant additives [5].

A substance must comply with several requirements before it can be considered for application as a flame-retardant in a specific polymer applied for a specific purpose. A flame-retardant must be inexpensive, stable to heat and in some cases to light and preferably colorless. It must not drastically alter the physical and mechanical properties of the final product and it must be stable at temperatures in which the product is formed. To be effective it should decompose around the same temperature at which the polymer itself begins to decompose, which is normally between 200 and 300°C [6–9].

Another requirement is that the flame-retardant should not itself release toxic components that might be dangerous either immediately or in the long run [4].

Concerning halogen compounds, the effectiveness of halogen-containing flame-retardants increases in the order of F<Cl<Br<I. It is noticeable that; fluorine and iodine based flame-retardants are not applied in practice because neither type interferes with the combustion process at the right point. Fluorine cannot become effective as a radical interceptor in the gas phase due to its strong

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1388–6150/$20.00

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bond to carbon. Iodine in contrast is attached to carbon so loosely that it is liberated by even a negligible energy supply; as a result, the polymer's properties (e.g. light stability) are affected and the flame-retardant effect is already lost in the combustion's temperature range or in the zone of pyrolysis [2].

Of the two remaining halogens, bromine is the most efficient since its weaker bonding to carbon enables it to interfere at a more favorable point in the combustion process. It is assumed, moreover, that the effective agent, HBr, is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone. In contrast with it, HCl, which is generated over a wider temperature range and is present at lower concentrations, is thus less effective [10]. Hence flame-retardants containing bromine are usually more effective, on a molar basis, than those containing chlorine, on the other hand, bromine atoms are much heavier and their compounds are more costly than cholorine components.

However despite the high cost of bromine relative to chlorine, and despite a significant increase in the mass of the polymer caused by the application of bromine compounds, the brominated flame-retardants are generally preferred [4]. It is noticeable that in order to meet both the desired flame-retardancy and desired mechanical properties of the product, most bromine containing flame-retardants are used as additives, usually should not be more than 30% of the mass of the final product.

There are different theories illustrating the attempts that have been made to explain the flame-retardancy action of various treatments. One of these theories is allocated to the free radical theory. This theory relies on the interruption of the basic chain reaction of combustion via halogen compounds, which are generally used as flame-retardants.

Actually there are various radicals in the vapor phase at the combustion's zone. In general $^{\bullet}$H, $^{\bullet}$OH and the like are the most active radicals, which can support combustion, so that their removal can help to suppress the flame. To achieve this target it would be ideal if these active radicals could be converted to less active ones. It is mentionable that all halogens are effective in eliminating the active free radicals [11].

The objective of this study is to compare the effect of ammonium bromide and ammonium chloride as non-durable flame-retardant finishes incorporated onto cotton fabric.

Experimental

Materials

All fabrics were a plain construction, weighing 144 g m^{-2}, unfinished 100% cotton, laundered and dried. They were 22 by 8 cm strips cut along the warp direction and pre-washed in hot distilled water. The specimens were dried at 110°C for 30 min in an oven, cooled in a desiccator and weighed with an analytical precision.

Bath treatment

With the exception of the first set, all other specimens were impregnated with suitable concentrations of ammonium bromide and/or ammonium chloride at 20°C. Afterwords they were squeeze rolled and dried horizontally in an oven at 110°C for 30 min [12–21]. They were then cooled in a desiccator and re-weighed with an analytical balance so that the suitable add-on presented onto the samples were obtained.

Methods

Flammability test

A vertical tester for determination of the flammability of thermoset fabrics has been designed by the corresponding author and named as Mostashari's flammability tester. It is similar to the procedure described in DOC FF 3-71 [22] (Fig. 1). It is a rectangular aluminum frame cut on from one of its smaller sides. It has internal splits for inserting the fabric. The frame has also five even numbers of holes in each of its parallel legs, so that pining of the fabric has been possible inside it. The specimens were then pinned tightly to the frame and held vertically in a retort stand by clamps with the lower edge 1.9 cm above the top of a 3 cm yellow flame of a Bunsen burner, and an ignition time of 3 s was observed. This procedure was conducted in order to avoid harsh conditions for ignition. It is mentionable that the time of ignition was subtracted from the total combustion's duration, and then the rest was reported as the burning time. Standard deviation of burning time when untreated samples were burned was ±1.06 for an average of 5 tests. However for 'the

Fig. 1 Mostashari's flammability tester with an untreated cotton fabric before the accomplishment of the experiment

salt treated fabrics' this figure was around ±1.30. In fact the pad squeeze process resulted certain amounts of variability. The length of 'char' was measured after each test to the nearest cm. The flammability test was conducted in a switched-off fan fume-cupboard, prior the fulfillment of the combustion; however the exhaust ventilator had been turned on for about 5 min, after each burning, so that the consumed toxic gases were conducted away from the environment and fresh air could enter around the experimental apparatus.

It is worthy to mention that the burning rates could be calculated by means of dividing the length of the combusted samples in cm by the burning times in sec. This method was also introduced in the previous published articles [12–21].

According to the above-mentioned test, an aluminum frame with the following specification has been used: two strips of 3 mm aluminum double-sheet, 22.5 by 1.5 cm are cut, perforated and welded at right angles to a shorter 9 cm strip. The circumstances of the specimens and environment were in average temperature ranged between 20 and 22°C and the relative humidity of 65±2%. The fabrics were conditioned nightlong before the fulfillment of the flammability test. It is mentionable that all samples were pinned tightly to frame and held vertically in a retort stand by clamps with the lower edge 1.9 cm above the top of a Bunsen burner with a 3 cm yellow flame, and then an ignition time of 3 s was observed. This procedure was conducted in order to avoid harsh ignition conditions. All samples were tested with accuracy of determining the burning time of ≈0.1 s. Repeatability of the burning time was ±5% for an untreated fabric. This figure was much lower for salt-treated specimens. This indicates the presence of inhomogeneities in the treated fabrics. The flammability test was conducted in a put out fume-cupboard before the accomplishment of the combustion. However, the exhaust ventilator had been turned on for about 5 min, after each burning, so that the fresh air could be available around the apparatus, and the consumed toxic gases could be conducted away from the environment. Finally, the length of 'char' was measured after each test to the nearest cm and fabrics possessing 0.5 cm char length or less than this figure were considered as flame-retarded.

Thermogravimetric analysis

Thermal analysis was carried out for untreated, flame-retarded cotton fabrics and also pure ammonium bromide and or ammonium chloride, by using Thermogravimetric analyzer (TGA V5.1A DuPont 2000). All of the specimens were heated from room temperature up to 600°C in the presence of air. The heating rate was 10°C min^{-1} during all experiments.

Results and discussion

The experimental results are listed in Table 1. Vertical flame test was carefully conducted to ascertain the add-on values on the subject of the burning times in s (column 5). In column 4 the percents of ammonium bromide and/or ammonium chloride are given respectively. In column 6 char lengths are illustrated. In column 7 the states of the fabrics after the fulfillment of the testes are given. CB means completely burnt and FR means flame-retarded. It can be attributed from the above-mentioned experimental results that the optimum add-on values to impart flame retardancy expressed in g anhydrous ammonium bromide and ammonium chloride per 100 g fabrics were individually obtained to be about 3.5–3.89 and 17.31–17.99%, respectively. It is mentionable that the mode of action of halogen containing compounds to act as flame-retardants are in compliance with the free-radical theory [23, 24]. According to the above-mentioned theory, the mechanism taking place in the gas phase during combustion is believed to involve the formation of high-energy OH, H, O and the like radicals formed during combustion which can support the afore-mentioned process, so that their removal or conversion can help to snuff out the flame. That is: to achieve this target it would be beneficial if these active radicals could

Table 1 Comparison between the effect of deposited ammonium bromide and ammonium chloride on the flame-retardancy imparted to cotton fabric (woven construction weighing 144 g m^{-2})

Set No.*	Treating solution NH_4Br molarity	Treating solution NH_4Cl molarity	Percent (add-on) drying at 110°C and weighing	Burning time/s	Char length/cm	State** of the fabric
1	untreated	–	–	25	–	CB
2	0.20	–	2.65	16	–	CB
3	0.22	–	3.50	–	0.5	FR
4***	0.25	–	3.89	–	0.5	FR
5	–	1.50	13.50	27	–	CB
6	–	1.85	17.31	–	0.2	FR
7***	–	2.00	17.99	–	0.1	FR

*Average of 5 tests for each set. **CB stands for completely burnt. FR means flame-retarded. *** Confirmatory tests using excessive quantities of salts.

be converted to less active ones. Actually this suppression is believed to happen by chlorine or bromine compounds when used as flame-retardants:

$$\mathrm{RX}+{}^{\cdot}\mathrm{H}\rightarrow\mathrm{HX}+{}^{\cdot}\mathrm{R}\qquad (X=\mathrm{Cl\ or\ Br})$$

It is worthy to notice that $^{\cdot}$R is a less active radical than $^{\cdot}$H. It is also mentionable that halogenated flame-retardants absorb the required amounts of energy and the C–X (X=halogen) bonds will break homolytically. The free halogen atoms formed by this process react with the polymer's hydrogen atoms, generating hydrogen halide molecules. These HX molecules also play an important role in hindering the chain reaction that happens during the propagation of fire or combustion process. They may for instance, inhibit or deactivate $^{\cdot}$OH radicals as follows:

$${}^{\cdot}\mathrm{OH}+\mathrm{HBr}\rightarrow\mathrm{H_2O}+{}^{\cdot}\mathrm{Br}$$

$${}^{\cdot}\mathrm{OH}+\mathrm{HCl}\rightarrow\mathrm{H_2O}+{}^{\cdot}\mathrm{Cl}$$

Then the newly formed free halogen radicals re-form HX by capturing free hydrogen radical present in the gaseous phase or by reacting with the polymer's body:

$${}^{\cdot}\mathrm{H}+{}^{\cdot}\mathrm{X}\rightarrow\mathrm{HX}$$

$$\mathrm{RH}+{}^{\cdot}\mathrm{X}\rightarrow\mathrm{HX}+{}^{\cdot}\mathrm{R}$$

Various other reactions are proposed. The significant overall effect is that; the halogen atoms withdraw energy from the combustion-propagation zone or from the burning region, so that the flame-retardancy is achieved [4, 23].

Burning process of cellulose fibers

Burning of this material involves two thermal decomposition processes, i.e. combustion and pyrolysis [25]. Thermal decomposition of cellulose produces solid residues, liquid components and volatile gases when it is heated without oxygen. Combustion of cellulose is an oxidation process of this compound under heat, which consumes flammable gases, liquids, and solid residues produced in the pyrolysis of the materials, and results in excess amount of heat. Burning of substances may involve two different types of fires: gas-state and solid-state, based on the nature of the fire. The first type is combustion of flammable gases and volatile liquids; where the solid-state burning is an oxidation of solid residues (mainly carbon). It is worthy to notice that the temperature of the flame burning is lower than that of the solid-state burning [26]. The later would cause more thermal decomposition (pyrolysis) of the materials. Thermal pyrolysis generates more flammable products, which then could fuel the burning of more materials with flame, resulting fire spreading. The cycle of this combustion process is self-sustainable and could cause severe damage to the materials and unexpected fatal tragic events.

The pyrolysis of cellulose is a very complex phenomenon accompanied by chemical process and is commonly believed to involve two different mechanisms. One of them is a process of dehydration and charring of cellulose, producing water, carbon dioxide and solid residues. While according to the second mechanism, the cellulose produces nonvolatile liquid glucose by depolymerization, and glucose cleavage continues, producing low molecular mass products, which are more flammable. If there is oxygen existing, the decomposed products of glucose will be oxidized, liberating much more energy and heat to promote more cellulose cleavage. The reciprocity of these two reactions exists throughout the thermal decomposition of cellulose [25].

Thermal analysis and the pyrolysis of cellulose

Thermal analysis was carried out at a heating rate of 10°C min^{-1}. DTG and TG of cotton sample reveal that the pyrolysis of cellulose includes three stages: initial, main and char formation decomposition. The related temperature, speed and mass loss of every stage can be found from the TG curves.

TG of pure cotton fabric (Fig. 2) demonstrates three stages: in the initial stage, where the temperature range is below 300°C, the most important changes are in some physical properties and little mass loss. Here, the damage to the cellulose occurs mostly in amorphous region of the polymer. However the main pyrolysis stage occurs in the temperature range of 300–370°C. In this stage, the mass loss is very fast and important. Most of pyrolysis products is assigned to be formed at this stage. Glucose is one of the major products, together with all kinds of combustible gases [27].

Ultimately above 370°C dehydration and charring reactions tends to be completed. The curves illustrate that; pure ammonium bromide is mainly decomposed at 300°C. However the treated flame-retarded cotton fabric with optimum amount of this chemical

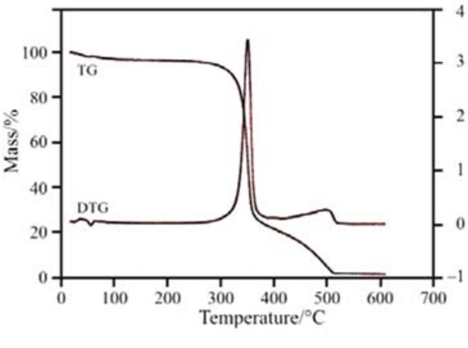

Fig. 2 TG and DTG of untreated (UT) cotton fabric

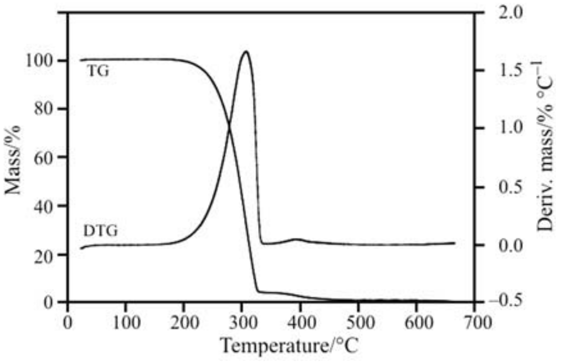

Fig. 3 TG and DTG of pure ammonium bromide supplied by Merck Co.

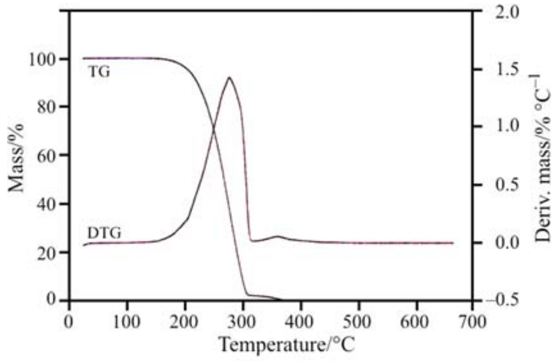

Fig. 5 TG and DTG of pure ammonium chloride supplied by Merck Co.

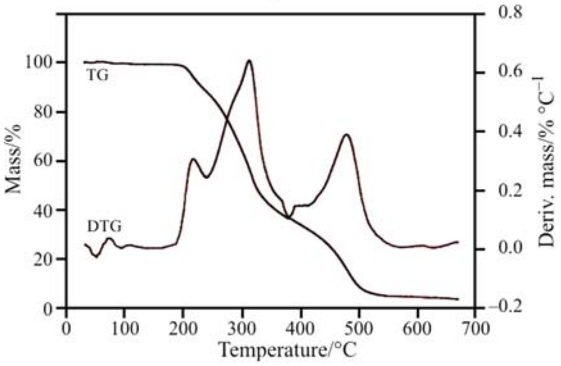

Fig. 4 TG and DTG of flame retarded (FR) cotton fabric by ammonium bromide

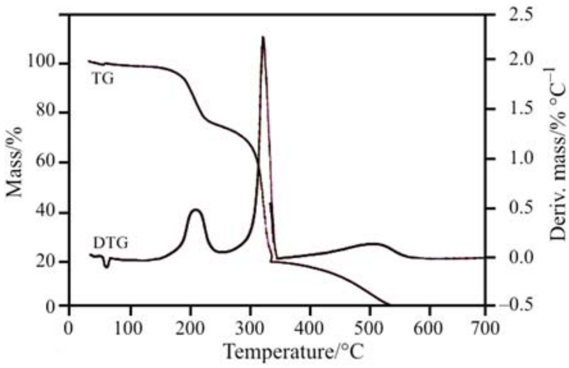

Fig. 6 TG and DTG of flame retarded (FR) cotton fabric by ammonium chloride

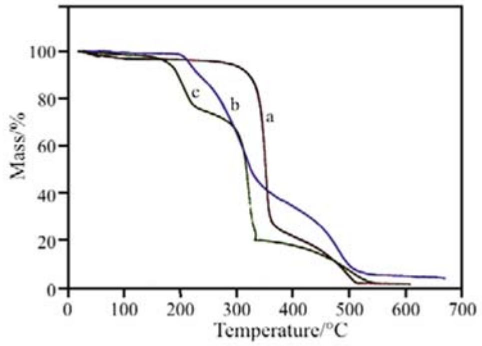

Fig. 7 The combined curves. a – TG spectra of UT cotton fabric, b – TG spectra of FR cotton fabric by ammonium bromide, c – TG spectra of FR cotton fabric by ammonium chloride

showed two major mass losses around 310 and 460°C, respectively (Figs 3 and 4).

The corresponding decomposition temperature for pure ammonium chloride and the treated fabric at its optimum range of flame-retardation zone is around 310 and 280°C, respectively (Figs 5 and 6). The combined curves are represented in Fig. 7. The spectacular mass loss around 310°C (curves b and c) for both treated fabrics with the halogen-containing flame retardants illustrate that the samples degrade almost at the vicinity of thermal decomposition range of cellulose which is about 325°C. The treated cotton with NH_4Br at the optimum content for flame-retardancy acted earlier and sustained its action at the thermal degradation zone in a longer duration and smoother manner in regard to ammonium chloride supported cotton fabric. Hence the higher efficiency of ammonium bromide in regard to ammonium chloride on the flame-retardancy could be deduced.

The similarity of the major mass loss regarding these temperature shows that the action of the aforementioned salts is via losing hydrogen–halides and water vapor in a punctual duration of the thermal decomposition of cellulose. Therefore the justification of the flame retardancy of these salts via free radical theory [23, 24] would be reasonable. Moreover the TG results probably explain the Lewis acidic effects of these salts used as flame-retardants. In fact the pH of their 0.1 molar solution determined via universal paper is about 5 for both solutions of ammonium bromide and/or ammonium chloride. The plausible mechanism of the flame-retardancy using these types of flame-retardants relies on the chemical theory suggested by Little [24]. This theory explains the formation of solid carbon residue i.e. the generation of char rather than volatile pyrolysis products when the polymer is subjected to thermal degradation are promoted. That is: the decomposition of cellulose substrate could be pushed to form carbon residue (char) and water vapor via the catalytic dehydration process shown below:

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

Ultimately the liberated gases such as NH_3, CO_2, H_2O, HBr and HCl by using these flame-retardants may assist to interrupt the burning process i.e. the atmosphere in the vicinity of the inflamed cotton substrate is changed, resulting the dilution of the flammable gases generated during combustion process. These gases may act as a blanket, preventing or making very difficult the access of air oxygen [23].

Therefore, the combination of fuel, oxygen and heat i.e. fire triangle [4, 28] to sustain the burning process will be ruptured.

Conclusions

In this article a comparison between the efficiency of ammonium bromide and ammonium chloride on the flame-retardancy imparted to cotton fabric has been examined and commended via our flammability tester and also by the thermogravimetric analysis of untreated and treated fabrics. Both salts treated fabrics demonstrated a desirable flame-retardancy. However ammonium bromide is much effective than ammonium chloride, so its minor treatment with reaction concentration is needed to gain the same efficiency for fire retardation. Their actions have been assigned because of the liberation of free halogen radicals in a punctual duration of the thermal degradation of cellulose. Hydrogen halides generated in the combustion's zone of cotton substrate is assigned to act as a blanket, preventing the access of air oxygen or to play as a diluant of the flammable gases, causing to snuff out the combustion. Furthermore, the acidic nature of the applied salts to the cotton fabric made it susceptible to form char and water vapor via the catalytic dehydration during the combustion.

Ultimately by using our vertical flammability tester the superiority of ammonium bromide relative to ammonium chloride in the ratio of 3.50/17.31 regarding the impartation of flame-retardancy to cotton fabric has been experienced. It is to be noted that selecting the above-mentioned water-soluble salts in despite of their unutilizablity for the flame-retardancy of garments, could provide some beneficial assessments to be put in practice for some other commercial purpose such as insulators, plastics and polymers.

Acknowledgements

The authors are grateful to Gilan University for financial assistance of this research project.

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Received: June 20, 2008
Accepted: October 14, 2008

DOI: 10.1007/s10973-008-9373-8