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XRD CHARACTERIZATION OF THE ASHES FROM A BURNED CELLULOSIC FABRIC IMPREGNATED WITH MAGNESIUM BROMIDE HEXAHYDRATE AS FLAME-RETARDANT

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The effect of magnesium bromide hexahydrate [$MgBr_2 \cdot 6H_2O$] as a nondurable finish on the flammability of 100% cotton fabric, (woven construction, massing 150 g m^{-2}) has been investigated. The laundered bone-dried, massed fabrics were impregnated with various concentrations of the aqueous above-mentioned salt solutions by means of squeeze rolls and drying in an oven at 110°C for 30 min. The specimens were then cooled in a desiccator, re-massed with an analytical balance and kept under standard conditions before the fulfillment of the vertical flame spread test.

After several experiments the optimum add-on values to impart flame-retardancy expressed in g anhydrous magnesium bromide hexahydrate per 100 g fabric were determined to be about 5.6%. The ashes of the treated specimens were subjected to X-ray diffraction analysis (XRD), and the result was compared with data for pure MgO powder and/or $MgBr_2$ specimens. Consequently the existence of MgO was detected in the ashes.

Keywords: *flame-retardancy, free-radical theory, gas theory, magnesium bromide hexahydrate, XRD*

Introduction

Although in the last decade there has been an increase in the number of hetero-elements used in flame-retardants, the commercial market is still dominated by compounds containing halogens notably, chlorine and bromine. They are exceptionally efficient and may be incorporated as either additive or as reactive [1].

The use of halogenated additives in polymers also has drawbacks, e.g. they tend to produce environmental and health problems due to the evolution of corrosive and obscuring smoke during combustion, which gained great concern in Europe nowadays [2].

Nevertheless highly brominated organic compounds are still among the most widely used flame-retardants for plastics. The function of brominated flame-retardants is based upon hydrobromic acid (HBr) evolution through the thermal decomposition of the retardant during the course of combustion occurs often at above 1000°C [3].

Over the past decade and at the international level, there has been interest in the determination of brominated flame-retardants (BFRs) in consumer's matrices [4].

Halogen-containing flame-retardants mainly act in the gas phase, resulting in the release of more toxic gases and smoke during combustion [5].

These flame-retardants or their degradation products stop the radical mechanism of the burning process that takes place in the gas phase. The high-reactive radicals such as $HO^{\cdot}$ and H, etc., can react in the gas phase with other radicals, like halogenated radicals $X^{\cdot}$ resulted from flame-retardant's degradation, so less reactive radicals which decrease the kinetics of the combustion are created.

To be efficient for trapping radicals, it is necessary to reach the flame in gas phase [6].

The aim of this investigation is to study the effect of deposited magnesium bromide hexahydrate as a nondurable finish for the impartation of flame-retardancy onto cotton fabric; moreover XRD analysis of the ashes after the low treated specimen was consumed has been of interest in this research project.

Experimental

Samples preparation

All fabrics were a 'plain' construction, massing 151 g m^{-2}, unfinished 100% cotton, laundered and dried. They were 22×8 cm strips cut along the warp direction and pre-washed in hot distilled water. The samples were then dried horizontally at 110°C for 30 min in an oven, cooled in a desiccator and massed with an analytical precision.

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With the exception of the first set, all other samples were impregnated with several independent concentrations of magnesium bromide hexahydrate at 20°C. Afterwards they were squeeze rolled and then dried horizontally in an oven at 110°C for 30 min, They were then cooled in a desiccator and re-massed with an analytical balance, so that the suitable add-on presented onto the fabrics were obtained. All of the specimens were kept nightlong under ordinary conditions before the fulfillment of the flammability test. This method has been introduced in previous publications of the corresponding author including in this journal [7–16].

Fig. 1 Mostashari's Flammability Tester with a low addition of magnesium bromide hexahydrate applied onto a cotton fabric during the test

Fig. 2 Mostashari's Flammability Tester with a low addition of magnesium bromide hexahydrate applied onto a cotton fabric at the end of the experiment

Methods

Flammability test

A vertical flame spread test method, following the procedure described in DOC FF 3-71 [17] was employed to determine the flammability of fabrics. It has been designed and named as Mostashari's Flammability Tester (Figs 1 and 2). This method has been previously described [7–16].

XRD analysis

X-ray diffraction (XRD) measurements were performed on a Philips PW1840 diffractometer with the use of CuK_α radiation of copper at room temperature. XRD patterns were recorded using an automatic divergence slit system.

Results and discussion

The experimental results are summarized to identify the burning characteristics of the specimens in Table 1. The add-on percents of magnesium bromide hexahydrate are shown in column 3. The vertical flame spread tests were carefully conducted to clarify the add-on values on the burning times in sec are given in column 4. The states of the samples at completion of testing are illustrated. CB for completely burned, PB for partly burned and FR for flame-retarded these are shown in column 5. The char lengths in cm are illustrated in column 6. The burning rate is calculated by means of dividing the length of fabrics by the burning times in s; these data are given in column 7.

The results show that inadequate quantities of this salt used as the flame-retardant decreased the burning times and hence increased the burning rates. This outcome is in compliance with the scientific literature suggested by Reeves and Hammons [18]. They found that inefficient amounts of certain flame-retardant finishes accelerate the combustion process,

Table 1 The effect of deposited 'magnesium bromide' on the flame-retardancy imparted to cotton fabric (plain 150 g m^{-2})

Set* No.	Treating solution magnesium bromide (molarities)	Percent (add-on) drying at 110°C and weighing	Burning time/s	State of the fabric**	Char length/cm	Burning rate/ cm s^{-1}
1	untreated	–	27	CB	–	0.81
2	0.025	1.5	15	CB	–	1.46
3	0.05	1.62	12.3	CB	–	1.78
4	0.75	3.04	7.3	PB	7	0.96
5	0.1	4.69	2	PB	4.2	2.1
6	0.125	5.6	–	FR	2	–
7***	0.15	6.73	–	FR	1.3	–

*Average of 5 tests for each set of samples. **CB stands for completely burned, PB for partly burned and FR stands for flame-retarded.
***Confirmatory tests using excessive amounts of the additives. Note: For flame-retarded (FR) samples, the char length ≤2.0 cm

i.e. a decrease in burning time and an increase in the burning rate is the outcome. In fact the fabrics impregnated with magnesium bromide hexahydrate followed suit this phenomenon. In the present experience by deposition of inadequate amounts of this salt, the imperfect rapid burning deformation has also occurred and a decrease in burning time and an increase in the burning rate were the resultant. Plausibly this is due to the relative rigidity donated to the cotton substrate by the use of this salt. It seems that the heat feedback into the bulk's surface of the cellulosic substrate made it susceptible to participate in a rapid, uncompleted surface combustion. However if sufficient quantities of the above-mentioned substance is deposited into the cotton fabric, the char conducts away the heat from the cellulosic substrate at a comparable rate, which is being supplied by the flame, so the flame-retardancy is achieved.

By application of 0.125 molar solutions of magnesium bromide hexahydrate an acceptable flame-retardancy into the cotton fabric was experienced. This outcome was obtained by several treatments and the consequent vertical flame spread tests. Data concerning additive content at 110°C (mass%) illustrated about 5.6% of its addition showed to be fairly sufficient to impart flame-retardancy for the cotton fabric.

The plausible mechanism of the flame-retardancy by using this flame-retardant could be referred in compliance with the free-radical theory [19, 20]. According to this theory, the mechanism taking place in the gas phase during combustion is believed to involve the formation of high-energy OH, H, O and alike radicals formed during combustion. In fact they can support burning process, so that their removal or conversion may help to suppress the flame. To achieve this target it would be beneficial if these radicals could be converted to less active ones. In general this suppression is believed to occur via chlorine or bromine compounds when applied as flame-retardants:

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

It is mentionable that ${}^{\cdot}R$ is a less active radical than ${}^{\cdot}H$. It is also noticeable that the halogenated flame-retardants absorb the required quantities of energy and the bonds between carbon-halogen will break homolytically. The free halogen atoms formed by this process react with the polymer's hydrogen atoms; hence hydrogen halide molecules are generated. These molecules also play an important role in stopping the chain reaction that occurs during the propagation of fire or combustion process. They may for instance, inhibit the generation of ${}^{\cdot}OH$ radicals; described in the following reaction [20, 21].

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

The newly formed halogen radical then, regenerates HX via capturing free hydrogen radical present in the gaseous phase or by reacting with the polymer's body:

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

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

Various other reactions are proposed in the literature. The major overall effect is that; the heavy halogen atoms withdraw energy from the combustion–propagation zone or from the burning region.

Thus the generated HX ultimately acts as a catalyst. After all, hydrogen halides as non-flammable gases they could also form non-combustible protective gas layers interfering with the accessibility of air oxygen, so stopping the combustion process is the resultant [21–23].

It is worthy to mention that burning of a material involves two thermal processes, i.e. combustion and pyrolysis [24]. Regarding to the thermal decomposition of cellulose, it produces solid residues, liquid components and volatile gases when it is heated without oxygen. Combustion of cellulose is an oxidation process of the compound under heat, which consumes flammable gases, liquids, and solid residues produced in the pyrolysis process of the materials and results excess quantities of heat.

It is generally agreed that radicals play a significant role in the complicated reaction mechanism of gas-phase combustion. In fact reactive radicals formed during the combustion such as ${}^{\cdot}OH$, ${}^{\cdot}O$, ${}^{\cdot}OR$ and alike take part an important role in the chain reaction of burning. Their formation is strongly endothermic, but when they react with each other or with other reactive species present in the gas phase, a large amount of heat is released back into the combustion zone, supporting the burning process [12, 21].

The pathway of the hydrated magnesium bromide deposited into the rich oxy-containing substrate i.e. cotton fabric, after loosing its hydration water molecules and bromine radicals in the combustion propagation zone, is assumed due to the generation of magnesium oxide.

Hence at this stage a profound investigation to probe the remained ashes has been of interest for continuation of this study.

After the treated specimen with a low add-on content of the salt was burned completely the ashes concerning the treated cotton possessing insufficient amount of magnesium bromide to achieve flame-retardancy, were collected.

X-ray diffraction (XRD) analysis with the use of CuK_{α} radiation of copper was then carried-out.

XRD patterns were recorded for ashes of consumed cotton impregnated by $MgBr_2{\cdot}6H_2O$ and, a

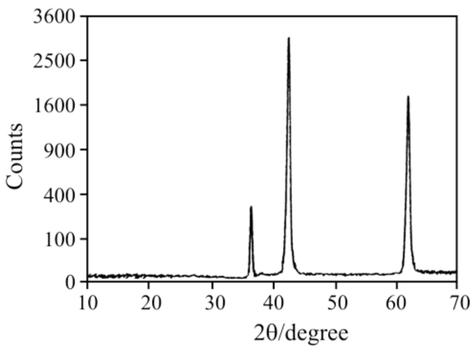

Fig. 3 XRD pattern of the consumed ashes of a cotton fabric impregnated by magnesium bromide hexahydrate

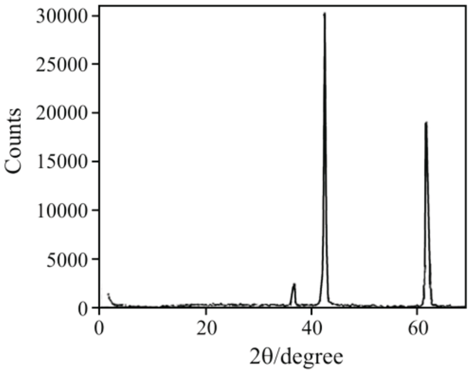

Fig. 4 XRD pattern of pure MgO specimen

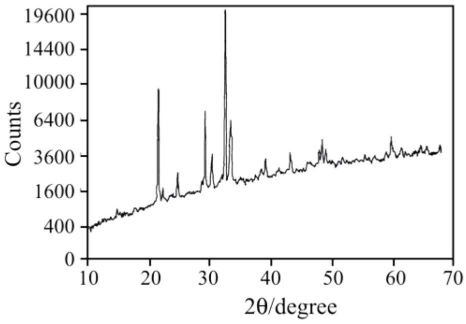

Fig. 5 XRD pattern of pure $MgBr_2$ specimen

comparison for ashes of MgO powders was then accomplished. XRD patterns of the ashes demonstrate two main peaks at $2\theta=42.515$ and 61.905 (Fig. 3). These values correspond to the peaks of 42.845 and 62.250, present in the pure MgO (XRD patterns in Fig. 4). Note the XRD patterns of the ashes do not display any significant peak that would indicate the presence of other compounds such as $MgBr_2$, etc. (Fig. 5). It is mentionable that the formation of MgO during combustion of the treated specimen could be then deduced. On the other hand the flame-retardancy action of the remained MgO in the consumed ashes could be referred due to Dust or Wall Effect Theory suggested by Jolles and Jolles [25]. According to this theory 'if a high enough concentration of dust is present in the air, no flame can propagate'. This phenomenon is suggested due to the absorption and dissipation of heat by the inert dust, causing a diminished temperature to be feedback into the bulk of polymer. It is named as Dust or Wall Effect [20, 25]. The above-mentioned hypothesis seems to be also in accordance with the 'Thermal Theory'. It suggests, 'the heat of combustion can be dissipated away from the un-burnt medium with a rate equal to the rate of heat feed-back of the heat into the bulk of the fuel (polymer)' [26]. Therefore the target of flame-retardancy could be achievable. Ultimately the generation of this oxide as an insolating protective layer may assist the formation of coating at the surface of the substrate, leading to snuff out the flame.

Conclusions

The pathway of the deposited hydrated magnesium bromide to donate flame-retardancy to a cotton fabric during the combustion, verifies an oxidation–reduction process under the access of atmospheric oxygen into the burning medium.

The existence of magnesium oxide in the consumed ashes of impregnated samples by XRD analysis supported this hypothesis. That is: no traces of magnesium bromide could be detected in the ashes. The action of this salt in the combustion zone may be considered on the basis of the suppression via free-radical theory, implying the inhibition by bromine radicals during the combustion process leaving magnesium oxide in the consumed ashes. The existence of this oxide was proven via XRD analysis.

The latest-mentioned material performs the role as a heat dissipater discussed in 'Thermal Theory'. This oxide could also coat the remaining substrate as an insolating protective layer during the combustion process, leading to snuff out the flame.

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