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THERMAL DECOMPOSITION PATHWAY OF A CELLULOSIC FABRIC IMPREGNATED BY MAGNESIUM CHLORIDE HEXAHYDRATE AS A FLAME-RETARDANT

S. M. Mostashari[*] *and H. F. Moafi*

Chemistry Group, Faculty of Science, Gilan University, P.O.Box 1914, Rasht, Iran

We have investigated the effect of magnesium chloride hexahydrate [$MgCl_2 \cdot 6H_2O$] as a nondurable finish on the flammability of 100% woven cotton fabric, (plain construction, with a density of 144 g m^{-2}, the number of yarns 21/10 mm). The laundered bone-dried, massed fabrics were impregnated with suitable concentrations of aqueous solution of the above-mentioned salt, by means of squeeze rolls. They were then dried horizontally in an oven at 110°C for 30 min. The optimum add-on value after the fulfillment of vertical flame spread test to donate flame-retardancy onto cotton fabric was obtained to be in the range of 6.73–8.30 g of the salt per 100 g fabric. Thermogravimetry (TG) of pure cotton, treated cotton and the salt was accomplished, and their TG curves were compared and commented. The results obtained are in favor of the 'gas dilution theory', chemical action theory and also in compliance with the 'free radical theory'. The formation of sal ammoniac was proven by sprinkling concentrated ammonia upon the inflamed treated specimen.

Keywords: *chemical action theory, flammability, flame-retardancy, free radical theory, gas dilution theory, magnesium chloride hexahydrate, thermogravimetry*

Introduction

With the daily increasing stringent requirements on the fire safety of materials, searching for new heat and flame-resistant polymers has attracted considerable research activity during the last 30 years [1–5]. Most of the immediate surroundings are combustible clothes, furnishings, and much of the construction materials in dwelling work and places, the interior of cars, buses, airplanes, wood, papers, textiles and synthetic polymers, etc. all burn vigorously and ignite readily. Whereas human being have been always afflicted by unwanted fires, so it is not surprising that they have sought ways to reduce the combustibility of their surroundings. In this connection early chemists tried a variety of concoctions to reduce the flammability of materials [6, 7]. In fact there are different physical and chemical theories for flame-retardation or flameproofing. However the emphasize of this article is concentrated into chemical action theory as well as gas theory and free radical theory.

According to Free Radical Theory flame-retardants dissociate into radicals that will interrupt the chain propagating and branching steps in the combustion process. Concerning halogens, the efficiency of the flame-retardant increases in the order of $F < Cl < Br < I$. This corresponds with the decreasing stability of the carbon halogen bonding. Fluorine-containing additives because of their high bond strength and stability towards higher temperatures are too ineffective and also expensive.

Hence its use could not be applicable. Although the iodine compounds are effective but they are very unstable and therefore, limited in use, so in practice, only chlorinated and brominated flame-retardants are widely used. Because of the relatively low carbon-bromine bond energy bromine containing compounds are generally preferred. They decompose at between 200 and 300°C. In fact bromine-containing flame-retardants gained an increasing market share nowadays. Since chlorine flame-retardants are relatively moderate in cost and due to a significant mass increase in the substrate donated by bromine components, sometimes chlorinated flame-retardants are preferred [8]. The implications concerning other theories are discussed hereinafter in the text.

The aim of this study is to investigate the flame-retardancy action of magnesium chloride hexahydrate on cotton fabric. In addition the thermogravimety (TG) supported our investigation. Moreover the existence of hydrochloric acid during the burning process of a treated cotton fabric has been demonstrated. The objective salt used in this investigation i.e. magnesium chloride is a colorless, crystalline salt, deliquescent in nature and exceedingly soluble in water. It is mentionable that this salt loses water and

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[*] Author for correspondence: smmostashari@yahoo.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

hydrochloric acid when heated and ultimately leaves a residue of the oxide [9].

$$MgCl_2·6H_2O \rightarrow Mg(OH)Cl+HCl(g)+5H_2O$$

$$Mg(OH)Cl \rightarrow MgO+HCl(g)$$

Experimental

Materials (sample preparation)

In this article, we developed a bath method treatment for donation of flame-retardancy into the cotton fabric by magnesium chloride hexahydrate. All fabrics used, were woven ‘plain’ construction massing 144 g m^{-2}, unfinished 100% cotton, laundered and dried, the numbers of yarns were 21/10 mm. The fabrics were 22·8 cm strips cut along the wrap direction and pre-washed in hot distilled water. They were then analytically massed. Except the first set, other bunches of specimens were dipped and impregnated into a 200 mL bath of suitable solutions of the salt at 20–22°C for 10 min. They were then squeezed rolled and dried horizontally in an oven at 110°C for 30 min, cooled in a desiccator, remassed using an analytical balance, hence their add-on percent could be determined. The samples were then conditioned overnight in a relative humidity ranged between 65 and 67% and a temperature ranged between 20 and 22°C before the vertical flame spread test. The procedure was described in the previous reports [10–19]. Their flame-retardancy were also determined using our flammability tester. The optimum figure has been obtained by several experiments (Table 1).

Methods

Thermogravimetry (TG)

Thermal analysis of a treated specimen at its optimum addition to impart flame-retardancy was accomplished. TG curves have been obtained for specimens using a TGA V5.1A DUPONT 2000 Thermal Analyzer. It was used to determine the mass loss during thermal degradation of a pure cotton fabric (1.0961 mg), the treated one with magnesium chloride hexahydrate (1.1017 mg), at the optimum addition and the pure magnesium chloride hexahydrate (1.2634 mg) were put in practice. To carry out thermogravimetry the pulverized fabrics were scratched by a razorblade, so that their pulverization could be applicable. The specimens were heated from 20 to 600°C in air atmosphere at a heating rate of 10°C min^{-1}.

Flammability tester

A vertical flame spread test method similar to the procedure described in DOC FF 3-71 [20] was employed to determine the flammability of the fabrics. It has been designed and named as Mostashari’s Flammability Tester (Fig. 1). It has also been introduced in the previous articles [10–19, 21, 22].

Mohr analytical method

Each piece of finished cotton fabric, 22 by 8 cm, with the treatment by magnesium chloride solutions was selected.

The fabric was dried in an oven at 110°C for 30 min, cooled in desiccator and massed in an analytical balance. It was then put into a 100 mL conical flask containing 50 mL of distilled water. Afterwards it was boiled for 30 min by hot distilled water. Each sample was then cooled and shaken. Each remained extracted

Table 1 The effect of deposited magnesium chloride hexahydrate on the flame-retardancy imparted to cotton fabric (woven, plain construction massing 144 g m^{-2})

Set No*.	Treating solution $MgCl_2·6H_2O$ molarity	Percent(add-on) drying at 110°C and massing	chlorine**/%	Burning time/s (sd***)	Burning rate/cm s^{-1}	Char length/cm	State**** of the fabric
1	Untreated	–	–	25(±1.08)	0.88	–	CB
2	0.25	5.80	1.90	20(±1.33)	1.10	–	CB
3	0.275	6.44	2.15	7(±2.97)	1.14	8	PB
4	0.30	6.73	2.23	–	–	0.5	FR
5	0.40	8.30	2.80	–	–	0.5	FR*****

*Average of 5 tests for each set,
**These figures determined via the Mohr analytical method,
***Sd stands for standard deviation,
****CB stands for completely burnt. PB means for partially burnt. FR means for flame-retarded,
*****Confirmatory tests applying excessive amount of magnesium chloride hexahydrate,
Note 1: For flame-retardancy (FRs) samples the char length ≤2.0 cm,
Note 2: Percent (add-on) means, the mass of addition for impregnated dry fabrics×100

Fig. 1 Identification of hydrogen chloride by concentrated ammonia, the formation of sal ammoniac as a white smoke upon the burning sample has been demonstrated

solution was transferred into a 100 mL volumetric flask and diluted with distilled water to the appropriate volume. The amount of anhydrous magnesium chloride in the finished fabric was calculated by titration of chloride anion via Mohr method.

The chloride anions were determined by titration with a standard 0.01 normal solution of $AgNO_3$, using 5% K_2CrO_4 solution as an indicator.

Qualitative analysis concerning generation of hydrogen chloride

Detection of hydrogen chloride generated during the flaming process of a finished fabric by magnesium chloride was accomplished via sprinkling of concentrated ammonia by using a sprinkler upon the burning zone of an inflamed treated fabric. The formation of a white smoke known as ammonium chloride (sal ammoniac) was obviously observed (Fig. 1).

$$HCl(g)+NH_3(g)\rightarrow NH_4Cl(g)$$

This verifies the existence of hydrogen chloride formed upon the burning zone. Actually it correlates with the production of HCl which can obviously lead to extensive charring of the cellulosic substrate, reducing the amount of volatile gases and also suppress the generation of flammable decomposition products, where are discussed hereinafter.

Results and discussion

The experimental results are summarized in Table 1. The vertical flame spread test was carefully conducted to determine the burning time. The burning rates were calculated by dividing the length of sample (in cm) by the burning time in sec. It can be concluded from the tabulated results on the burning time that the range of 6.73–8.30% addition of the afore-mentioned salt is fairly sufficient to donate flame-retardancy to the cotton fabric. In fact magnesium chloride hexahydrate has an acidic nature (pH≈5), the plausible mechanism of its flame-retardancy can be rationalized using the chemical action theory [23]. This theory indicates that the acidic nature of a salt as a flame-retardant could promote the formation of solid char rather than volatile pyrolysis products when the polymer is subjected to thermal degradation. Ideally the carbon present in cellulose could be confined to the solid products and water vapor. Hereupon during the thermal decomposition, the cellulosic substrate is pushed through a catalytic dehydration represented below:

$$(C_6H_{10}O_5)_n\rightarrow 6nC+5nH_2O$$

It is noticeable that the mode of action of halogen-containing compounds to act as flame-retardants is also in compliance with the free-radical theory [23, 24]. According to this theory, the mechanism taking place in the gas phase during combustion is believed to involve the formation of high-energy $^\bullet OH$, $^\bullet H$, $^\bullet O^\bullet$ radicals formed during combustion which can support the afore-mentioned process, so that their removal or conversion can help to suppress the flame. To achieve this target it would be beneficial if these active radicals could be converted to less active ones. In fact this suppression is believed to occur via chlorine or bromine compounds when used as flame-retardants:

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

It is worthy to mention that $^\bullet R$ is a less active radical than $^\bullet H$. It is also noticeable that the halogenated flame-retardants absorb a significant amount of energy. Moreover the bonds between carbon-halogen will break homolytically. The free halogen atoms formed by this process react with the polymer's hydrogen atoms, generating hydrogen halide molecules. These molecules also play a significant role in stopping the chain reaction that occurs during the propagation of fire or combustion process. They may, for instance, inhibit or deactivate $^\bullet OH$ radicals [24, 25].

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

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

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

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

Different 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 HX ultimately acts as a negative catalyst. After all hydrogen halides as non-flammable gases could also form non-combustible protective layers, interfering with or stopping the combustion process [25–27].

Thermogravimetry

The TG curve of untreated cotton fibers (Fig. 2) confirm the data cited in the scientific literature. That is: pyrolysis of cellulose includes three stages: initial, main, and char decomposition [28]. The correlative temperature and the trend of mass loss for every stage can be found from TG curve. In the initial stage, where the temperature range is below 300°C, the most important changes of the fabric are in some physical properties with a little mass loss. Here, the damage on cellulose occurs mostly in the amorphous region of the polymer. The main pyrolysis stage occurs in the temperature range of 300–370°C. At this stage, the mass loss is very fast and significant. Most of pyrolysis products are produced in this stage. Glucose is one of the major products, together with all kinds of combustible gases [28].

Generally speaking, at this stage the pyrolysis of cellulose takes place in the crystalline region of the fibers. According to the literature, the char pyrolysis occurs at the temperature above 370°C. In fact during the process of dehydration and charring reactions a competition between the productions of glucose, with the dehydration and charring reactions happens [28]. The mass decomposition continues to dehydration and decarboxylization, releasing more water and carbon dioxide and other residues. So that the carbon content in the decomposed products becomes higher and higher, and charred residues are formed. It is noticeable that despite the exact temperature ranges of cellulose the pyrolysis may vary depending on different cellulosic substrate and the experimental conditions.

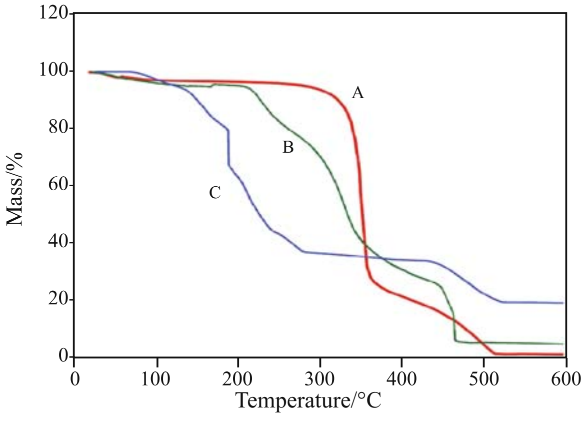

Fig. 2 The combined curves of untreated and treated cotton fabrics with the optimum addition of magnesium chloride to impart flame-retardancy, TG spectra of A – pure cotton fabric, B – FR cotton fabric, C – pure magnesium chloride hexahydrate

The pyrolysis of the flame-retarded sample, finished by magnesium chloride shows the similar three stages, but at a lower decomposition temperature (Fig. 2). Note that the decomposition temperature concerning the finished fabric is about 30°C below the temperature of untreated one. While this figure for pure magnesium chloride hexahydrate is much lower, in fact it is around 190°C.

Actually hydrated magnesium chloride showed a spectacular mass loss at 190°C. This is because of the majority of its hydration water is lost at this temperature and onset of hydrolysis to give HCl. However at 480°C a minor mass loss is displayed in the TG curve (Fig. 2).

It seems that the sixth hydration water of the hexahydrate salt is lost at this temperature. Similar work gave extensive data concerning the effect of heat on $MgBr_2\cdot 6H_2O$ [29]. It indicated that the above-mentioned temperature occurs at 180°C and onset of hydration to give HBr. On the basis of this work, it is not surprising that this salt and alike prove to demonstrate a good flame-retardancy. The production of acid can obviously lead to extensive charring of the cellulosic substrate, reducing the amount of volatiles and inflammable decomposition products. Therefore chemical action theory [23] could also be rationalized.

It is mentionable that the generation of HCl in the gas phase will inhibit the normal oxidation processes as described earlier. Moreover its qualitative identification has also been indicated herein before in this article, proves this hypothesis.

Concerning the treated cotton fabric with this salt at its optimum addition of the flame-retardancy, the degradation started at 220°C, this path is followed at 320 and 450°C respectively. Note that at the first stage of mass loss i.e. at 220°C exceeded the temperature range for pure magnesium chloride hexahydrate. It seems to be correlative with the hydrogen bonding between hydrated salt and the cellulosic substrate. This mutual attraction ultimately caused the liberation of water vapor and hydrogen chloride at a punctual duration, helpful to suppress the flame. Hence 'gas dilution theory' and 'free-radical theory' would be rationalized to justify its action [23, 24].

The results of the second and third rows of Table 1 show under the optimum limit addition of this salt, a decrease in the burning time and an increase in the burning rate was the outcome. This observation is in favor of the literature stated by Reeves and Hammons [30]. They distinguished that the inefficient quantities of certain flame-retardants accelerate the burning process of fabrics, i.e. by deposition of insufficient quantities of some flame-retardants, the imperfect rapid burning deformation occurred and a decrease in burning time and an increase in the burning rate were the outcome. Plausibly, this is due to the relative rigidity donated to the cotton substrate by the use of some additives, such as the afore-mentioned salt. It is likely 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 adequate amount of the above-mentioned salt are deposited onto the cotton fabric, the dust 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.

Concerning the pathway of the deposition of this salt during combustion, it verified the existence of magnesium oxide in the consumed ashes of the treated specimens by XRD analysis [31]. Hereupon the inhibiting action of chlorine radicals during the combustion, leaving magnesium oxide in the consumed ashes was proved.

Conclusions

In this article the action of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) deposited as a flame-retardant onto cotton fabric has been investigated and commented. The above- mentioned chemical displayed a favorable flame-retardancy. This is due to its ability for generating its hydration water in a punctual duration of thermal degradation zone of the cellulosic substrate. Another role of this salt seems to be due to the liberation of chlorine radicals to suppress the flame, by conversion of active radicals such as $^{\bullet}OH$, $^{\bullet}H$, $^{\bullet}O^{\bullet}$ to less active ones yielding the hydrogen chloride gas. The generation of this gas during the burning process was demonstrated by sprinkling the concentrated ammonia upon the flaming zone of a finished fabric. Consequently a white smoke of sal ammoniac was generated. Hydrogen chloride can also play as a protective layer interfering with or stopping the combustion process. The results obtained by thermogravimetry support this hypothesis, indicating the sensible mass loss concerning the dehydration of treated cellulose which occurred at a punctual duration of the thermal degradation zone of the polymeric substrate.

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