Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 933–936

TG OF A COTTON FABRIC IMPREGNATED BY SODIUM BORATE DECAHYDRATE ($Na_2B_4O_7 \cdot 10H_2O$) AS A FLAME-RETARDANT

S. M. Mostashari and F. Fayyaz*

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

The effect of sodium borate decahydrate as a nondurable treatment on the flammability of 100% cotton fabric (woven plain 150 g m^{-2}) has been investigated in this paper. The laundered bone-dried massed samples were impregnated with suitable concentrations of sodium borate decahydrate. Each bunches of fabrics were dipped into individual aqueous solutions of the salt, followed by means of squeeze rolls and drying at 110°C. By using a 'vertical flame spread test' the optimum add-on values to impart flame-retardancy onto cotton fabric was determined to be as 4.24 g salt per 100 g fabric. The objective of this study is thermogravimetry (TG) investigation of pure cotton, treated one with the salt at its optimum efficiency. So that outcomes could be compared and commented, finally the results obtained are in favor of 'Chemical action theory', 'Condensed phase retardation', 'Dust or wall effect theory' and also 'Gas dilution theory'.

Keywords: *chemical action theory, condensed phase retardation, dust or wall effect theory, gas dilution theory, sodium borate decahydrate, TG*

Introduction

Recent developments in the chemistry of halogen-free flame retardant polymers involve polymers or reactive monomers that are inherently flame-retarding such as those containing phosphorous, silicon, boron, nitrogen and other miscellaneous elements [1]. Amongst them boron compounds are often considered to be good flame-retardants [2]. Boric acid and its salts have been used as flame-retardant additives since early 1800s, but they have been less studied than phosphorous, halogen and other compounds. The use of borates in enhancing the flame-retardancy of polymeric materials was reported earlier in the 20th century. Thus boron is found to exert its flame-retardant action on polymeric materials at a temperature well below that of the normal pyrolysis of these materials [3].

Borates (such as colemanite, ulexite, kernite, etc.) have a variety of applications in industry including glass, ceramics and detergents. These compounds are used as flame-retardants where they reduce flammability by melting and preventing contact of oxygen with the burning surface [4].

It was found that boric acid and borates have some efficacy in suppression of the flame-spread on wood surface [2], as well as cellulosic materials such as timber, particle board, paper, wood fiber and cotton products [4].

In this paper, we determined to investigate the effect of sodium borate deca-hydrate as a non-durable finish on 100% cotton fabric's flammability, so that its sufficiency could be judged for enhancing the flame-retardancy to donate into other materials such as plastics and polymers, etc. Moreover the TG/DTG curves for more justifications are put in practice.

Experimental

Materials (samples preparation)

A bath method treatment for donation of flame-retardancy into the cotton fabric by the salt was developed. The laundered, totally dried and massed specimens 'Woven' (plain) construction with a density of 150 g m^{-2} were dipped and impregnated into independent appropriate baths of the suitable concentrations of sodium borate deca-hydrate; the suitable addition to enhance flame-retardancy has been obtained by several experiments (Table 1).

With the exception of the first bunch, all other bunches of specimens were dipped and impregnated with suitable concentrations of aqueous sodium borate decahydrate solutions at 20–22°C. The applications were accomplished onto the fabrics by means of squeeze rolls and drying horizontally in an oven at 110°C for 30 min. afterwards the fabrics were cooled in a desiccator and re-massed by an analytical balance. All of the samples were kept nightlong under ordinary conditions before the fulfillment of the vertical flammability test.

* Author for correspondence: smmostashari@yahoo.com

1388–6150/$20.00

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

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

Set[a] No.	Treating solution (molarities)	Percent (add-on) drying at 110°C and massing	Burning time/s (Sd)[b]	Applied moles	Char length/cm	Burning rate/cm s^{-1}	State of the fabric[c]
A	untreated	–	27±1.10	–	–	0.81	CB
B	0.025	1.21	13±1.36	$0.8 \cdot 10^{-4}$	–	1.69	CB
C	0.050	4.02	7.66±1.39	$2.9 \cdot 10^{-4}$	6.6	0.86	PB
D	0.075	4.24	1.33±1.41	$3.0 \cdot 10^{-4}$	1.4	–	FR
E[d]	0.100	5.84	–	$4.0 \cdot 10^{-4}$	0.5	–	FR

[a]Each experiment was repeated five times, and averaged. [b]Sd stands for standard deviation. [c]CB stands for completely burned, PB for partly burned and FR stands for flame-retarded. [d]Confirmatory tests using excessive amounts of the salt. Note: for flame-retarded samples the char lenght ≤2.0 cm

Methods

Flammability test

A vertical flame spread test method for the estimation of the fabric's combustibility has been designed and named as Mostashari's Flammability Tester (Fig. 1). The conditions of the fabrics and environment were on an average temperature ranged between 20–22°C and relative humidity (RH) ranged between 65–67%. This method following the procedure described in DOC FF 3-71 was employed [5].

Fig. 1 Mostashari's Flammability Tester with a low addition of sodium borate deca-hydrate applied onto a cotton fabric just before the end of the experiment. Uneven burned and carbonaceous areas in the fabric are shown in the figure

This method was also introduced in the corresponding author's published articles [6–12]. Its description has also been introduced in author's accepted articles in this journal [13–15].

Thermogravimetry

Thermogravimetry was conducted by using a TGA V5.1A DuPont 2000 with a heating rate of 10°C min^{-1} in air, all samples were heated from 20–600°C; this apparatus was used to determine the mass loss of the samples during thermal decomposition. Hence for a better understanding about the role of sodium borate deca-hydrate on the flame-retardancy of the cotton fabric, thermogravimetry of pure cotton and the treated fabric with this salt at its optimum addition was put in practice.

Results and discussion

The experimental outcomes are listed in Table 1; vertical flame spread test was carefully conducted to measure the burning times in s (column 4). The applied moles are given in column 5. The char lengths in cm are illustrated in column 6. The burning rates are calculated by means of dividing the combusted length of the fabrics by their burning times in s; column 7. In column 8 the states of the samples at completion of testing are shown. CB for completely burned, PB for partly burned and FR for flame-retarded. The results illustrate that inadequate quantities of sodium borate deca-hydrate applied 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 [16]. They stated that inefficient quantities of certain flame-retardant finishes accelerate the burning process, i.e. a decrease in burning duration and an increase in the burning rate is the resultant. In fact the fabrics impregnated with sodium borate deca-hydrate followed suit this phenomenon.

The pyrolysis of untreated cotton fabric (Fig. 2) indicates different major stages as follows: initial stage including two sections, i.e. up to 150°C no mass loss could be observed and up to 300°C which most significant changes of cellulose begins to occur in some physical properties accompanied by a little mass loss. At the above-mentioned stage the damage to cellulose often happens in its amorphous region [17]. The main pyrolysis stage occurs in the temperature zone between 300–370°C. At this stage the sample's mass loss is very fast and obvious. Major pyrolysis products are produced at this stage. Above 370°C dehydration and charring reactions tends to be completed. Figures 3 and 4 also illustrate TG spectra of the pure sodium borate deca-hydrate; and the treated cotton fabric with this salt, at the optimum addition to impart flame-retardancy, respectively.

It is clear that a complete dehydration of cellulose accounts for around 60% of its mass loss around

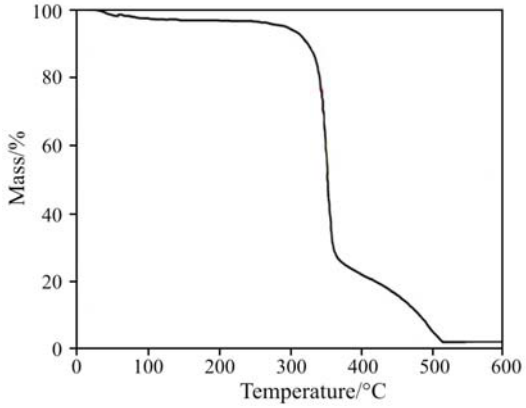

Fig. 2 TG of untreated (UT) cotton fabric

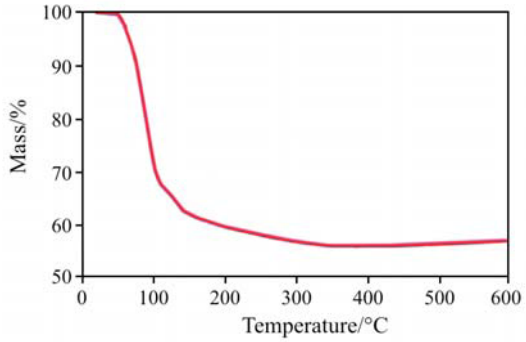

Fig. 3 TG of pure sodium borate decahydrate

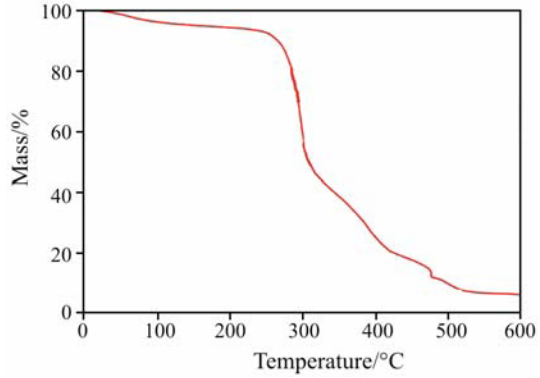

Fig. 4 TG of flame-retarded (FR) cotton fabric with sodium borate decahydrate at its optimum addition to impart flame-retardancy

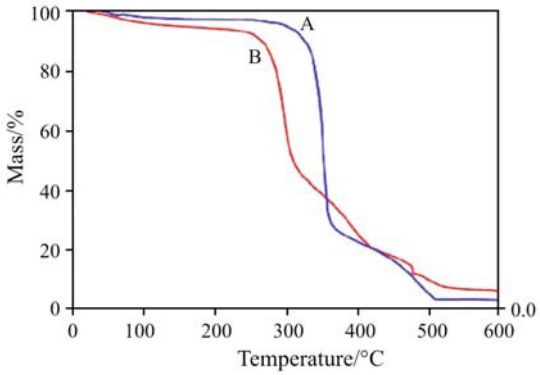

Fig. 5 Comparative TG curves A – pure pulverized cotton fabric, B – treated cotton fabric with sodium borate decahydrate at its optimum addition to impart flame-retardancy

350°C, in the presence of air. Whereas for pure sodium borate deca-hydrate (Fig. 3) the major mass loss occurs at around 90°C implying the lost of its hydration water. Concerning the treated fabric, the mass loss occurred at temperature around 290°C; implying that cellulose oxidation proceeds under this circumstance, accompanied by thermal dehydration of the substrate (Fig. 4). This implies that cellulose oxidation is pushed forward under this circumstance, accompanied by thermal dehydration of the substrate. The comparative curves could be seen in Fig. 5. It is significant that TG curve for the flame-retarded cotton fabric at its optimum percent of addition by the above-mentioned salt displayed a priority of losing its mass.

It seems that during combustion, the residue of the salt in the consumed substrate plays the role of dust or wall causing the heat absorption and dissipation. This was described in dust or wall effect theory, suggested by Jolles and Jolles [18]. According to this theory 'if a high enough concentration of dust is present in the air, no flame can propagate'. Therefore if sufficient amount of the remaining residues are present during the combustion process, they plausibly could act the role of dust or wall in the burning zone of the cellulosic substrate.

It is worthy to mention that the flame-retardancy action of the boron-containing compounds on polymeric materials is a chemical as well as a physical phenomenon. In fact it was found that inorganic boron compounds promote char formation in the burning process [1]. In addition to the usual char-forming catalytic effect, they have a rather low melting point and form glassy layer when exposed to high temperatures in fires. Actually it is found that this chemical promotes smoldering or glowing [2].

Thermogravimetry, TG curves of pure salt, untreated cotton fabric and the treated one with the salt at its optimum addition are displayed in Figs 2–4, respectively. TG curves of the salt show that below 150°C, all of its water of crystallization was lost. Comparative TG curves of untreated and the impregnated cotton fabric by the salt reveal this fact that the conditioned treated fabric lost a sensible portion of its mass around 300°C; this is about 50°C below the thermal degradation zone of untreated cotton fabric. This seems to be in correlating with the removal of water vapor via a catalytic action of the salt from the treated substrate.

On the other hand the observed burning characteristics of the treated fabrics also indicated the formation of char. The suitable mechanism of such flame-retardancy is in favor of chemical action theory [19].

According to this theory the action of certain flame and glow retardants is to promote the pyrolysis products when the polymer is subjected to thermal degradation. Ideally the carbon present in cellulose could be confined to the solid phase during the thermal decomposition, and then degradation could be pushed through the catalytic dehydration shown below:

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

The dehydration of cellulosic substrate could be catalyzed under the impression of dehydrating agents such as acidic or neutral species that form Lewis acids at high temperatures. Ideally they function only on heating, but are stable at normal temperature [20].

The effectiveness of this salt as a flame-retardant could also be justified via 'Gas dilution theory' [19, 21]. Referring to this action, some flame-retardants generate inert or not easily oxidizable gases such as CO_2, SO_2, H_2O, NH_3, etc. during thermal decomposition. Hence the atmosphere in the vicinity of inflamed substrate could be diluted and the accessibility of air oxygen into the flammable volatiles during the combustion's process becomes very difficult, so flame-retardancy could be achieved. It can be assigned that the impregnation of cotton substrate by this salt made it capable to expel water vapor under burning conditions. Its catalytic action through dehydration of the substrate could justify its flame-retardancy effect. The evidential thermogravimetry curves fortifies this hypothesis, indicating the dehydration of treated fabric occurs at a well-timed temperature zone, i.e. at a punctual duration of the thermal degradation of cellulose, so it may catalyze combustion of the substrate, by dehydrating activation mechanism.

Conclusions

Impregnation of sodium borate deca-hydrate onto cotton fabric demonstrated a favorable flame-retardancy. It is assigned that 'Gas dilution theory' and 'Condensed phase retardation', 'Chemical action theory' as well as 'Dust or wall effect theory', may be involved to justify its action that is: considering the collaboration of these hypotheses could provide a reasonable deduction. The comparative TG curves of untreated and treated cotton fabric with the salt at its optimum addition displayed a priority of losing sample's mass for the treated fabric around 275–325°C. This temperature zone is a favored range in regard with the thermal degradation zone of the cotton's substrate. TG curves, illustrated that the pure salt does not break down into oxide at the decomposition zone of the pyrolysing substrate, however its mass loss occurred around 100°C which is due to removal of its crystallization water, hence the remaining substance may act as dust or wall to absorb and dissipate the heat from the combustion's zone, causing a lowering of temperature, so its flame-retardancy could also be justified via dust or wall effect theory. Besides the above-mentioned deductions, due to its water solubility, it may not be applicable for textiles; nevertheless the outcomes of this research could be put in practice for other uses such as insulators, polymers and plastics, etc.

Acknowledgements

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

References

1 C. Martin, J. C. Ronda and V. Cádiz, 91 (2006) 747.
2 S. L. Levan and H. C. Tran, 1st International Conference on Wood Protection with Diffusible Preservatives: Proceedings 47355, November 28–30, 1990.
3 C. Martin, B. J. Hunt, J. R. Ebdon, J. C. Ronda and V. Cádiz, React. Funct. Polym., 66 (2006) 1047.
4 U. Atikler, H. Demir, F. Tokatli, F. Tıhmınlıoğlu, D. Balköse and S. Ülkü, Polym. Degrad. Stab., 91 (2006) 1563.
5 U. S. Department of Commerce Standard for Flammability of Children Sleepware (DOC.FF 3-71), Federal Register, 36, July 19, (1971).
6 S. M. Mostashari, Asian J. Chem., 17 (2005) 434.
7 S. M. Mostashari, H. Haddadi and Z. Hashempoor, Asian J. Chem., 18 (2006) 2388.
8 S. M. Mostashari, J. Appl. Fire Sci., 13 (2004–2005).
9 S. M. Mostashari and S. M. Golmirzadeh, Asian J. Chem., 17 (2005) 2007.
10 S. M. Mostashari and A. Darsaraei, Intern. J. Chem., 15 (2005) 89.
11 S. M. Mostashari, M. A. Zanjanchi and O. Baghi, Combustion, Explosion Shock Waves, 41 (2005) 426.
12 S. M. Mostashari and S. Z.Mostashari, Asian J. Chem., 17 (2005) 2331.
13 S. M. Mostashari and Y. Kamali Nia, J. Therm. Anal. Cal., 92 (2008) 489.
14 S. M. Mostashari, Y. Kamali Nia and F. Fayyaz, J. Therm. Anal. Cal., 91 (2008) 237.
15 S. M. Mostashari and S. Z. Mostashari, J. Therm. Anal. Cal., 91 (2008) 437.
16 W. A. Reeves and M. A. Hammons, Text. Res. J., 50 (1980) 245.
17 P. Zhu, S. Sui, B. Wang, K. Sun and G. Sun, J. Anal. Appl. Pyrolysis, 71 (2004) 647.
18 Z. E. Jolles and G. I. Jolles, Plastics Polymers, 40 (1972) 319.
19 J. H. Troitzsch, Chimica Oggi Chemistry Today, 16 (1998) 10, 14.
20 A. R. Horroks, JSDC, 99 (1983) 191.
21 S. M. Mostashari, The production of Flame-retarded Acetate Rayon, M. Phil. Thesis, University of Leads, (1978), pp. 1, 4.

Received: December 20, 2007
Accepted: January 4, 2008

DOI: 10.1007/s10973-007-8933-7