Journal of Thermal Analysis and Calorimetry, Vol. 91 (2008) 1, 237–241

THERMOGRAVIMETRY OF DEPOSITED CAUSTIC SODA USED AS A FLAME-RETARDANT FOR COTTON FABRIC

S. M. Mostashari[*]*, Y. Kamali Nia and F. Fayyaz*

Chemistry Department, Faculty of Science, The University of Gilan, Rasht, Iran

We have investigated the effect of caustic soda as a nondurable finish on the flammability of 100% cotton fabric (plain 180 g m^{-2}). On the contrary to the mercerization, during the impregnation process, no tension was applied. In order to attain the alkali cellulose onto the fabric, the subsequent neutralization was not followed. Each bunches of fabrics were dipped into individual aqueous solutions of sodium hydroxide, followed by means of squeeze rolls and drying at 110°C. After conditioning nightlong, by using our 'vertical flame test' the optimum add-on values to impart flame-retardancy into cotton fabric was determined as 1.3 g sodium hydroxide per 100 g fabric.

Thermogravimetry and derivative thermogravimetry (TG/DTG) of pure cotton, treated cotton with sodium hydroxide at its optimum efficiency to impart flame-retardancy into the fabric was fulfilled and the obtained curves were compared and commented. The effectiveness of this hydroxide is attributed to the heat dissipation by the remaining material in the consumed ash. The results obtained are in favour of 'dust or wall effect theory' and also gas dilution theory.

Keywords: *caustic soda, chemical action theory, condensed phase retardation, dust or wall effect theory, flammability, gas dilution theory, thermogravimetry*

Introduction

Today, flame-retardants (FRs) are used in a wide range to the materials from plastic coatings for wires and cables, in foams, textiles, furniture and upholsteries, in adhesives and wood, paper and construction materials, etc. The products used in these applications are either inherently flame-retarding materials and or protected substances with treatments by flame-retardant additives. In fact research and testing in apparel flammability has involved various approaches. The earliest use of flame-retardant materials is date back to the fourth century B.C., which the use of vinegar to impregnate wood had been recommended [1, 2].

Most early additives were water-soluble salts and devoted to cotton fabric. The interest in achieving fire-retardancy technology and chemicals that could be applied to cellulosic fabrics to impart flame-retardancy has improved sufficiently at the present centenary.

In our investigation the effect of caustic soda as a nondurable finish on 100% cotton fabric's flammability was studied. Contrary to the mercerization process [3] no tension was applied and the temperature of the bath was kept at 20°C. In order to retain the alkali cellulose formed on the surface of the fabric, the subsequent neutralization and washing was abandoned. It is mentionable that Mercer was the first who suggested treatment of cotton with 20% sodium hydroxide. He observed that when the hydroxide had been removed by treatment with acid and washing, the cotton increased in tensile strength, contracted in length, and had acquired a greater affinity for dyes. In fact the alkali had formed alkali cellulose; it is noticeable that the mercerized cotton is commercially desirable. The fabrics also acquire additional properties such as increased lustre, a greater capacity to respond to mechanical finishing processes, and softer to handle, etc. [4].

Experimental

Materials ad methods

Samples preparation

In this article we developed a bath method treatment for donation of flame-retardancy into the cotton fabric by caustic soda. The laundered, dried and massed specimens 'Woven' plain construction with a density of 180 g m^{-2} were dipped and impregnated into independent baths of the suitable concentrations of caustic soda; the figures have 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 hydroxide solutions at 20–22°C. The applications were accomplished onto the fabrics by means of squeeze

* Author for correspondence: smmostashari@yahoo.com

1388–6150/$20.00

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

Table 1 The effect of deposited 'caustic soda' on the flame-retardancy imparted to cotton fabric (woven plain 180 g m^{-2})

Bunch*	Treating solution (molarity)	Percent (add-on) drying at 110°C and massing	Applied moles	Burning time/s (Sd)**	Burning rate/ cm s^{-1}	Char length/cm	State of the fabric***
A	untreated	–	–	31±1.02	0.71	–	CB
B	0.06	1.03	0.026	21.2±1.34	1.04	–	CB
C	0.07	1.1	0.028	24±1.40	0.92	–	CB
D	0.08	1.3	0.032	–	–	0.3	FR
E	0.10	1.65	0.041	–	–	0.20	FR

*Each experiment was repeated five times. **Sd stands for standard deviation. ***CB stands for completely burned, FR stands for flame-retarded. Note: for flame-retarded samples the char lenght ≤2.0 cm

rolls and drying horizontally in the 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.

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 is originated under the impression of the procedure described in DOC FF 3-71 [5].

Fig. 1 Mostashari's flammability tester with a treated fabric inserted and pinned in its inner grooves, before to the fulfillment of the flammability test

The above-mentioned tester has also been described in the previous published investigations [6–8] and also it has been described in the corresponding author's accepted articles in this journal [9, 10]. It is a rectangular aluminum frame cut on from one of its smaller sides: it has inner grooves 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. According to the aforementioned test, the aluminum frame with the following specification has been applied: Two strips of 3 m aluminum double-sheet, 22.5 cm by 1.5 cm cut, perforated and welded at right angles to a shorter 9 cm strip. The specimens were 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. It is worthy to mention that in this experiment an ignition time of 3 s was observed. This procedure was conducted in order to avoid harsh condition for ignition. Repeatability of burning time was ±5% for untreated samples, repeatability for 'sodium hydroxide' treated fabrics was much worse. In fact the pad squeeze process resulted a certain amount of variability this also indicates the presence of inhomogeneities of the treatment. After the ignition, at the bottom edge, the total burning time at the nearest 0.1 s was determined with a stop-watch. 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. The length of 'char' was measured after each test to the nearest cm. The flammability test was conducted in a put out 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.

Thermogravimetry (TG)

Thermogravimetry is a technique, which measures the mass changes of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Hence for a better understanding about the role of sodium hydroxide on the flame-retardancy donated to cotton fabric, thermogravimetry of pure cotton (1.0768 mg) and the treated fabric with sodium hydroxide (1.9716 mg) at its optimum addition was accomplished. TG curves were obtained with a TG V5.1A DuPont 2000 Thermal Analyzer; this apparatus was used to determine the mass of the sample loss during thermal decomposition. To fulfill thermal analysis, a pulverized pure cotton fabric, and the treated one were put in practice. All samples were heated from 20 up to 510°C in air at a heating rate of 10°C min^{-1}.

Results and discussion

The experimental results are listed in Table 1. The vertical flame test was carefully conducted to measure the burning times in s (column 5). In column 8 the states of the samples at completion of testing are shown. CB for completely burned, and FR for flame-retarded. The char lengths in cm are illustrated in column 7. The applied moles are shown in column 4. The burning rates are calculated by means of dividing the length of the fabrics (22 cm) by their burning times in s; column 6. The results show that inadequate quantities of sodium hydroxide applied as the flame-retardant decreased the burning times and increased the burning rates. This outcome is in compliance with the scientific literature suggested by Reeves and Hammons [11]. 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 hydroxide followed suit this phenomenon. The TG curves illustrations displayed that up to 410°C, the treated specimen with caustic soda is almost thermally degraded, while untreated cotton, not. This means that at moderate temperature, the hydroxide catalyzes the combustion of char. That is; the carbon residue is possibly consumed be activation of oxygen via the assistance of the hydroxide. The pyrolysis of pure cotton fabric includes different major stages as follows: initial stage including two sections, i.e. up to 150°C no sample 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 sample loss. At the above-mentioned stage the damage to cellulose often happens in its amorphous region [12]. The main pyrolysis stage occurs in the temperature zone between 300–370°C (Fig. 2). At this stage the sample's mass loss is very fast and significant. Major pyrolysis products are produced at this stage. Above 370°C dehydration and charring reactions tends to be completed. Figures 3 and 4 also demonstrate TG spectra of the treated cotton fabrics with sodium hydroxide at the optimum addition to impart flame-retardancy, and the comparative curves, respectively. Actually the fabric supported by sodium hydroxide displayed a mass loss at lower temperatures.

It is important that TG curve for the flame-retarded cotton fabric at its optimum percent of addition by the above-mentioned hydroxide displayed a priority of losing its mass. In other words; complete dehydration of cellulose accounts for around 60% mass loss at 350°C, in the presence of air. Whereas for the treated fabric, the mass loss at temperature below 350°C; exceeds this limit. This implies that cellulose oxidation proceeds under this circumstances, accompanied by thermal dehydration of the substrate. It seems that the remained hydroxide in the consumed substrate is about 1.5% of the initial mass of the sample. This temperature is around 510°C, so at combustion's zone it 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 [13]. According to this theory 'if a high enough

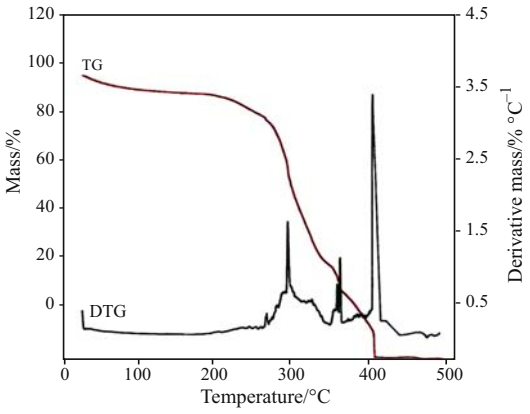

Fig. 3 TG and DTG curves of flame retarded (FR) cotton fabric with caustic soda at the optimum addition to impart flame-retardancy

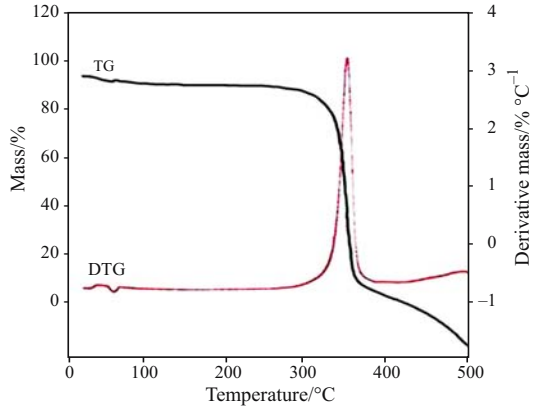

Fig. 2 TG and DTG curves of untreated (UT) cotton fabric

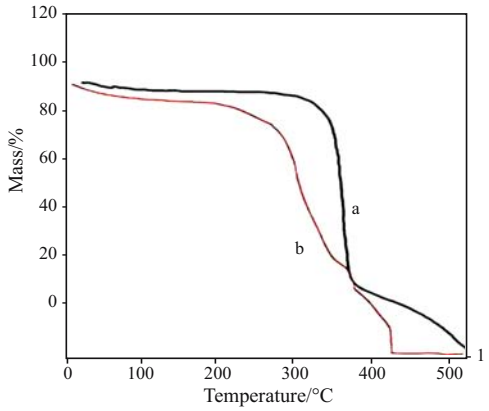

Fig. 4 a – TG curves of pure pulverized cotton fabric, b – treated cotton fabric with caustic soda at its optimum addition to impart flame-retardancy

concentration of dust is present in the air, no flame can propagate'. Therefore if sufficient amount of caustic soda is impregnated onto the fabric, it plausibly acts the role of dust or wall in the combustion's zone of the cellulosic substrate.

It is worthy to mention that; sodium hydroxide is highly stable at elevated temperatures and does not decompose on heating [14]. Hence it seems to remain intact in the consumed substrate and the absorption and dissipation of heat by its particles causes a lowering of temperature, so snuffing out of the flame is the resultant.

Concerning thermogravimetry, the TG curves of untreated cotton fabric and the treated one with sodium hydroxide at the optimum addition are displayed in Figs 2–4, respectively.

DTG and TG curves of untreated and the impregnated cotton fabric by sodium hydroxide reveal this fact that the conditioned treated fabric by the hydroxide lost a sensible portion of its sample around 300°C; that is about 50°C below to the thermal degradation zone of untreated cotton fabric. This seems to be in correlating with the removal of absorbed water and probably the carbon dioxide gained during the conditioning process overnight by the fabric before the accomplishment of the experiment.

On the other hand the observed burning characteristics of the treated fabrics also indicated the formation of char and the effectiveness of this hydroxide in suppressing the after-glow. The suitable mechanism of such flame and glow-retardancy is in favor of chemical action theory [15].

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 effectiveness of caustic soda as a flame-retardant could also be justified via 'gas dilution theory' [2, 16, 17]. 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 of combustion's products becomes very difficult, so flame-retardancy could be achieved. It can be assigned that the impregnation of cotton substrate by caustic soda made it capable to expel water vapor under burning conditions, so caustic soda could act as a dehydrating flame-retardant agent. The evidential thermogravimetry curves fortify 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.

Conclusions

Impregnation of sodium hydroxide deposited onto cotton fabric demonstrated an excellent flame-retardancy. It is assigned that both 'gas dilution theory' and 'condensed phase retardation' and also dust or wall effect theory, are involved to justify its action, i.e. considering the collaboration of these hypothesis could be beneficial to gain a reasonable deduction. The comparative thermograms of the untreated and treated cotton fabric with caustic soda at its optimum addition displayed a priority of losing sample's mass for the treated fabric around 280–300°C. This temperature is at a punctual duration range of the thermal degradation zone of the cotton's substrate. It seems that the hydroxide catalyzed the combustion of the substrate causing carbon residue, plausibly by activation at the atmospheric oxygen. Since this hydroxide does not break down into the oxide at the decomposition zone of the pyrolysing substrate, so it may act as dust or wall to absorb and dissipate the heat from the combustion's zone, causing a lowering of temperature, so that the flame-retardancy is achievable. Besides from the above-mentioned effect, releasing of water vapor and carbon dioxide gained during the conditioning process, may also assist the flame-retardancy. Because of corrosiveness and irritability of caustic soda to skin, its application for garments is ruled out. Independent of this failure, choosing cotton as a handy polymeric substrate has been beneficial to detect the high efficiency of caustic soda to combat the flame. So that it's probable application in insulators and some polymeric materials and plastics may be put in practice.

Acknowledgements

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

References

1 J. E. Ramsbottom, The Fire Proofing of Fabric, O. H. M. O., London 1947.
2 S. M. Mostashari, The production of flame-retarded Acetate Rayon, M. Phil Thesis, University of Leads, 1978, pp. 1 and 4.
3 D. S. Lyle, Modern Textiles, John Wiley, New York 1976, p. 94.

4 E. R. Trotman, Dyeing and Chemical Technology of Textile Fibres, Charles Griffin and Company Ltd., 4th Ed., London 1970, p. 62.
5 U. S. Department of Commerce Standard for Flammability of Children Sleepware (DOC.FF 3-71), Federal Register, Vol. 36, No. 146, July 19, 1971.
6 S. M. Mostashari, M. A. Zanjanchi and O. Baghi, Explosion and Shoke Waves, 41 (2005) 426.
7 F. M. Farhan, S. M. Mostashari and G. Ghazi Moghadam, Intern. J. Chem., 2 (1991) 163.
8 S. M. Mostashari, Intern. J. Chem., 13 (2003) 115.
9 S. M. Mostashari and Y. Kamali Nia, J. Therm. Anal. Cal., (2007), accepted.
10 S. M. Mostashari and S. Z. Mostashari, J. Therm. Anal. Cal., (2007), accepted.
11 W. A. Reeves and M. A Hammons, Text. Res. J., 50 (1980) 245.
12 P. Zhu, S. Sui, B. Wang, K. Sun and G. Sun, J. Anal. Appl. Pyrolysis, 71 (2004) 647.
13 Z. E. Jolles and G. I. Jolles, Plastics Polymers, 40 (1972) 319.
14 A. K. De, A Textbook of Inorganic Chemistry, Wiley Eastern Ltd., New Delhi 1983, p. 221.
15 A. R. Horroks, JSDC, 99 (1983) 191.
16 M. Kenser and W. J. Vos, J. Chem. Educ., (2001) 41.
17 J. H. Troitzsch, Chimica Oggi Chemistry Today, 16 (1998) 10.

Received: November 21, 2006
Accepted: April 17, 2007
OnlineFirst: October 26, 2007

DOI: 10.1007/s10973-006-8276-9