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THERMOGRAVIMETRIC ANALYSIS OF A COTTON FABRIC INCORPORATED BY 'GRAHAM'S SALT' APPLIED AS A FLAME-RETARDANT

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We have investigated the effect of 'Graham's salt' as a phosphorous containing flame-retardant applied onto cotton fabric. The optimum loading of this salt to impart flameretardancy has been determined to be about 36.78–41–31 g salt per 100 g cotton woven fabric (plain 144 g m^{-2}). Thermogravimetry of pure cotton, treated cotton fabric and the pure salt were accomplished. The curves were then compared and commented. They reveal that this salt thermosensibilized combustion of the treated substrate as a dehydrating agent. The results obtained fortified the 'Chemical Theory' and 'Coating Theory' evidenced the formation of carbonaceous residue upon the cellulosic substrate during the combustion.

Keywords: *chemical theory, coating theory, condensed phase retardation, flame-retardancy, thermogravimetry*

Introduction

The necessity for reduced flammability in different textiles has been increased by governmental legislations in many countries nowadays. This is because of the deaths caused by the ignition and subsequent flammability of garments. It is noticeable that other hazards may occur by fires such as the combined effects of smoke and toxic gases. It is declared that over half of the fatalities are due to the afore-mentioned side effects [1, 2].

As far as the household environment is concerned, children and older adults face a dramatically increased risk of dying in a home fire due to their limited cognitive and physical abilities [3].

The reason for selection of cotton fabric as a high oxy-content substrate to be impregnated with a flame-retardant is the ease of its ignition i.e. once a fragment of the substance is flamed; the charred residue will frequently continue to react through a solid-state glowing or smoldering oxidation. Hence due to its popularized demand, if no flame-retardation precaution is devised during the finishing process, significant fire hazards could be anticipated by the application of cellulosic materials. Therefore this fabric could be a good indicator for the assessment of the influential role of certain chemicals used for the purpose of flame and glow retardancy. It is mentionable that ideal candidates for commercial flame-retardants should be stable at normal temperatures and act only on heating. However this character should be considered among the other characters of flame-retardancy such as possessing high efficiency, low rate of combustion, low rate and amount of smoke generation, low toxicity and cost, etc.

The aim of this study is Thermogravimetry investigation of the commercial type of 'Graham's salt ($Na_6P_6O_{18}$)' which is an economically moderate substance could be deposited as a nondurable finish for the flame-retardancy of the cotton fabric, so that its effectiveness on the cotton's substrate during the degradation process could be assessed. The disadvantage of this chemical is its easily leach out properties, it may not be applied for textiles. Nevertheless, a better performance of flame-retardancy could be offered by using synergistic effect with nitrogen compounds and the outcomes may be put in practice for other commercial applications such as insulators, plastics, and polymers, etc.

This salt's history extends back nearly 150 years to the time when Thomas Graham described the formation of a glassy sodium polyphosphate mixture known as Graham's salt [4].

This salt is prepared by melting monosodium orthophosphate, followed by rapid cooling. Graham's salt hydrolyzes in aqueous solution, particularly under acidic condition, to sodium trimetaphosphate and sodium orthophosphate [5]. It is easily soluble in water, but not in organic solutions, absorbent to dampness, and turns sticky when absorbed humidity in air. It is possible to form solvent compound with metallic ions such as Pb^{2+} and Ag^{+} [6, 7].

In industry it is incorrectly called sodium hexametaphosphate [8]. This nomination is not correct due to it does not contain six [PO_4] units and is a high molecular mass polymer $(NaPO_3)_n$, which usu-

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ally has a mean molecular mass of 12000–18000, and up to 200[PO_4] units in the chain. Though mainly made up of long chains, it does contain up to 10% of ring metaphosphates and a little cross-linked material [7]. In overall, although this substance is in fact, more complex, the formula: $Na_6P_6O_{18}$ is generally ascribed to it [9]. The other names of this salt are Calgon S, glassy sodium, hexasodium salt [5]. Graham's salt is also used in the industry of soap, metal finishing and plating, pulp paper manufacture, synthesis of polymers, photographic products, textiles, scale removal and agriculture [10].

Experimental

Materials

All specimens were of 'plain' construction weighing 144 g m^{-2}, unfinished 100% pure cotton, laundered and dried. The fabrics were 22 cm by 8 cm strips cut along weft 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 weighed with an analytical balance.

Methods

Bath treatment

With the exception of the first set i.e. 100% pure cotton samples, all other sets of specimens were impregnated with suitable concentrations of Graham's salt solutions at 20–22°C, i.e. different sets of specimens except the first set were impregnated with suitable concentrations of Graham's salt. Actually the addition was continued until to achieve flame-retardancy. The continuation of addition by applying excessive quantities of Graham's salt into the last sets was repeated as a confirmatory cheek to make sure former add-ons efficiency.

The applications were fulfilled onto the fabrics by means of squeeze rolls and drying horizontally in an oven at 110 °C for 30 min. The fabrics were then cooled in a desiccator and re-weighed by an analytical balance. All of the samples were kept overnight under room condition before the vertical flammability test could be accomplished.

Flammability test

A vertical 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 and 22°C and relative humidity (RH) ranged between 65 and 67%. The similar procedure is described in DOC FF 3-71 [11].

The above-mentioned tester has also been described in the previous investigations [12–22]. 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. According to the aforementioned test, the aluminum frame with the following specification has been applied: Two strips of 3 mm aluminum double-sheet, 22.5 cm by1.5 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, and an ignition time of 3 s was observed. This procedure was conducted in order to avoid harsh condition for ignition i.e. yellow flame and 3 s ignition correlate with mild conditions, compared with hot blue flame and higher duration of ignition. So that, gaining more irreproducible results was avoided. Repeatability of burning time was ±5% for untreated samples, repeatability for 'Graham's salt' treated fabrics was much lower. In fact the pad squeeze process results a certain amount of variability. An ignition time of 3 sec, at the bottom edge with the accuracy of 0.1 s was observed with a stop-watch. 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 0.1 cm. The flammability test was conducted in a switched off 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. The purpose of this invention was

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

to introduce a new vertical flame spread testing method which could provide beneficial data for evaluation and development of flame-retarding materials to be compared with untreated samples. The advantages of this technique over existing textiles flammability tests is an innovation of a reliable handy economical method of evaluation concerning the flammability of termoset fabrics, especially when other techniques of flame spread are not available. Moreover the data concerning the flame-retardancy determined via this tester support the outcomes of TG/DTG curves of untreated and the flame-retarded specimens, as detailed hereinafter.

Thermogravimetry (TG)

Thermogravimetry is a technique, which measures the mass change 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 Graham's salt on the flame-retardancy confered to cotton fabric, thermogravimetry for the samples was carried-out. To determine the mass loss during thermal decomposition, a TG curve was obtained for each specimen by using a TGA V5.1A Dupont Thermal Analyzer. To fulfill thermogravimetry, a pulverized pure cotton fabric, the treated fabric with the salt at its optimum addition for flame-retardancy and the pure salt were carried-out. All samples were heated from 20°C in air at a heating rate of 10°C min^{-1}.

Results and discussions

The experimental results are listed synoptically in Table 1. The vertical flame test was carefully carried out to measure the burning time in s (column 4). In column 5 the burning rates are calculated by means of dividing the length of the combusted specimens in cm by their burning times in s. The char lengths in cm (after the tests) are given in column 6. The states of samples are illustrated in column 7. The function of concentration is so important, since insufficient addition of flame-retardant caused imperfect rapid combustion deformation. Hence a decrease in the burning duration and an increase in burning rate was the resultant. 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 into a rapid, uncompleted surface combustion. However if adequate amount of the above-mentioned additive is deposited onto the cotton fabric, the flame-retardancy is achieved.

Concerning the TG analysis, the comparative curves of untreated cotton and the impregnated sample with optimum amount of the salt and the pure salt

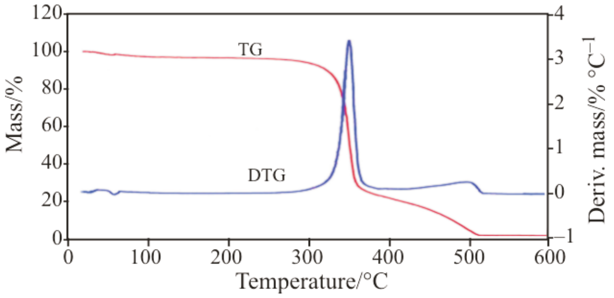

Fig. 2 TG and DTG curves of untreated (UT) cotton fabric

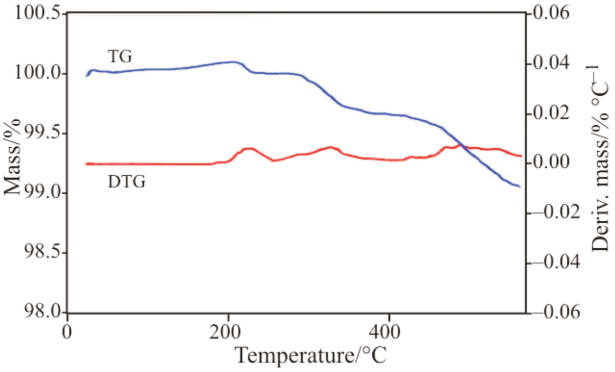

Fig. 3 TG and DTG curves of pure Graham's salt

Table 1 The effect of deposited 'Graham's salt' on the flame-retardancy imparted to cotton fabric (plain 144 g m^{-2})

Set*	Treating solution formality	(add-on) drying at 110°C /%	Burning time/s	Burning rate/cm s^{-1}	Char length/cm	State of the fabric**
A	Untreated	–	30	0.73	–	CB
B	0.40	33.63	19	1.15	–	CB
C	0.45	36.78	–	–	0.2	FR
D***	0.50	41.31	–	–	0.1	FR

*Average of 5 tests for each set.
**CB stands for completely burned, and FR stands for flame-retarded.
***Confirmatory tests applying excessive quantities of 'Graham's salt'. To explain the optimum values of addition confirmatory tests applying excessive amounts of additive were carried-out to make sure the former addition was sufficient.
Note: For flame-retarded (FRs) samples the char length ≤2.0 cm

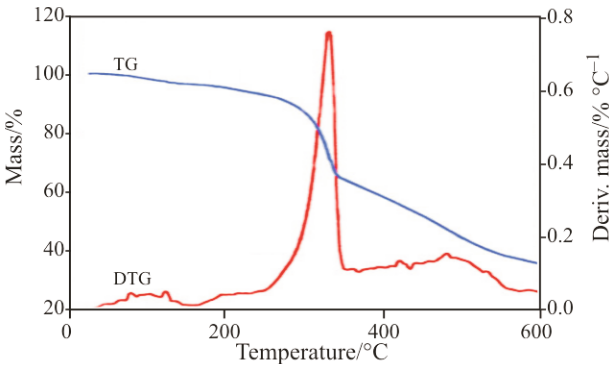

Fig. 4 TG and DTG curves of flame retarded (FR) cotton fabric by Graham's salt

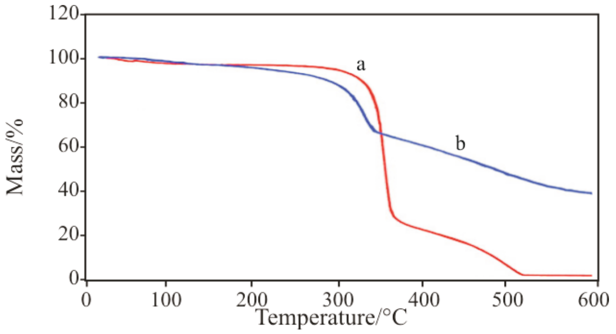

Fig. 5 TG comparative curves of a – untreated cotton fabric and b – treated cotton fabric by Graham's salt in the optimum addition of flame-retardancy

are illustrated in Figs 2 and 5, respectively. Meanwhile the TG slopes of pure Graham's salt and the treated cotton fabric by the Graham's salt are displayed in Figs 3 and 4, respectively.

Figure 5 illustrates that: the untreated specimen started a rapid decomposition at 330 °C and lost 98% of its mass at 500°C leaving a little ash (curve A). The treated conditioned specimen began to degrade at around 320°C (curve B). It is noticeable that actual major mass loss for the untreated cotton sample occurred at 340°C and above 80% of its mass is lost around this temperature. However the treated cotton sample lost the majority of its mass including its decomposition water in the vicinity of the degradation temperature of cellulose (curve B). Hence it can be deduced that the action of the Graham's salt in the cotton fabric is via liberating water vapor formed during the dehydration process of the treated cotton's substrate in a well timed limit of the thermal degradation of cellulose. It is mentionable that no major mass loss could be observed for pure Graham's salt around 330–350°C (Fig. 3) i.e. the stability of this salt at the decomposition's zone of cellulose is obvious. Thermogravimetry displayed a significant residue for the cotton substrate impregnated with the above-mentioned salt at higher temperatures up to 400°C (Fig. 4). It lost about 40% of its mass in a suitable range of the thermal decomposition of cellulose (curve B). i.e. cotton with above-mentioned addition of salt at the optimum flame-retardancy range has been rather thermosensibilized. This implies that cellulose oxidation proceeded under this circumstances, which is accompanied by thermal dehydration of the substrate.

This can be rationalized that Graham's salt as a phosphorous containing flame-retardant will act to push the cellulosic substrate to form and lose water molecules from its cellulosic chains in a well timed limit of its thermal degradation. Hence the char formation can also be attributed via its action. A suitable mechanism describing the role of this salt and alike flame-retardants considers the total decomposition of cellulose as the reaction shown below [23]:

$$–(C_6H_{10}O_5)_n – \rightarrow (6C+5H_2O)_n$$

The dehydration is catalyzed by the presence of dehydrating agents such as acidic or neutral species that form Lewis acids at high temperatures. They are effective and stable in flame-retardants at normal temperatures and function only on heating and show to be ideal for commercial purposes.

Our experimental observation displayed the formation of a thick char during burning. This agrees with the suggestions concerning the application of phosphorous compounds as flame-retardants [24–26]. It is mentionable that Troitzsch [25] suggested that phosphorus flame-retardants mainly influence the reactions occurring in the condensed phase. They are particularly effective in high some materials such as cellulose should be converted in high oxy-content materials such as cellulose and oxygen containing plastics. They are converted by thermal degradation, eliminating water from the pyrolysing substrate causing it to char, i.e. phosphoric acid formed, esterifies and dehydrates the oxygen-containing polymer and causes charring. This is in favor of Chemical Theory implying to the confinement of carbon content of the substrate to solid phase, during the thermal degradation, resulting its decomposition via catalytic dehydration to yield carbon and water vapor, so flaming could not proceed. However, Jolles and Jolles [26] stated that phosphorus compounds generate phosphoric acid on heating, to result a polymeric metaphosphoric acid. Where it is a stable coating material and coats the surface of the polymer, causing it to a carbonaceous residue. Therefore the Coating Theory could be justified. According to this theory low melting chemicals capable of forming a layer of fused material on the surface of substrate during combustion are formed, so layers impervious to air could exclude the reach of oxygen, hence its flame-retardancy is achieved.

Actually the activity of Graham's salt (sodium polymetaphosphate) despite possessing phosphate at its construction, in combustibility's terms is confined. This capability is rather hidden with regard to the effectiveness of other phosphates. Indeed this salt has a complex polymeric structure described in the scientific literature [7]. Therefore its efficiency to impart flame-retardancy is declined due to the involvement of phosphates in the polymeric chain.

Conclusions

Graham's salt deposited onto the cotton fabric to impart flame retardancy demonstrated a tendency towards these phenomena. This behavior is assigned to its multiple physiochemical characteristic, which is in compliance with different flame and glow-proofing theories. According to our experimental results the optimum add-on values of Graham's salt to donate flame and glow retardancy into cotton sample was about 36.78–41.31% of the mass of the dried fabric. This result is optimal due to its lower addition causes completely burning. However, this quantity of the Graham's salt is quite efficient to impart flame-retardancy for cotton fabric, i.e. the continuation of burning or charring of the specimens could not be detected.

The TG/DTG curves illustrated an increase in the mass of the remained residue, when Graham's salt was applied onto the cotton fabric. That is: the dehydration of cellulosic substrate treated by this salt occurred in a well timed limit of its thermal degradation zone, and promoted the formation of solid char rather than the generation of flammable volatile pyrolysis products. The comparative TG/DTG curves of untreated and treated cotton fabric with optimum addition of Graham's salt have been monitored and displayed a priority of mass loss concerning the treated fabric around 300°C. This is around the well timed temperature of thermal degradation zone of cotton's substrate which is about 350°C. It implies that this treatment has affected the pyrolysis process of the substrate to produce more char, so the production of flammable volatiles could be confined to yield solid phase and water vapor, to justify Chemical Theory towards flame-retardancy. Thermogravimetry's results are alongside of our flame-spread test, i.e. they fortify each other, and both of them are appropriate for this investigation. Moreover the results of the tests could illustrate a general pathway concerning flammability's prediction of textiles. The above-mentioned data, address a type of cotton fabric, nevertheless other types of cotton fabric have the same formula, but their physical construction of texture i.e. thickness, text of yarns (or counts), geometrical shape of fabric, the compression of tissues etc. could effect these outcomes. The results could also be used for other thermoset fabrics.

It may be recommended the use of the above-mentioned salt in conjunction with other flame-retardants such as nitrogen compounds to gain a better manifestation on the flame-retardancy, i.e. applying the synergistic effect may be beneficial to improve the afore-mentioned performance. However due to its water solubility it is not applicable for garments, but the results may be put in practice for other tissues and applications for insulators, plastics and polymers. It seems that the wall of the bulk's body of such polymers and/or plastics may preserve the salt's wash-fastness by means of preventing its chance to be in contact with water.

Ultimately the efficiency of Graham's salt as a polymeric (complex) phosphorous containing chemical used as a flame-retardant implied that the ability of the flame-retardancy depends on the structural nature, as well as the physicochemical characteristics of the substrate. overall the efficiency of Graham's salt is rather low, its attainment declined due to the involvement of phosphates in its structural polymeric chain, so higher content of this chemical is needed.

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