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Thermal Degradation and Burning Behaviour of Cotton, Polyester and Polyester/Cotton Blended Upholstery Fabrics

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Abstract: Upholstery cotton, polyester and Polyester-Cotton blended upholstery fabrics were treated with phosphorous containing flame retardant chemical. Oxidative thermal degradation and flaming characteristics of these upholstery fabrics before and after treatment was studied using Thermogravimerty, Differential Thermal Analysis and vertical flammability techniques. From TG output, mass loss profile of control fabrics was compared with that after treatment. Form DTA data, the activation energy of fabrics during decomposition was calculated. Heat of combustion of fabric before and after treatment was also evaluated. Observed fundamental properties of thermal analysis were correlated with vertical flammability result. There is complete change in degradation path of all fabrics after they are treated with flame retardant chemicals. Also, mass loss and activation energy vary drastically after chemical treatment. Activation energy of treated samples was found decreased after treatment. Presence of an endotherm in initial stages of thermal degradation and decrease in exotherm during the final decomposition of treated fabric was noted to be well correlated with reduced flame spread rate and char length.

Key words: Upholstery fabrics · Flame Retardant · Mass loss · TG · DTA · Thermal Degradation · Activation Energy · Vertical flammability · Char length · Speed of flame spread

INTRODUCTION

Flammability of cellulose based and synthetic upholstery textile materials has been recognized as an important parameter for many years. Fortunately, the cellulose has a chemical composition that makes it particularly amenable to treatment which can offer cotton to resist both flaming and glowing combustion. Phosphorous containing flame retardants (FR) have been regarded as most simple but effective chemical treatments for celluloses. [1]. Cotton (C) cellulose normally decomposes below 300°C and under dehydration, depolymerization and oxidation, release of CO, CO_2 and carbonaceous residual char results. Tar and leaveglucosan are formed at around 300°C [2]. Polyester (P) normally melts and flows under the influence of the temperature at above 260°C. In case of Polyester, the thermal decomposition is initiated by scission of an alkyl-oxygen bond and the material decomposes via the formation of cyclic or open chain oligomers, with olefinic or carboxylic end group at above 510°C [3]. There are many reports that phosphorous based compounds are effective for polyesters as well [4]. Because of the vast differences in physical and chemical properties of cotton and polyester, blend of polyester-cotton (PC) poses problems as far as the flammability of fabric is concerned. In blended fabric, polyester which has melting point at 250-260°C, tends to wick on the cotton char resulting in phenomenon called "scaffolding". Because of this, it is impossible to predict, in advance, flammability of cotton-polyester blended fabric on the basis of knowledge of individual fibres. [5-7].

It has been noted by many investigators [8, 9] that a proper selection of appropriate laboratory test method are essential for assessing flame retardancy. Basis for this is the need to understand the pass/fail criteria as the function of the end use of the textile product. FR materials have also been studied on the basis of their fundamental properties of thermal analysis which may include thermal degradation and heat flow

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[10]. Since the thermal degradation is a combination of both physical and chemical processes that involve decomposition and oxidation and depend upon Activation energy (E_a), it is thought to be an important factor in study of the material.

Many studies have been reporting E_a on pure synthetic polymer and cotton based cellulose materials in fibre form [11-14]. However, little information is available on thermogravimetric analysis and flammability of textile upholstery materials containing cotton and polyester in blended form in the fabric stage. Upholstery materials being most vulnerable to fire accidents require to be studied for the flaming characteristics upon addition of FR chemicals.

MATERIALS AND METHODS

Three commercially available upholstery fabrics samples viz., 100% cotton, 100% Polyester and a Polyester/Cotton (45/55) were treated with 350 gram per liter (gpl) of phosphorous containing flame retardant chemical. Such treated fabrics were analysed for various characteristics as explained below.

Thermal Analysis: Thermogrvimetric (TG) and Differential Thermal Analysis (DTA) were carried out on control and treated fabric samples by using TG analyser (SDT-600 model of TA Instruments, USA). The samples were heated from ambient temperature to 800°C with 10°C/min ramp in normal atmosphere. Thermograms associated with TG and DTA for control and treated samples were obtained from instrument output. Detailed information with respect to mass loss, degradation onset temperature was obtained from these thermograms for both samples before and after treatment. Three method advocated by Broido [15], Coats-Redfern (C-R) [16] and Horowitz-Metzger (H-M) [17] were adopted for calculating E_a. The different equations employed to evaluate the activation energy are as follows.

$$Broido's\ Method: \quad In\left[In\frac{1}{y}\right] = -\frac{Ea}{R}\frac{1}{T} + \left[\frac{R}{Ea}\frac{A}{\beta}T_{max}^2\right]$$

$$C-\text{R's Method}: \quad \text{In}\left[-In(y)/T^2\right] = In\left[\frac{AR}{\beta Ea}\left(1-\frac{2RT}{Ea}\right)\right] - \frac{Ea}{RT} \quad forn=1 \rightarrow O$$

$$H-M\text{'s Method} \quad In\left[-Iny\right] = Ea\frac{Ea\theta}{R(DT_{max})^2} \quad forn=1 \rightarrow O$$

Where, y is fraction of initial molecules not yet decomposed, T is absolute temperature, T_{max} the absolute temperature of maximum reaction rate, β is rate of heating, A the frequency factor and R is universal gas constant, DT_{max} maximum decomposition temperature and $\theta = T - DT_{max}$.

A graphical plot of left hand side of each of the equation 1, 2 and 3 versus 1000/T [18] was obtained for each major thermal decomposition events for all the samples.

Flammability Test: The treated fabrics were cut into two parts. One part of samples was washed using ISO 6330 standard wash procedure for 3 cycles. Vertical flammability of control, treated fabric samples and treated fabric after washing was tested adopting standard test procedure as prescribed in NFPA 701 [19]. The parameters viz., char length and afterglow were measured. Rate of flame spread was calculated using formula as below.

$$Rate\ of\ flame\ spread\left(\frac{m}{m}\right) = \frac{charlength(mm)}{X + After\ flame(s)^2} \rightarrow O$$

Where X is flame application duration (12 s)

Observations with respect to char length, afterglow and after-flame were recorded from the test. From these observations Rate of flame spread was calculated using equation No 4 given above.

RESULTS AND DISCUSSION

Thermal Degradation: Plot of thermal degradation of different fabrics both before and after treatment are given in 1a (Cotton control), 1b (cotton treated), 2a (polyester control), 2b (polyester treated), 3a (polyester-cotton blended control) and 3b (polyester-cotton blended treated). Different data observed during thermal decomposition and measured values from TG and TDA curves are given in Table 1.

Cotton Control: TG curve in Fig 1a shows three steps of mass loss. In the initial step, a mass loss of 7.5% was observed at temperature range of 30-110°C. 72% of mass gets decomposed in one single step between 250 - 400°C due to de-hydration of cotton and oxidative thermal decomposition to CO, CO_2 and formation of carbonaceous char [15, 16]. Onset point of this mass loss is 310°C. This mass loss is associated with a major exotherm which has peak at 332°C. In the third step, residual char which

Table 1: Decomposition characteristics of upholstery materials before and after treatment with FR compound

		Maximum Mass loss		Char Content	Endotherm	Exotherm
Sample No	Onset Temp. (°C)	Temp. (°C)	Loss (%)	(%)	Peak Temp. (°C)	Peak Temp. (°C)
Control						
C	310	105 250-400	7.5		---	332
			72.4	16.1	---	440
P	410	350-470	82.0	16.0		617
PC	314	105	4.5	13.1	47	500
		200-350	41.4			
		360-500	35.5			
After Treatment						
C	234	78	6.9	30.6	62	326
		180-257	39.8		203	441
		250-480	29.7			
P	354	82	6.7	18.6	197	522
		300-450	74.8			
PC	244	81	6.8	27.4	200	418
		150-270	20.3			
		310-420	48.2			

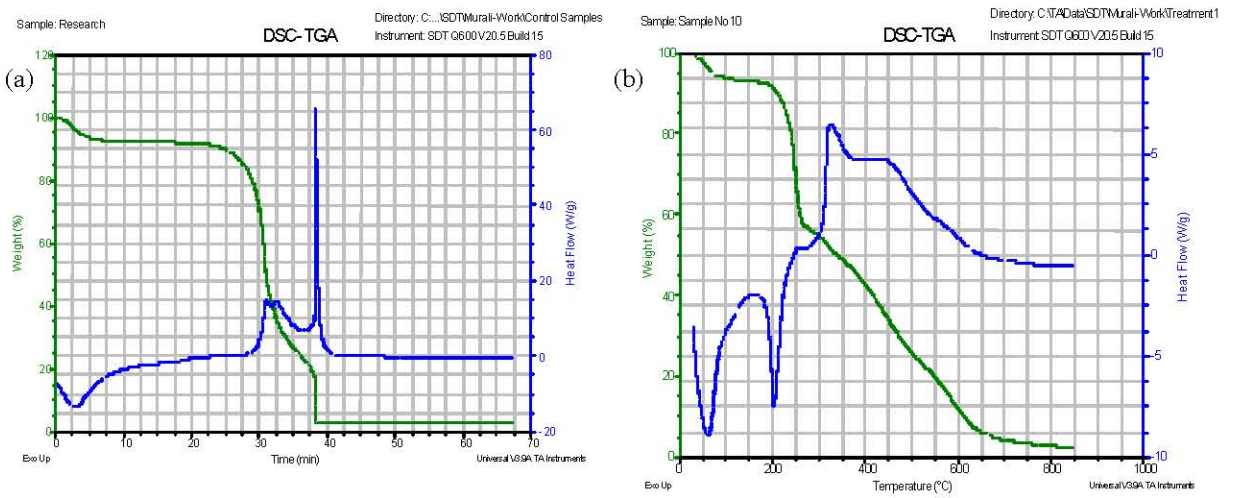

Fig. 1a,b: (a) TG and DTA of Cotton (Control)
(b) TG and DTA of Cotton (After treatment)

was formed in second step, undergoes oxidative decomposition and this resulted in a mass loss of 20.5% and associated with a sharp and large exotherm with a peak at 440°C. Mass loss curves are sharp with least slope.

Cotton after Treatment: From Figure 1b, it is seen that after chemical treatment onset temperature of thermal decomposition of cotton occurs at relatively low temperature (233.8°C) when compared to control cotton. Also, complete decomposition of cotton observed in 2 steps in control sample is now noted to be spread to 3 steps in treated sample. In Figure 1b, the 7.5% mass loss was observed due catalytic dehydration of cotton at low temperature. In Figure 1b, two endotherms with peak at 61°C and at 203.5°C were observed due to dephosphorylation and acid catalysed dehydration of treated cotton [20]. In second stage a mass loss of 37.8% was observed. This mass loss curve shows that the rate of decomposition has become slower and in turns mass loss lesser. Onset temperature of decomposition for this step for treated cotton has shifted almost by 100°C lower side when compared to control. Next major mass loss (29.7%) was observed between 250-480°C due to oxidative decomposition of char products which has resulted in an exotherm with a peak at 325°C and that at 440°C is due to oxidation of char.

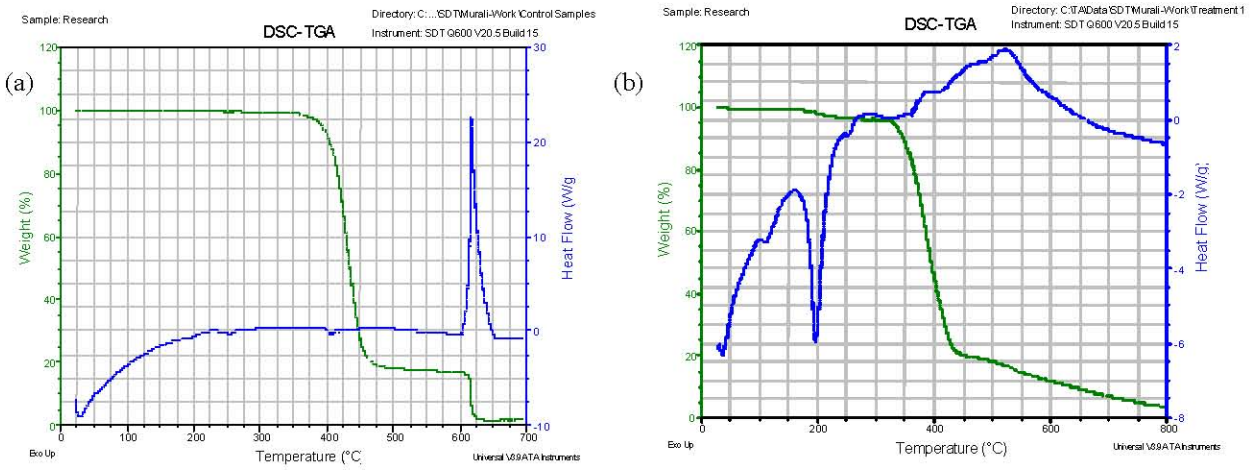

Fig. 2a,b: (a) TG and DTA of Polyester (Control)
(b) TG and DTA of Polyester (after treatment)

Polyester Control: TG curve (Fig. 2a) of the polyester shows in first step a sharp mass loss of 82% in temperature range 350-470°C. This mass loss has onset point at 410°C. This is due to thermal decomposition of polyester into CO_2 and carbonaceous char and this char undergoes oxidative decomposition at 600°C resulting in a mass loss of 16.0% [21]. A sharp exotherm with a peak at 617°C was observed during decomposition of this char.

3.1.4. Polyester After treatment: TG curve (Fig. 2b) shows a small mass loss due to catalytic dehydration. Next major mass loss is 74.8% observed in range of 300-450°C and this has occurred at lower temperature and at a slower rate when compared to control sample. Onset temperature of this major mass loss has shifted in treated samples to lower range almost by 75°C to 354°C. Char for treated sample has increased by 2.6%. Contrary to two endotherms observed in treated cotton, one endotherm was only observed in Fig 2b for treated polyester due to dephosphorylazation of treated chemical. A sharp exotherm appearing at 617°C in control sample (Fig 2a) is seen as a broader exotherm in treated sample of polyester with peak at lower temperature at 522°C (Fig 2b). It was reported that cross linking of applied phosphorus with polyester may increase the volatility of molten polymer in combustion zone, thereby lowering rate of transport of combustible pyrolysis product to flame [12]. In final stage of major mass loss, there are enough radical scavengers released to decrease speed of mass loss.

PC Control: It is observed from TGA curve that, control P/C fabric shows 2 major and 2 minor mass losses in TG curve (Fig 3a). Initially, 4.5% loss was observed in 30-110°C range and it is due to dehydration of fibres mainly of cotton. In second and third step, mass losses of 41.4% (200-350°C) and 35.5% (360-500°C) were observed respectively. Between 475-700°C, TG curve shows a mass loss of 13.1% which is also associated with an exotherm with peak at 500°C. Mass loss in PC blended fabric may be explained as follows. Thermal degradation of cotton begins at a temperature well below that required for thermal degradation of polyester. Thus cotton acts as initial source of ignition in polyester-cotton blended fabric. Therefore, second step of mass loss is mainly due to complete decomposition of cotton and partial decomposition of polyester. Polyester component furnishes additional fuel to gas phase and as polymer temperature is raised heat is produced from combustion of cotton decomposition products. Additional fuel increases vigour of gas phase oxidation [9].

PC after Treatment: From the Figure 3b, it is observed that onset point of thermal decomposition (223°C) and initial major mass loss (20.3% at 150-270°C) were observed to get shifted to lower temperature. Second major mass loss of 48.2% is observed between 310-420°C. At this point, cotton which is major portion in blend undergoes complete decomposition. As in polyester treated fabric, one endotherm is observed at 200°C. Enhanced char content (27.4% undergoes oxidative decomposition at 450 - 700°C which results in a broad exotherm with a peak at 418°C. The exotherm has also got shifted to lower temperature.

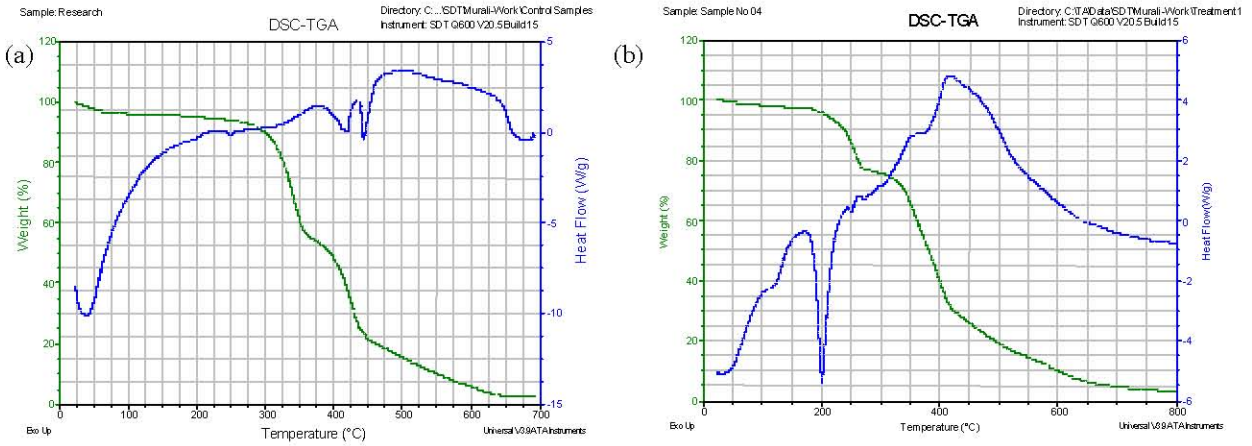

Fig. 3a,b: (a) TG and DTA of PC (Control)
(b) TG and DTA of PC (After treatment)

When compared the control samples, the mass loss in treated samples have become slower. This is evident from slopes of TG curve of Fig. 1b, 2b and 3b. Applied FR chemical starts releasing phosphoric acid at around 250°C. NH_3 and H_2O are released upon further heating phosphorus based chemical and this is resulted in appearance of endotherm at 196.7°C [22]. DTA curve of treated fabric indicates that there is one additional endotherm in 190-200°C as the result of chemical treatment. This endotherm is responsible for considerable mass loss in cotton and polyester-cotton blended samples. It may be noted from DTA curves of all three samples after treatment that exotherm in final stage of thermal decomposition has become broader and prolonged when compared to respective DTA of control samples. In control samples this exotherms are much sharper and peak was at higher temperature (□ 100°C). This indicates that heat release is distributed within a broad exotherm covering wide area resulting in major decrease in releasing rate of heat and combustible gases which fuel flaming combustion reaction. When compared to the control samples, it is evident that treated samples posses lower decomposition temperature, decreased heat release rate and increased char yield. The applied phosphorous based FR compound acts in condensed phase. In condensed phase mechanism, added FR chemical alter pyrolytic path of substrate and reduces drastically amount of combustible gases and favours formation of carbonaceous char and water [22]. Application of FR chemical containing phosphorous releases inert or not easily oxidizable phosphorous radicals, which slow down process of oxidative decomposition of cotton, polyester either in pure form or in blend form. Release of phosphorous radical in the form of NH_3, Phosphoric acid and H_2O leads to mass loss along with an endotherm at around 200°C.

Vertical Flammability: Observations of vertical flammability test are given in Table 2.

From Table 2, it could be noted that all three fabrics when subjected to the vertical flammability test burn their entire length and does not meet criteria of NFPA 701. Afterglow was observed in cotton and polyester-cotton sample for longer durations. The burning behaviour of all materials seems to have changed after the treatment. Char length in cotton and polyester-cotton samples reduced drastically and they meet requirement of NFPA 701 criteria. Although, reduction in char length was observed in polyester fabric, this fabric still fails to confirm to the requirement. FR chemical reduced after flash duration in the sample. Effect of FR chemical on these parameters was seen to be reduced after the treated-fabric was washed for 3 cycles. It is stated that effect of flame retardant chemicals remains in fabric even after the fabric waswashed for 3 cycles, but at reduced level [23]. It may be seen from Table 2 that rate of flame spread in vertical direction has reduced in all samples. Though char length of polyester fabric after treatment did not meet the criteria, highest reduction in flame spread (> 50%) was observed in this case. The reduced mass loss rate observed in TG curves for all samples after treatment can be correlated with reduced rate of flame spread. Observed burning characteristics of treated samples also indicate that formation of char and effectiveness of chemical in suppressing burn rate as well as afterglow duration are highly significant. Suitable mechanism for such flame and

Table 2: Result of Vertical flammability test

		I. Char length (inches)			II. After Glow (s)		
Sample	Weight (oz yd^{-2})	Control	After Treatment	After Treatment and washing	Control	After Treatment	After Treatment and washing
Cotton	7.8	12.5	8.3	8.9	145	0	0
Polyester	5.5	12.5	2.6	7.5	0	0	2
PC	6.8	12.5	2.0	8.1	335	0	12
		III. Rate of flame spread in vertical direction (mm/s)			IV. After Flame (s)		
Cotton		9.0	3.9	6.7	10	2	8
Polyester		13.8	6.2	6.1	21	2	19
PC		8.2	4.4	4.3	26	16	22

Table 3: Calculated Activation Energy (E_a)

	Briodo's Method (kJ/mol)		C-R's Method (kJ/mol)		H –M's Method (kJ/mol)	
Sample	Control	Treated	Control	Treated	Control	Treated
C	191.9	82.1	178.9	73.3	140.1	72.8
P	374.4	224.5	342.2	192.2	317.1	180.0
PC	150.8 (I)	83.2 (I)	134.4 (I)	73.2 (I)	134.4 (I)	64.3 (I)
	111.6 (II)	44.2 (II)	85.4 (II)	37.4 (II)	65.2 (II)	71.6 (II)

glow retardancy is in favour of chemical action theory [24, 25, 26, 27]. According to this theory, action of phosphorus flame retardants is to promote pyrolysis of products when substrate is subjected to thermal degradation. Ideally, carbon present in cellulose and polyester could be confined to solid phase during thermal decomposition and then degradation could be pushed through catalytic dehydration.

Activation energy: E_a calculated using the equation 1, 2 and 3 for all three samples before and after treatment is given in Table 3. E_a given in table were calculated as described above from DTA curves for both control sample and treated samples using the equation 1, 2 and 3. As there were two major mass loss steps in thermal decomposition of PC fabric, the E_a is calculated for both events. From table 3, it is observed that a drastic decrease occurs in E_a values for all samples after treatment [14 and 28]. Values calculated using three different equation although yield different results they were found to be in a narrow range. There observed reduction in E_a predicted by all methods after treatment was found to be same extent. Reduction in E_a implies that amount of burning material in last stage is considerably lesser. This is due to fact that less flammable products are formed or continuous burning of products is hindered. Overall thermal decomposition and E_a profile of sample under decomposition has changed after treatment with flame retardant chemicals which corroborates fact that treated samples are highly flame retardant. This has been proved in vertical flammability test.

CONCLUSION

Mass loss profile of upholstery cotton, polyester and polyester-cotton fabrics changed completely after the fabric was treated with FR compound. Pyrolytic profile was completely shaded by added that of FR chemicals. A rapid increase is noted in thermal energy absorption by system in initial stages of decomposition and there is also drop in exothermic heat and E_a. Initial thermal decomposition profile of treated samples shows the presence of endotherm which suggests that heat is consumed by expulsion of moisture and this has resulted in reduction of further flame propagation. This is in correlation with reduced char length. After the application of FR compounds, mass loss splits into many small steps and final step of mass loss is associated with a broad exotherm. These exothermic peaks are prolonged compared to their counterpart for control samples. This suggests that heat release is distributed between broader peaks covering wider area, resulting in a major reduction in rate of heat release and combustible gases thus reducing supply of fuel to further flaming. Char length, afterglow and rate of flame spread for fabrics after treatment were reduced drastically. This reduction continued to prevail even after washing the fabrics although quantum of FR chemicals was noted to be lower after washing.

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