

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

¹K.S. Muralidhara and ²S. Sreenivasan

¹Laboratories, Textiles Committee, Govt of India,
Min of Textiles, P. Balu Road, Prabhadevi, Mumbai-440025
²CIRCOT, Adenwala Road, Mumbai, India

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 the treatment was studied using Thermogravimetry (TG), Differential Thermal Analysis (DTA) and vertical flammability techniques. From TG output, the mass loss profile of control fabrics were compared with that after treatment. From DTA data, the activation energy of fabrics during decomposition was calculated. The heat of combustion of fabric before and after treatment was also evaluated. The observed fundamental properties of thermal analysis were correlated with the vertical flammability result. There is complete change in the degradation path of all fabrics after they are treated with flame retardant chemicals. Also the mass loss and activation energy vary drastically after the chemical treatment. The activation energy of treated samples was found decreased after the treatment. The presence of an endotherm in the 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 the cotton to resist both the flaming and glowing combustion. Phosphorous containing flame retardants have been regarded as most simple but effective chemical treatments for celluloses. [1]. Cotton cellulose normally decomposes below 300°C and under dehydration, depolymerization and oxidation, release of CO, CO₂ and carbonaceous residual char results. Tar and leaveglucosan are formed at around 300°C [2]. Polyester 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 the phosphorous based compounds are effective for polyesters as well [4]. Because of the vast differences in the physical and chemical properties of cotton and polyester the blend of polyester and cotton poses problems as far as the flammability of fabric is concerned. In the blended fabric polyester which has melting point at 250-260°C, tends to wick on the cotton char resulting in the phenomenon called “scaffolding”. Because of this, it is impossible to predict in advance the 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 that a proper selection of appropriate laboratory test method are essential for assessing the flame retardancy. The 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 [10].

Since the thermal degradation is a combination of both physical and chemical processes that involve decomposition and oxidation and depend upon the activation energy (E_a), it is thought to be an important factor in the 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 fabric samples viz. 100% cotton (C 10), 100% Polyester and a Polyester/Cotton (45/55) were treated with 350gpl of phosphorous containing flame retardant (FR) chemical. Such treated fabrics were analysed for various characteristics as explained below.

Thermogravimetric Analysis: Differential Thermal Analysis (DTA) and Thermogravimetry (TA) were carried out on the control and treated fabric samples by using a 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. The thermograms associated with TG and DTA for control and treated samples were obtained from the instrument output. Detailed information with respect to mass loss, degradation onset temperature were obtained from these thermograms for both the samples before and after treatment. Three methods advocated by Broido [15], Coats- Redfern (C- R) [16] and Horowitz- Metzger (H- M) [17] were adopted for calculating the activation energy, E_a . The different equations employed to evaluate the activation energy are as follows.

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

C- R's Method:

$$\ln \left[-\ln(y) / T^2 \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} f_{omn}$$

H- M's Method:

$$\ln[-\ln y] = E_a \frac{E_a \theta}{R(DT_{max})^2} f_{omn} = 1 \longrightarrow \text{O}$$

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 E_a is the activation energy, 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 the samples was washed using ISO 6330 standard wash procedure for 3 cycles. The 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. The rate of flame spread was calculated using the formula as below.

$$\text{Rate of flame spread} \left(\frac{\text{mm}}{\text{s}} \right) = \frac{\text{Char length (mm)}}{x + \text{After flame (s)}} \longrightarrow \text{O}$$

Where:

X is flame application duration (12 seconds).

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: The 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 the thermal decomposition and the measured values from TG and TDA curves are given in Table 1.

Cotton Control: The TG curve in Fig 1a shows three steps of mass loss. In the initial step, a mass loss of 7.5% was observed at the temperature range of 30-110°C. 72 % of mass gets decomposed in one single step between

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

Sample No	Onset Temp. (°C)	Maximum Mass loss		Char Content	Endotherm	Exotherm
		Temp. (°C)	Loss (%)	(%)	Peak Temp. (°C)	Peak Temp. (°C)
Control						
C	310	105	7.5	16.1	---	332
		250 – 400	72.4		---	440
P	410	350 – 470	82	16		617
P/C	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			
P/C	244	81	6.8	27.4	200	418
		150 – 270	20.3			
		310 – 420	48.2			

250-400°C due to the de-hydration of cotton and oxidative thermal decomposition to CO, CO₂ and formation of carbonaceous char [15, 16]. The onset point of this mass loss is 310°C. This mass loss is associated with a major exotherm which has the peak at 332°C. In the third step, the residual char which was formed in the 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. The mass loss curves are sharp with least slope.

Cotton after Treatment: From the Figure 1b, it is seen that after the chemical treatment the onset temperature of thermal decomposition of cotton occurs at relatively low temperature (233.8°C) when compared to the control cotton. Also the complete decomposition of cotton observed in 2 steps in control sample is now noted to be spread to 3 steps in the treated sample. In the Figure 1b, the 7.5% mass loss was observed due the catalytic dehydration of cotton at low temperature. In the Figure 1b, two endotherms with peak at 61°C and at 203.5°C were observed due to the dephosphorylation and acid catalysed dehydration of treated cotton [20]. In the 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 the mass loss lesser. The onset temperature of decomposition for this step for treated cotton has shifted almost by 100°C lower side when compared to control. The next major mass loss (29.7 %) was observed between 250-480°C due

to the 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 the oxidation of char.

Polyester Control: The TG curve (Fig. 2a) of the polyester shows in first step a sharp mass loss of 82 % in the temperature range 350-470°C. This mass loss has the onset point at 410°C. This is due to the thermal decomposition of polyester into CO₂ 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 the decomposition of this char.

Polyester after Treatment: The TG curve (Fig. 2b) shows a small mass loss due to the catalytic dehydration. The next major mass loss is 74.8 % observed in the range of 300-450°C and this has occurred at lower temperature and at a slower rate when compared to the control sample. The onset temperature of this major mass loss has shifted in treated samples to lower range almost by 75°C to 354°C. The char for the treated sample has increased by 2.6%. Contrary to the two endotherms observed in treated cotton, one endotherm was only observed in Fig 2b for treated polyester due to dephosphorylation 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

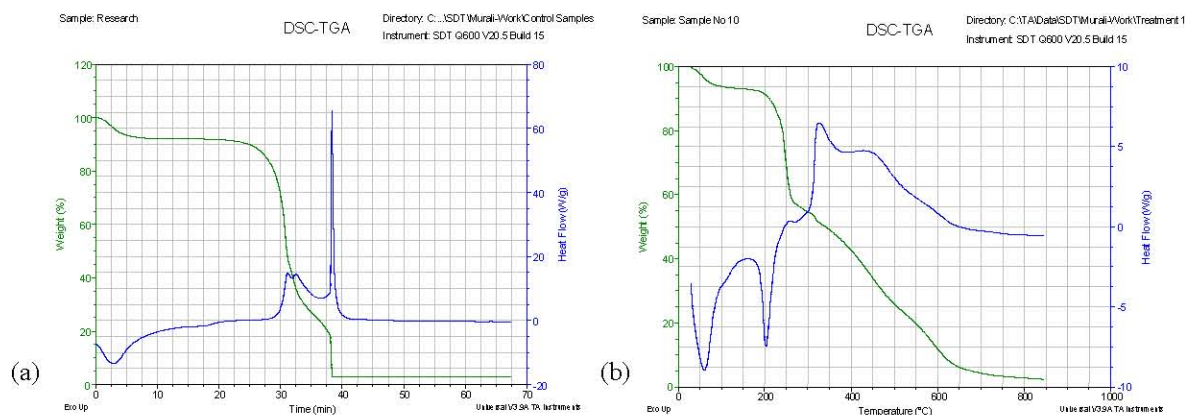


Fig. 1a: TG and DTA of Cotton (Control)

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

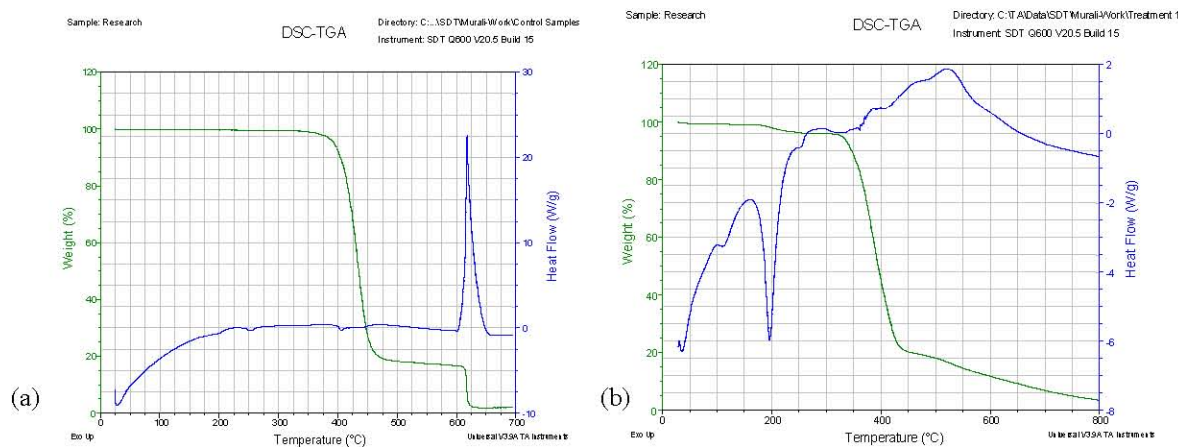


Fig. 2a: TG and DTA of Polyester (Control)

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

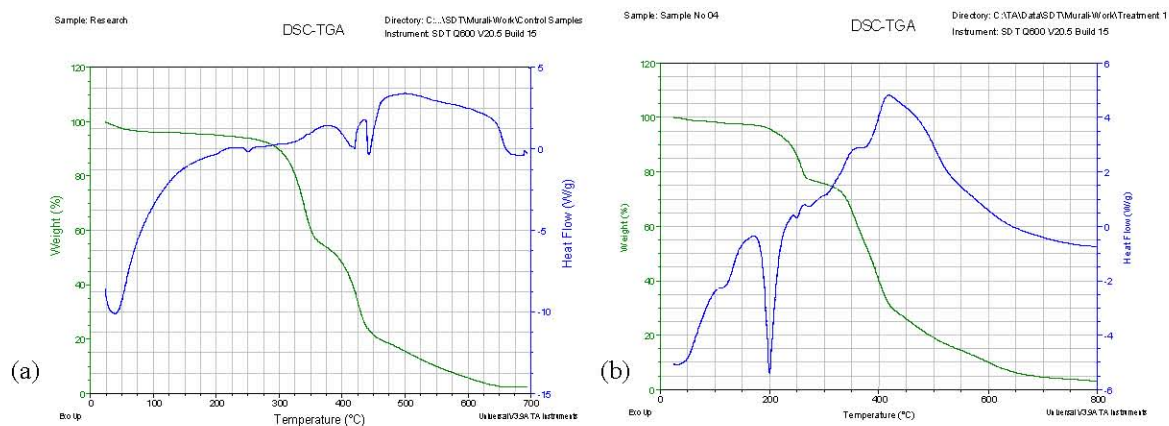


Fig. 3a: TG and DTA of Polyester - Cotton (Control)

Fig. 3b: TG and DTA of Polyester - Cotton (After treatment)

applied phosphorus with polyester may increase the volatility of the molten polymer in the combustion zone, thereby lowering the rate of transport of the combustible pyrolysis product to the flame [12]. In the final stage of major mass loss, there are enough radical scavengers released to decrease the speed of the mass loss.

P/C Control: From the Fig. 3a, it is observed from the TGA curve that, the control P/C fabric shows 2 major and 2 minor mass losses in the TG curve (Fig. 3a). Initially, 4.5 % loss was observed in 30-110°C range and it is due to the dehydration of fibres mainly of cotton. In the 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. The mass loss in the P/C blended fabric may be explained as follows. The thermal degradation of cotton begins at a temperature well below that required for thermal degradation of polyester. Thus the cotton acts as the initial source of ignition in the polyester-cotton blended fabric. Therefore, the second step the mass loss is mainly due to the complete decomposition of cotton and partial decomposition of polyester. The polyester component furnishes the additional fuel to the gas phase and as the polymer temperature is raised the heat is produced from the combustion of cotton decomposition products. The additional fuel increases the vigour of the gas phase oxidation [9].

P/C after Treatment: From the Figure 3b, it is observed that the onset point of thermal decomposition (223°C) and the initial major mass loss (20.3% at 150-270°C) were observed to get shifted to lower temperature. The second major mass loss of 48.2% is observed between 310-420°C. At this point, the cotton which is the major portion in the blend undergoes complete decomposition. As in the polyester treated fabric, one endotherm is observed at 200°C. The 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.

When compared the control samples, the mass loss in treated samples have become slower. This is evident from the slopes of TG curve of Fig. 1b, 2b and 3b. The applied chemical APP starts releasing phosphoric acid at around 250°C. NH_3 and H_2O are released upon further heating the phosphorus based chemical and this is resulted in appearance of endotherm at 196.7°C [22]. The 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 the DTA curves of all the three samples after treatment that the exotherm in the final stage of thermal decomposition has become broader and prolonged when compared to respective DTA of control samples. In the control samples this exotherms are much sharper and the peak was at higher temperature ($\square 100^\circ\text{C}$). This indicates that the heat release is distributed within a broad exotherm covering wide area resulting in major decrease in releasing rate of heat and the combustible gases which fuel the flaming combustion reaction. When compared to the control samples, it is evident that the treated samples possess lower decomposition temperature, decreased heat release rate and increased char yield. The applied phosphorous based FR compound acts in condensed phase. In the condensed phase mechanism, the added FR chemical alter the pyrolytic path of the substrate and reduces drastically the amount of combustible gases and favours the formation of carbonaceous char and water [22]. The application of flame retardant chemical containing phosphorous releases inert or not easily oxidizable phosphorous radicals, which slow down the process of oxidative decomposition of cotton, polyester either in pure form or in blend form. The 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: The observations of the vertical flammability test are given in the Table 2.

From the Table 2, it could be noted that all the three fabrics when subjected to the vertical flammability test burn their entire length and does not meet the criteria of NFPA 701. Afterglow was observed in cotton and polyester-cotton sample for longer durations. The burning behaviour of all the materials seems to have changed after the treatment. The char length in cotton and polyester-cotton samples reduced drastically and they meet the requirement of NFPA 701 criteria. Although the reduction in char length was observed in P fabric, this fabric still fails to confirm to the said requirement. The FR chemical reduced the after flash in the sample. The effect of FR chemical on these parameters was seen to be reduced after the treated fabric were washed for 3 cycles. It is stated that the effect of flame retardant chemicals remains in the fabric fabrics even after the fabric was washed for 3 cycles, but in a reduced level [23]. It may be seen from the Table 2 that the rate of flame spread in vertical direction

Table 2: Result of Vertical flammability test

Sample	Weight (oz yd ⁻²)	I. Char length (inches)			II. After Glow (s)		
		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
P/C	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
P/C	8.2		4.4	4.3	26	16	22

(P/C = Polyester-Cotton blended)

Table 3: Calculated Activation Energy (E_a)

Sample	Briodo's Method		C- R's Method		H-M's Method	
	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
P/C	150.8 (I)	83.2 (I)	134.4 (I)	73.2 (I)	134.4 (I)	134.4 (I)
	111.6 (II)	44.2 (II)	85.4 (II)	37.4 (II)	65.2 (II)	71.6 (II)

has also reduced in all the samples. Though the char length of polyester fabric after treatment did not meet the criteria, the highest reduction in flame spread (> 50%) was observed in this case. The reduced mass loss rate observed in TG curves for all the samples after treatment can be correlated with the reduced rate of flame spread. The observed burning characteristics of the treated samples also indicate that the formation of char and the effectiveness of the chemical in suppressing the burn rate as well as afterglow duration are highly significant. The suitable mechanism for such flame and glow retardancy is in favour of chemical action theory [24-27]. According to this theory, the action of phosphorus flame retardants is to promote the pyrolysis of products when substrate is subjected to thermal degradation. Ideally, the carbon present in cellulose and polyester could be confined to the solid phase during the thermal decomposition and then degradation could be pushed through the catalytic dehydration.

Activation Energy (E_a): Activation energy calculated using the equation 1, 2 and 3 for all the three samples before and after the treatment is given in Table 3.

Activation energies given in the table were calculated as described above from the DTA curves of both the control sample and treated samples using the equation 1, 2 and 3. As there were two major mass loss steps in the

thermal decomposition of P/C fabric, the E_a is calculated for both the events. From the table 3, it is observed that a drastic decrease occurs in E_a values for all the samples after treatment [14, 28]. The 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 the methods after treatment was found to be the same extent. The reduction in E_a implies that the amount of burning material in the last stage is considerably less. This is due to the fact that less flammable products are formed or continuous burning of products is hindered. The overall thermal decomposition and E_a profile of the sample under decomposition has changed after treatment with flame retardant chemicals which corroborates the fact that treated samples are highly flame retardant. This has been proved in the vertical flammability test.

CONCLUSION

The mass loss profile of the upholstery cotton, polyester and polyester-cotton fabrics changed completely after the fabric was treated with FR compound. The pyrolytic profile was completely shaded by the added FR chemicals. A rapid increase is noted in thermal energy absorption by the system in the initial stages of decomposition and there is also drop in exothermic heat

and activation energy. Initial thermal decomposition profile of treated samples shows the presence of endotherm which suggests that the heat is consumed by expulsion of moisture and this has resulted in reduction of further flame propagation. This is in correlation with the reduced char length. After the application of FR compounds, the mass loss splits into many small steps and the 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 the 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. The char length, afterglow and the rate of flame spread for fabrics after treatment were reduced drastically. This reduction continued to prevail even after the washing the fabrics although the quantum of FR chemicals was noted to be lower after washing.

REFERENCES

- Drake, G.L., 1980. (Jr) Flame Retardant for Textiles in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, Vol. 10, Wiley Interscience, NY, 420ff.
- Hendrix, J.E., G.L. Drake and R.H. Barker, 1972. Pyrolysis and Combustion of Cellulose. III. Mechanistic Bases for the Synergism involving organic Phosphate and Nitrogenous Bases, J. Appl. Polymer. Sci., 16: 257.
- Montaudo, G., C. Puglisi and F. Samperi, 1993. Primary Thermal Degradation Mechanism of PET and PBT, Polymer degradation stability, 42: 13-28.
- Weil, E.D., 1999. Recent developments in Phosphorous based Flame retardants, Proc 3rd Beijing Sym, Flame Retardants and Flame Retardant Matter, Beijing, pp: 177-83.
- Hendrix, J.E. and Robert H. Barker, XXXX. Flammability and Flame Retardation of Cotton-Polyester Blend].
- Shukla, L. and P. Arya, 1998. Flame Retardant based on Poly (Fluorophosphazene) and organo brominated compound for the polyester/cotton shirting Textile Dyer and Printer. 35/5, pp: 16-18.
- Kubakawa, H., K. Takahashi, S. Nagatani and T. Hatakeyama, 1999. Thermal Decomposition behavior of Polyester/Cotton blended fabric treated with Flame Retardants (Japanese) World Textile Abstract, 5517: 298-305.
- Meyere, J., Van Hoeyland P. Vnitex and V. Everaert, 2005. The development of flame retardant Textiles World Textile Abstract 2005/12, pp: 4-9.
- Hossein Najafi, 2009. Improvement of Burning Properties on the Cotton/Polyester/Lacra Blend Fabric with Nano Silicone Material in Nano Silicone, World Applied Sciences J., 6(11): 1532-1539.
- Leonard, E. and A. Godfrey, 1970. Thermogravimetric Analysis (TGA) Studies of Flame-Retardant Rayon Fibers, Textile Res. J., 40(2): 116-126.
- Ping Zhu, Shuying Sui, Bing Wang, Kai Sun and Gang Sun, 1987. A study of pyrolysis and pyrolysis products of flame-retardant cotton fabrics by DSC, TGA and PY-GC-MS, Textile Research J., 57(3): 161-167.
- Anderson, D.A. and E.S. Freeman, 1961. The kinetics of the thermal degradation of Polystyrene and Polyethylene [J]. J. Polymer Sci., 54: 253-261.
- Kaur, B., I.S. Gur and H.L. Bhatnagar, 1987. Thermal Degradation Studies of Cellulose Phosphates and Cellulose Thiosulphates, Angew. Makromol. Chem., 147: 157-183.
- Dahiya, J.B. and Krishnakumar, 2009. Flame Retardant Study of Cotton coated with Intumescent Kinetics and effect of Metal Ions, J. Sci and Ind Res., 68: 548-554.
- Broido, A. and A. Simple, 1969. Sensitive Graphical Method of Treating Thermogravimetric Analysis Data: Part A-2 [J]. J. Polym. Sci., 7: 1761-1773.
- Coats, A.W. and J.P. Redfern, 1964. Kinetic Parameters from Thermodynamic data Nature, 201: 68-69.
- Horowitz, H.H. and G. Metzger, 1963. Anal. Chem., 35: 1464.
- Ashok, M.A. and B.N. Achar, 2008. Thermal decomposition kinetics and solidstate, temperature dependent, electrical conductivity of charge-transfer complex of Phenothiazine with Chloranil and Picric acid, Indian Academy of Sci. (Mater Sci.), 31(1): 29-35.
- NFPA 701, Standard Method for Fire tests for Flame retardant textiles and Films, 1989 Edition. pp: 701-5.
- Horrocks, A.R. and JSDC, 99: 191.
- Hilado, C.J. and Flammability Hand Book, 1996. Technomatic Publishing Co. Stamford Conn.
- Kandola, B. and A.R. Horrocks, 1996. Flame Retardant Treatment of Cellulose and their influence on the Mechanism of Cellulose, J. Macromol. Sci. Rev. Macromol. Chem. Phys., 36(4): 7-21.

23. Sander, R.R., 1990. How can the low flammability of a cotton blend fibre type be retained in textile printing, *Melliand Textilbericht* (English version, 1, E29,
24. Van Krevelen, D.W. and P.J. Hoftyzer, 1976. *Properties of Polymer*, Elsevier Scientific Publishing Co. New York. pp: 523-536. Van D.W. Krevelen, *Flame Resistane of Polymeric Materials*, *Polymer*, 16(8): 615-620.
25. Brauman, S.K., 1977. Phosphorous fire Retardant in Polymers, I. General Mode of Action, *J. Fire Retardant Chemistry*, 4: 18-37.
26. Levchik, S.V., G. Camino, L. Costa and G.F. Levchik, 1995. Mechanism of action of Phosphorous based flame retardant in Nylon 6. I. Ammonium Polyphosphate, *Fire. Mat.*, 19: 1-10.
27. Menachem Lewin and Edward D. Weil, 2001. Mechanism and modes of action in flame retardancy of polymers, *Fire Retardant Materials* edited by A.R Horrocks and D. Price, Woodhead Publishing Limited. pp: 31-68.
28. Gao Ming and Dai Qiu, 2006. Studies of Thermal Degradation of Cellulosic Fibres Treated with Flame Retardatns, *The Chines J. Proces Engg.*, 6(2): 242-246.