



Adaptation of Pyrolytic Conduit of Polyester Cotton Blended Fabric with Flame Retardant Chemical Concentrations

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Abstract

Thermal degradation of polyester – cotton blended fabric material was analysed after addition of phosphorous based flame retardant chemical at different concentration levels viz., 50GPL, 150GPL, 250GPL, 300GPL and 350GPL. The thermogravimetric curve of control sample showed two steps of degradations with two major onset points. A step wise and progressive budging in thermal degradation kinetics with increase in concentration level was observed for this material. The thermal degradation onset point was progressively shoved to lower temperature with increase in chemical concentration. Two step mass loss observed in control sample was modified to be in three steps in treated samples. The mass loss curve progressively became flat with increasing chemical concentration in the sample. As a result of chemical application, an additional endotherm was emerged near 200^oC. The depth of this endotherm increased with increasing chemical concentration. Mass loss was also analysed in three different temperature intervals. The mass loss in first and third temperature interval increased from 9% (control) to 24% (350GPL) and 11% (control) to 39% (350GPL) respectively as the concentration increased. Also, the mass loss decreased from 70.9 % in control to 35 % for 350GPL treatment implying that the less amount of mass was decomposed due to non accessibility of free oxygen. There observed a drastic decrease in exotherm energy with minor shifting in peak point after the treatment. The activation energy was observed to be progressively decreasing from 267.6kJ/mole for control to 140.3 kJ/mole for sample of 350GPL treatment.

Keywords: Polyester, pyrolytic, conduit, cotton blended fabric.

Introduction

Hendrix *et al.*, in their flammability measurement and thermal decomposition of textiles article have demonstrated that calorimetric method of measurement of thermal decomposition of textile fibres are best method to measure the efficiency modification due to added FR chemicals in fibre. They have clearly established the efficiency modification of phosphorous based FR chemical on cotton in their research article. Further, they stated that the phosphorous based compounds which decompose prior to their interaction with cellulose have efficiencies which are limited by inherent efficiency of phosphorous oxides and acid. Thus molar efficiency could only be altered by the use of treating reagents which are either thermally stable up to the temperature of cellulose pyrolysis or which thermolyse to form some different types of intermediates¹. Phosphorous based FR chemicals are known to be effective on cellulose substrates. It has been postulated that the phosphorous based FR chemical acts completely in condensed phase to alter the fuel producing reaction in cellulose substrate. While discussing the action of phosphoric acid on degradation of cotton substrate, Hendrix *et al.*, have argued that the endothermic pyrolysis reaction of cotton fabric occurred at progressively lower temperature as increasing amount of phosphoric acid present in the substrate². They further exhibited that the incorporation of increasing amount of phosphoric acid reduces over all heat of combustion and also resulted in

increasing amount of char formation. In another study, Barker has shown that the endothermic decomposition reaction becomes two-stage pyrolysis decomposition in presence of phosphoric acid. They related this two-stage decomposition to catalysed decomposition and catalysed phosphorylation of cotton³.

Flammability of cellulose and synthetic textile fibres has been independently recognized as an important area of textile research for many years. Due to their unique nature, cotton, polyester and their blends are normally found as general textile. Cotton cellulose normally decomposes below 300^oC and under dehydration, depolymerization and oxidation, releasing CO, CO₂, and carbonaceous residual char results at later temperatures⁴. On the other hand polyester normally melts and flows under the influence of the temperature at above 260^oC. 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^oC⁵. Due to the tremendous differences in the physical and chemical properties of polyester and cotton, the blend of polyester-cotton (P/C blend) poses problems as far as the flammability and thermal degradation of blend fabric is concerned. During the thermal degradation of P/C blend, cotton begins to decompose at a temperature well below that required for thermal decomposition of polyester. Thus the cotton acts as

the initial source of ignition in the blend. The polyester which has melting point at 250–260°C, tends to wick on the cotton char resulting in the phenomenon called scaffolding⁶. 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 oxidation³. Because of this, predicting the flammability of cotton – polyester blended fabric on the basis of knowledge of individual fibres is a doubtful phenomenon⁷⁻⁹.

Phosphorous containing flame retardants (FR) have been regarded as most simple but effective chemical treatments for celluloses and for polyesters as well^{10,11}. As the result, the phosphorous based FR chemicals are used to chemically treat P/C blended textile fabric to modify them as flame retardant textiles. FR textile materials have also been studied on the basis of their fundamental properties of thermal analysis which may include thermal degradation, decomposition and heat flow¹². 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 thermal degradation kinetics of cotton and polyester fibres as individual. However, the kinetic data on blend of these materials are very few^{13,14}. Also, we find hardly any studies on thermal degradation kinetics of P/C blended material with varying FR chemical concentration.

Material and Methods

Material: An upholstery P/C blended fabric (polyester 62% and cotton 38%, GSM 502) was treated with phosphorous containing flame retardant (Flamex DP 100 Nova-Transfer, India). Concentrations selected for application were 50 gram per litre (GPL), 150 GPL, 250 GPL, 300 GPL and 350 GPL. The chemical solution was prepared in water and applied using pad-dry-cure method. After the application, differential thermal analysis (DTA) and thermogravimetry (TG) were carried out on the control and treated fabric samples by using a SDT – 600 model instrument (TA instruments, USA).

Method: The samples were subjected to controlled heating condition in a closed furnace and temperature was raised from ambient to 800°C with 10°C/min ramp under normal atmosphere. Thermograms associated with TG and DTA for control given in figure 1 and treated samples given in figure 2 were obtained from the instrument output. The weight loss curves of all samples were pooled in one plot given in figure 3a and heat flow curves of all the samples were pooled together in one plot given in figure 3b. This is done to establish the stepwise modification in decomposition patten with varying FR chemical concentration. Detailed information with respect to mass loss, degradation onset temperature was obtained from these thermograms given in figure 1 and 2 for samples of control and after treatment given in table 1. To evaluate the

mass loss pattern during thermal degradation, mass loss data obtained from TG curve was analysed at three different temperature intervals viz., 30–250°C (A), 250–500°C (B) and 500–800°C (C) and the same is presented in table 2.

The other aim of the thermogravimetric analysis was to find out reliable values of activation energy of degradation. The method advocated by Broido was adopted for calculating the activation energy, E_a ¹⁵. The Briodo's equation employed to evaluate the activation energy are as follows.

$$\ln \left[\ln \frac{1}{y} \right] = -\frac{E_a}{R} \frac{1}{T} + \left[\frac{R}{E_a} \frac{A}{\beta} T_{max}^2 \right] \quad (1)$$

Where, y is fraction of initial molecules not yet decomposed, T is absolute temperature (°K), T_{max} the absolute temperature of maximum reaction rate, β is rate of heating (°C/min), A the Arrhenius pre-exponential factor (s^{-1}) and E_a is the activation energy (kJ/mol), R is universal gas constant (8.314 J/mol). A plot of $\ln (\ln 1/y)$ versus $1000/T$ for various stages of weight yielded straight line and slope of which is equal to E_a/R . E_a was calculated from intercept of slope of the plot given in table 3.

Results and Discussion

Mass loss and Heat flow observation: Before treatment the sample lost about 9% of mass mainly due to desorption of moisture. Two major mass loss was, one around 303°C (41.5%) and 393°C (47.1%) observed. The onset point of this mass loss was respectively placed at 290°C and 374°C. This mass loss was mainly attributed to the loss of polymer due to decomposition. There observed an endotherm around 65°C with enthalpy of reaction 2351 J/g. A sharp and shooting exotherm was observed with relatively high enthalpy of reaction (5225 J/g) with peak at 478°C. Compared to mass loss curve of control sample given in figure 1, the mass loss curves of treated samples given in figure 2 are shaper and have least slope. From the figure 1, it is noted that the control sample exhibited two major stages of mass loss. Due to high enthalpy of exothermic reaction no residual char was left out in the final stage (after 400°C). This may be due to the reason that the char component of cotton portion of blend served as additional fuel to the decomposition of polyester which under the influence of heat degrade completely without leaving any char remnant.

After the treatment, it can be observed the treated samples of all the treatments have three distinct stages of mass loss given in figure 2. Also from the table 1, it is noted that the onset point of first stage was 290°C for control sample was shifter to lower temperature 214°C for sample of 350 GPL treatment. It is pertinent to note that the onset point of second stage observed at 374°C for control sample was abruptly shoved to 402°C for 50GPL treatment and progressively heaved for samples at subsequent higher concentration and finally settled at lower temperature at 326°C. In contrast to the control sample, the treated samples exhibited three major mass loss events.

Table-1
Thermogravimetric data of samples

Concentration (GPL)	On Set Point (°C)	Max Weight Loss		Endotherm		Exotherm	
		(%)	Temp (°C)	Energy	Temp (°C)	Energy	Temp (°C)
Control	290	41.5	303.6	1605	67	5225	478
	374	47.1	393.4				
50	207	20.5	246	2256	61	3276	433
	402	45.0	449	438	201		588
	601	27.5	622				
150	214	24.0	240	2252	63	3636	442
	395	35.5	447	603	201		571
	612	15.3	607				
250	212	22.7	238	1959	60	2840	556
	389	33.5	442	853	202		739
	630	32.0	627				
300	214	20.7	240	1750	58	2690	330
	323	40.0	372	797	203		460
	634	29.0	632				
350	214	22.7	234	2523	51	3959	332
	326	32.6	384	866	200		412
	667	34.7	628				

Table-2
Mass loss data of samples at different temperature intervals

Concentration (GPL)	Major Mass Loss Events			Activation Energy (E _a) (kJ/mole)
	30 ^o C-250 ^o C Stage A	250 ^o C-500 ^o C Stage B	500 ^o C-800 ^o C Stage C	
Control	8.9	82.0	0.0	267.7
50	27.6	42.6	27.6	141.1
150	29.8	36.0	30.8	135.6
250	27.3	37.0	32.8	132.8
300	25.0	35.7	36.9	140.0
350	23.7	35.0	39.2	140.6

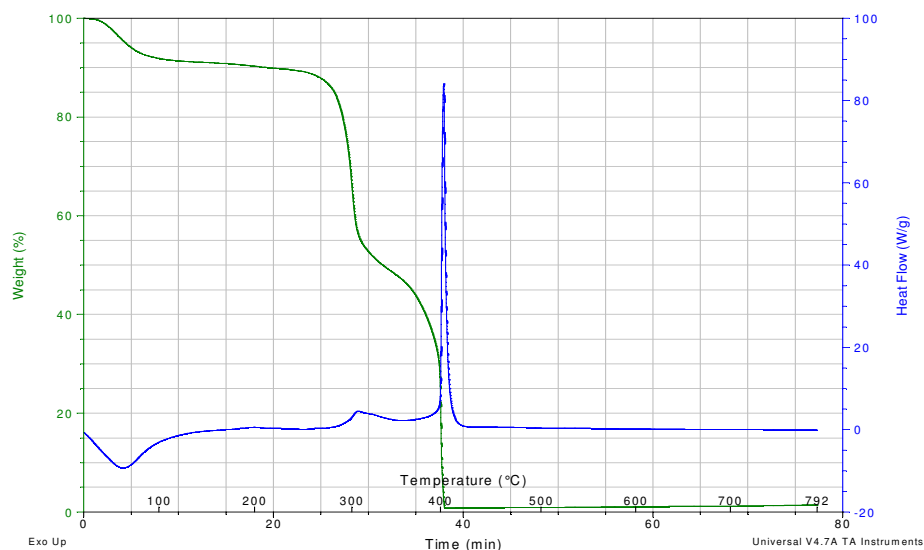
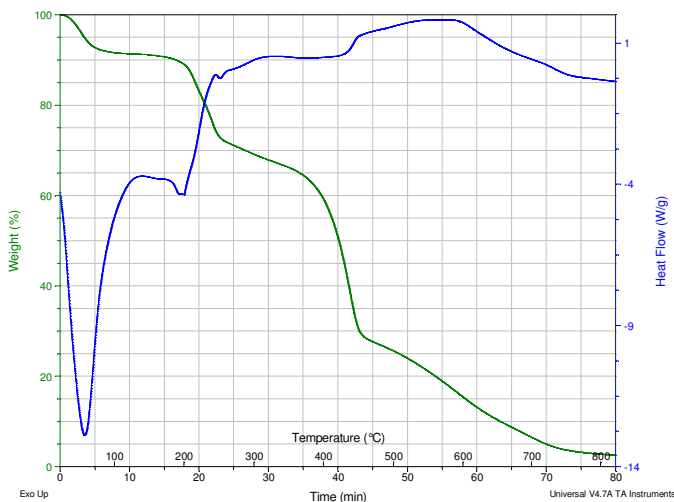
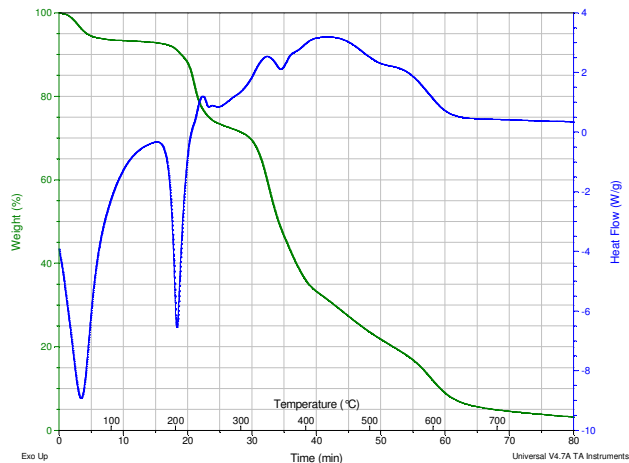


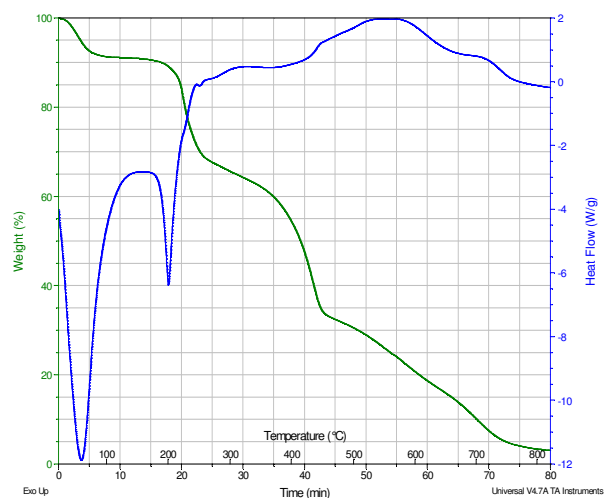
Figure-1
Weight loss and heat flow curved of control P/C sample



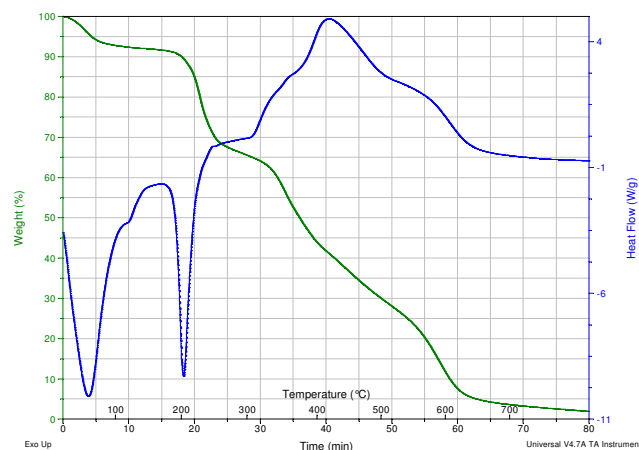
a. After 50GPL treatment



d. After 300 GPL treatment



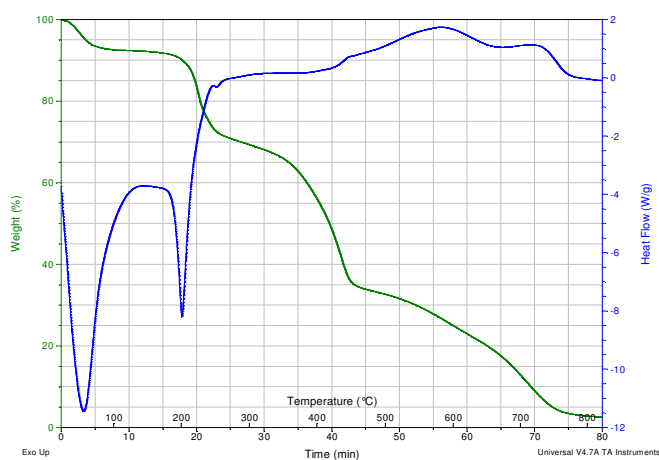
b. After 150GPL treatment



(e: After 350GPL treatment)

Figure-2

Weight loss and heat flow curved of treated P/C sample (Figure a-d)



c. After 250GPL treatment.

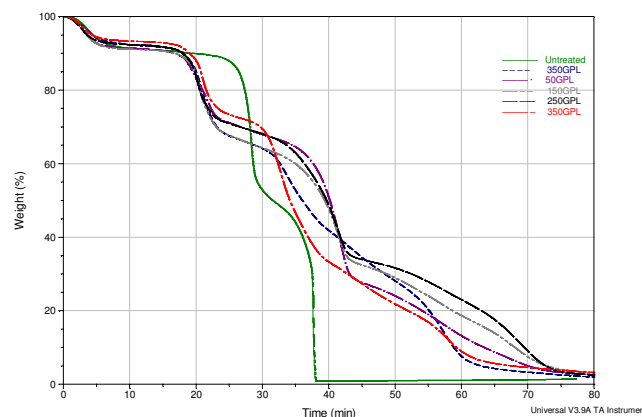


Figure 3a

Shift in weight loss curve due to treatment

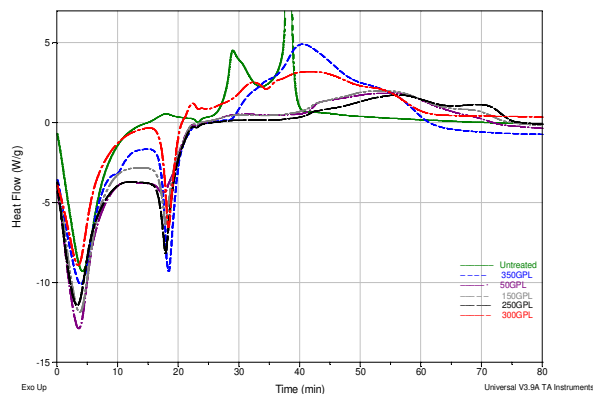


Figure 3b
 Shift in heat flow curve due to treatment

The DTA curve of the all samples demonstrated that an endotherm at a temperature $\approx 60^{\circ}\text{C}$ associating with a weight loss 5 - 6% due to desorption of moisture. This endotherm in control sample progressively grew broader with increasing concentration in treated samples. This wide endotherm in treated samples suggests that application of FR chemicals enabled the blended fibres to absorb more moisture, which is expelled by absorption of more thermal energy. The DTA curve of treated samples exhibits a second endotherm at $\approx 200^{\circ}\text{C}$ given in figure 2. This large endotherm peaking around 200 – 205 $^{\circ}\text{C}$ was associated with a concomitant weight loss (30 – 40%). This second endotherm was entirely absent in control sample given in figure 1 and therefore it is entirely accredited to the applied FR chemical in samples. The presence of second endotherm in treated samples may be explained as follows. Phosphorous FR chemical releases inert or not easily oxidizable phosphorous radicals, which slow down the process of oxidative decomposition of substrate. The release of phosphorous radical in the form of ammonia, phosphoric acid, and water vapour leads to mass loss along with an endotherm at around 200 $^{\circ}\text{C}$ ¹⁶.

As a result of application of FR chemical, a quantity of mass is left out after 500 $^{\circ}\text{C}$ for 50GPL treatment. This mass is regarded as char. The char degraded at higher temperature at 601 $^{\circ}\text{C}$ for 50GPL treatment and progressively rose at 667 $^{\circ}\text{C}$ for 350GPL treatment. The control sample showed a sharp and shooting exotherm with single peak at hovering 478 $^{\circ}\text{C}$. The exotherm in treated samples was found reduced but developed into broader, prolonged and got split into bimodal with peak temperature point of exotherm reducing progressively with increasing concentration. In the control sample this exotherms was much sharper and the peak was at higher temperature ($\geq 100^{\circ}\text{C}$). 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 mass loss observed in the samples was analysed between three temperature ranges. Table 2 reveals that the added FR chemical gradually customized the pyrolytic path of P/C blend sample. The two stage mass loss observed in control sample was altered to three stages after the treatment. It is noted that the most of the mass (82.0%) in control samples was decomposed in the temperature range B. Only 9% of mass was decomposed in range temperature A and no mass was left out for decomposition at C. After the treatment, the mass loss in range A increased to 27.6% for 50GPL treatment and to 29.8% for 150GPL treatment. The mass loss was then decreased slightly in samples of further higher treatment. The mass loss observed for 350GPL treatment was 23.7%. At this range the mass loss was mainly due evolution of various non flammable gases from added chemical and augmented moisture from textile fibre. The observed mass loss in range B was reduced to 43% after the 50GPL treatment. In the range B, the mass decomposed was mainly textile fibre. The FR chemical containing phosphorous as active content released inert or not easily oxidizable phosphorous radicals. These radicals are poor in oxygen and hindered the process of oxidative decomposition of P/C blend. As the result and due to non accessibility to atmospheric oxygen, hindered oxidations lead to reduced mass loss in the range B. The mass loss in range C was increased considerably to $\approx 25\%$. As the increase in concentration to 50 GPL, 150GPL, 250GPL, 300 GPL and 350GPL, the mass at stage C was also increased to 25%, 28%, 31%, 33%, 37% and 39% respectively. Therefore it may be stated that more and more char was created due to hindered fibre decomposition at temperature range B. This char gets decomposed at higher temperature (stage C). As a result of FR chemical application, the one major step mass loss (82%) observed in control samples was split into three major events. And the decrease/increase in mass loss at all the three stages is gradual and ensued with increase in chemical concentration.

Activation energy (E_a): As there are two distinct stages of mass decomposition in the control sample, one pertaining to decomposition of cotton and other pertaining to polyester, the activation energy (E_a) for control and treated samples was calculated for two stages given in table 2. The control sample exhibited 146.3 kJ/mole and 121.4 kJ/mole in the first and second part of decomposition respectively. It may be seen from the table 2, that the 2nd step mass loss leads more E_a value than the first step. The application of FR chemical at different concentrations gradually reduced the E_a to minimum. The drastic decrease in E_a values occurred for all the treatment¹⁷. The progressive 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.

Conclusion

As a result of FR chemical application, the one major step mass loss (71%) observed in control samples was split into three major events. The mass loss in temperature range B decreased drastically. The mass loss increased considerably in other two stages. And the decrease/increase in mass loss at all the three stages is gradual and ensued with increase in chemical concentration. In the treated samples, an additional endotherm (near 200°C) was observed in addition to one at around 60°C. This additional endotherm was entirely due to release of non oxidizable phosphorous radicals which, by the way of heat consuming, reduced the mass loss in stage B. As the result more mass was observed at stage C. The reduction in exotherm during decomposition of mass at the stage C indicates that the material was decomposed less vigorously leading to decreased activation energy. The increasing in FR chemical concentration, the P/C blend material progressively became non thermal degradable.

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