

Thermal Degradation Kinetic Data of Polyester, Cotton and Polyester-Cotton Blended Textile Material

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Abstract: Polyester (P), cotton (C) and Polyester-Cotton (PC) blended fabrics were treated with 350gpl of phosphorous containing flame retardant (FR) chemical. Oxidative thermal degradation of these fabrics before and after the treatment was studied using Thermogravimetry (TG) - Differential Thermal Analysis (DTA). From TG output, quantitative mass loss of samples was calculated at definite temperature interval. Mass loss profile of control fabrics were compared with that after treatment. From DTA data, activation energy of fabrics during decomposition was calculated using Broido's, Coats-Redfern as well as Horowitz-Metzger methods. There is complete change in degradation profile of all fabrics after treatment. The onset temperature of treated fabrics was advanced by 55°C, 75°C and 115°C for polyester, cotton and PC respectively. In final stage of mass loss, treated samples exhibited a pair of closely spaced and broad exotherm. The exothermic peak appeared at 100°C lower temperature in treated samples. Presence of an endotherm in the initial stages (near 180°C) of thermal degradation and decrease in exotherm during the final decomposition of treated fabric was noted. Activation energy treated samples was less compared to that of control samples. Drop in activation energy was observed in all method of calculation.

Key words: Flame Retardant • Mass loss • TG • DTA • Thermal Degradation • Activation Energy

INTRODUCTION

Flame retardancy in textile is a desirable property. Textile fabrics are made fire resistant by application of flame retardant (FR) chemical compounds. Effect of FR chemicals on textile include effect of additive on mode of thermal degradation of polymer in order to produce fuel poor pyrolysis paths, external flame retardant coating to exclude oxygen from the polymer surface, internal barrier formation to prevent evolution of combustible gases, inert gas evolution to dilute fuel formed in pyrolysis and dissipation of heat away from flame front. Some of the flame-retardants applied on fabrics do not burn themselves but dilute the flammable gases produced by the decomposition of the polymer to a concentration below the flaming point [1].

In recent years the application of Thermogravimetry (TG), Differential Scanning Calorimetry (DSC) and Differential Thermal Analyzer (DTA) to study the combustion and pyrolysis behaviour of textiles has gained a wide acceptance among researchers. Attempts

have been made to calculate influencing kinetic data during thermal degradation [2, 3]. Studies have been reported [4-6] on thermal degradation and activation energy (E_a) values of synthetic polymer and cellulose based materials separately. E_a is usually calculated using independent equations as suggested by Broido, Coats-Redfern (C-R) and Horowitz-Metzger (H-M) [6-8].

In this paper an attempt is made to determine kinetic data viz., thermal degradation onset temperature, mass loss at definite temperature range and E_a of some of important textiles polymers and their blends. Attempt is also made to compare the E_a values calculated using different methods. The calculated E_a was analysed with the other thermal kinetics like mass loss and exothermic reaction during major decomposition of samples.

MATERIALS AND METHODS

Experimental: Three textile samples were selected for the purpose of study. First sample contained pure Polyester mono component (P), second sample

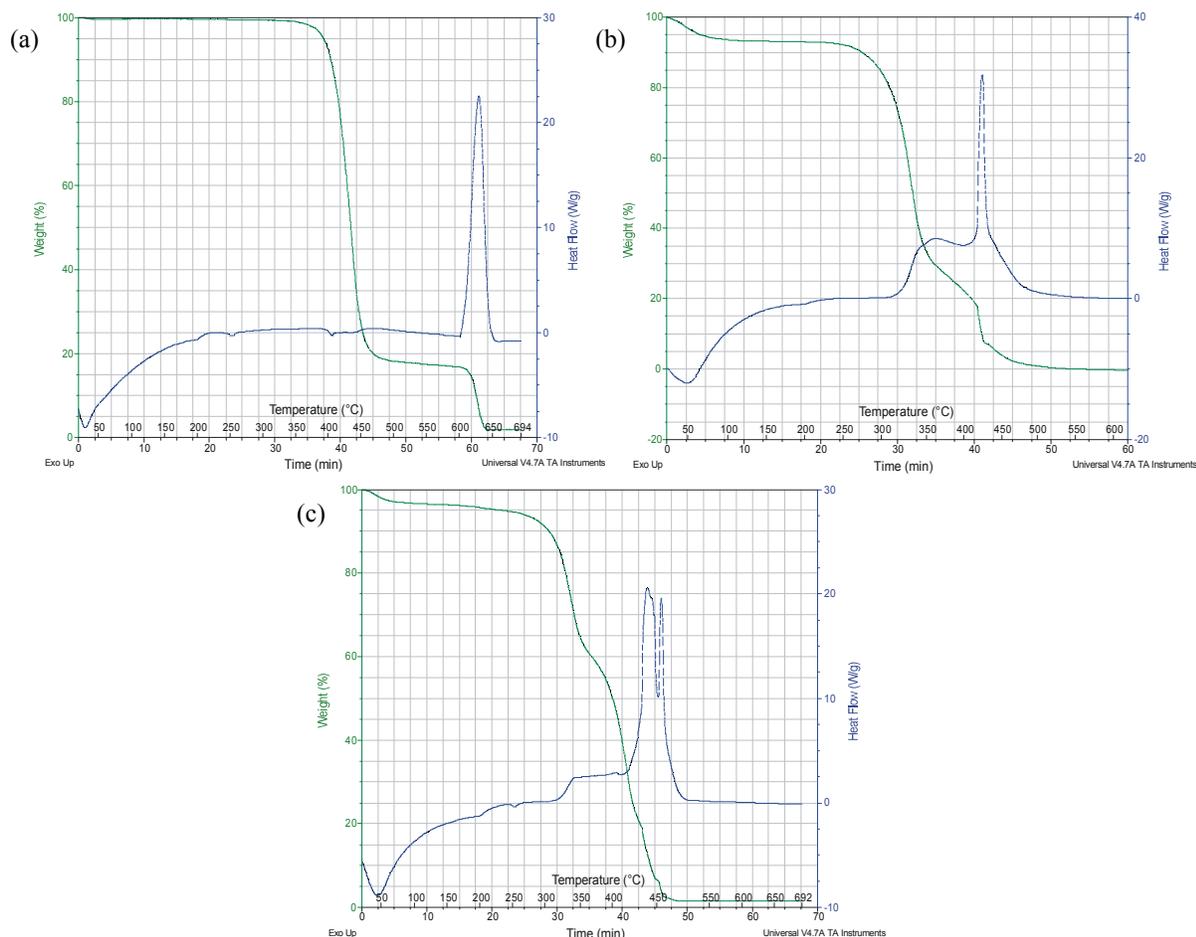


Fig. 1: TG and DTA of control: a) P; b) C and c) PC

contained pure cotton mono component (C) and third sample contained polyester (45%) and cotton (55%) blend (PC). These samples were thoroughly washed to remove any added finish and then treated separately with a phosphorous containing FR chemical (DP-100 - Nova Transfers, India; application concentration 350gpl) using Pad-Dry-Cure method.

Differential Thermogravimetric Analysis: Differential Thermal Analysis (DTA) and Thermogravimetry (TG) were carried out by using the SDT-600 Model of TA Instruments, USA. Thermograms were recorded under temperature rise rate of 10°C per minute. Finely powdered sample was heated from ambient to 300°C in nitrogen atmosphere and changed over to oxygen atmosphere later. Analysis on mass loss and heat flow was carried out from ambient temperature to 800°C. Thermograms associated with TG and DTA for control samples (Fig. 1)

and samples after treatment (Fig. 2) were obtained. Based on the observation of mass loss data at all temperature intervals in TG curve, the total mass loss of individual sample was estimated in three temperature intervals, first between 30-200°C, second between 200 - 500°C and third between 500 - 800°C (Table 1).

Various researchers [9] put forward integral method, which can be applied to thermogravimetric data assuming order of reaction and from which the activation energy (E_a) can be estimated. In thermogravimetric measurement, the mass conversion is typically calculated as

$$y = \frac{m_0 - m}{m_0 - m_f} \quad (1)$$

Where y is fraction of initial molecules not yet decomposed and equal to; m_0 represents initial sample mass in an experiment, m denotes current mass and m_f

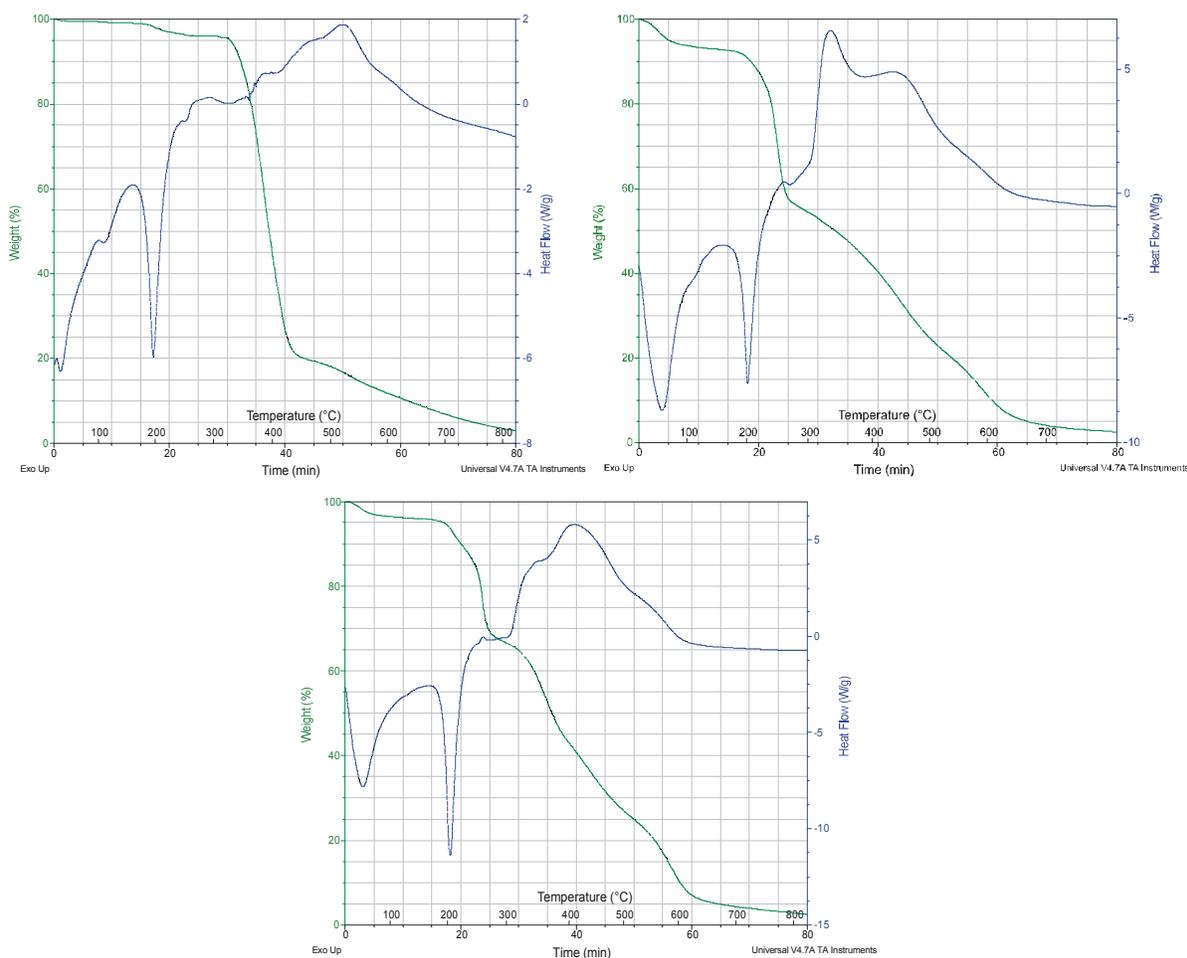


Fig. 2: TG and DTA of FR Treated: a) CP; b) CF and c) CS

Table 1: Mass loss (%) events at different temperature intervals

Sample	Condition	Temperature interval (°C)		
		1 st Stage (30-250)	2 nd Stage (250-450)	3 rd Stage (450-800)
P	Control	0.3	81.2	18.2
	After treatment	3.6	43.3	41.7
C	Control	4.8	69.9	22.3
	After treatment	28.9	29.3	39.2
PC	Control	3.1	89.1	6.6
	After treatment	8.7	32.6	58.7

represents final mass. Kinetic studies assume that the isothermal rate of conversion, dy/dt , is a linear function of the reactant concentration loss and of temperature-independent function of the conversion, y that is:

$$\frac{dy}{dt} = kf(y) \quad (2)$$

Where $f = (y)$ is the reaction model that depends on the mechanism of degradation. The function 'k' is always described by Arrhenius expression:

$$k = Ae^{-\frac{E_a}{RT}} \quad (3)$$

Where A is pre exponential factor (also called as Arrhenius constant), is assumed to be independent of temperature, E_a is activation energy, T is absolute temperature and R is universal gas constant. The combination of equation 2 and 3 gives the following relationship.

$$\frac{dy}{dt} = Af(y)e^{-\frac{E_a}{RT}} \quad (4)$$

When temperature of sample is changed under controlled and constant heating rate ($\beta = dT/dt$), the variation in degree of conversion of mass can be analyzed

Table 2: Activation energy (E_a) of samples

Sample	Condition	Broido Method	Activation Energy (kJ/mol)		
			C-R Method	H-M Method	Temperature Range (°C)
P	Control	374.4	342.3	317.4	330-480
	After treatment	224.5	192.2	180.0	320-460
C	Control	196.5	187.6	157.0	220-350
	After treatment	38.9	24.3	22.3	150-300
PC	Control	134.9 &	127.6 &	123.5 &	250-365 &
		165.7	143.3	88.6	370-440
	After treatment	105.6 &	102.1 &	99.9 &	150-300&
		54.4	30.4	35.6	310-520

as a function of temperature, which depends on time of heating. Therefore, reaction rate may be written as follows.

$$\frac{dy}{dt} = \frac{dy}{dT} \frac{dT}{dt} = \beta \frac{dy}{dT} \quad (5)$$

Thus, change in mass vs temperature can be written as

$$\frac{dy}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} f(y) \quad (6)$$

Integral form of Eq. 6 from initial temperature, T_o , corresponding to a degree of conversion m_o , to a peak temperature, T_p , can be written as.

$$\int_0^y \frac{dy}{f(y)} = \frac{A}{\beta} \int_{T_o}^{T_p} e^{-\frac{E_a}{RT}} dT \quad (7)$$

Using an approximation, Broido rearranged [6] the Eq. (7) as.

$$\ln \left[\ln \frac{1}{y} \right] = -\frac{E_a}{R} \frac{1}{T} + \left[\frac{R}{E_a} \frac{A}{\beta} T_{\max}^2 \right]_a \quad (8)$$

In Broido's approximation, the order of thermal degradation is considered as first order and the calculations are done accordingly. Assuming the order of equation, Coats and Redferd [7] developed an integral method for analysis of thermogravimetric data as below.

$$\ln \left[\frac{-\ln(1-y)}{T^2} \right] = \ln \frac{AR}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] - \frac{E_a}{RT} \quad \text{for } n=1 \quad (9)$$

The Horowitz and Metzger [8] modified the equation as below

$$\ln(1-y) = \frac{E_a(T-T_p)}{R(T_p)} \quad \text{for } n=1 \quad (10)$$

For both C-R and H-M methods, the correlation coefficient values among the reaction of different orders are considered. The values of 'y' were determined at different temperature interval from TG curve of instrument output. A plot of $\ln(\ln 1/y)$ in case of Broido's method, $\ln[-(1-y)/T^2]$ in case of C-R method and $(1-y)$ in case of H-M method; versus $1000/T$ for major degradation events yielded straight line and slope. This slope is equal $-E_a/2.303R$ [10]. E_a values of all the samples are presented in Table 2.

RESULT AND DISCUSSION

Thermogravimetric Analysis of Control Samples:

The mass loss observed in the first temperature range is mainly due to dehydration of fibres. In second temperature range, polyester, cotton and polyester cotton blend samples experienced a mass loss of 84.5%, 89% and 90% respectively (table 1) and degradation onset temperature is 410°C and 310°C and 365°C respectively (fig. 1). The mass loss in these samples is due to thermal decomposition into CO_2 and carbonaceous char in case of polyester; oxidative decomposition into CO , CO_2 and formation of carbonaceous char in case of cotton [11, 12]. PC sample, in the second temperature range, actually exhibited two distinctive mass loss peaks one between 200-350°C (41%) and second between 350-500°C (36%). Mass loss in the PC samples may be explained as follows. Thermal degradation of cotton begins at a temperature well below that required for thermal degradation of polyester. Thus the cotton acts as initial source of ignition in polyester-cotton blended fabric. Therefore, in second step, the mass loss is mainly due to complete decomposition of cotton and partial decomposition of polyester. The polyester component furnishes additional fuel to gas phase and as polymer temperature is raised, heat is produced from the combustion of cotton

decomposition products. Additional fuel increases the vigour of gas phase oxidation [13]. The char component undergoes oxidative decomposition in the third temperature range resulting in another major mass loss. The mass loss observed for polyester, cotton and polyester cotton blend samples is 16.5%, 7.0% and 7.5% respectively (table 1). Sharp exotherm was observed in all the samples in DTA curves (fig. 1) during major thermal degradation. The peak temperature of these exotherm was observed at 620°C for polyester sample, at 440°C for cotton sample and 445°C and 500 °C for PC sample.

Thermogravimetric Analysis of Treated Samples:

The TG and DTA curves (fig 2) of all treated samples exhibited a mass loss trend which different from the one observed for their control samples. The mass loss curves become less steep in treated samples indicating that the decrease in rate of mass loss and the major mass loss is appeared to be split into 2 or more events. An endothermic event was observed at $\approx 60^\circ\text{C}$ in cotton and PC samples and this is due to catalytic dehydration of treated samples. This is vindicated in increase of mass loss in first temperature range. Another sharp endothermic event was observed in treated samples at $\approx 180^\circ\text{C}$ may be due to release of phosphorous radical in the form of NH_3 , Phosphoric acid and H_2O leads to mass loss along with an endotherm [14]. Mass loss was observed to be decreased in second temperature range when compared to control samples. Application of flame retardant chemical containing phosphorous active content 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 drop in mass loss in second temperature range was more in case of cotton samples and PC. Also, the mass loss in the third temperature range increased which shows that the applied FR chemical act as char promoter. Onset temperature of degradation for polyester, cotton and PC samples was 355°C, 235°C and 250°C respectively and they occurred at 55°C, 75°C and 115°C lower temperature for polyester, cotton and PC samples respectively when compared to that of control samples. It may be noted from DTA curves (fig 2) that after the treatment, exothermic event in the final stage of thermal decomposition appeared as closely spaced pair of events and has become broader and prolonged when compared to that of control samples. Exothermic peak appeared at relatively lower temperature (522°C for polyester, 325°C for cotton and 410°C for

PC sample). In control samples this exotherms are much sharper and the peak was at higher temperature (100°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 chemical acts in condensed phase. In the condensed phase mechanism, the added FR chemical alters the pyrolytic path of substrate and reduces drastically the amount of combustible gases and favours formation of carbonaceous char and water [15].

Activation Energy (E_a): The sample P and C have single and continuous major mass loss event and therefore has one E_a value. The sample PC has two distinctive mass loss events and hence has two E_a values pertaining to first stage (due to initial degradation of cotton) and second stage (due to combined degradation of un-burnt cotton portion and polyester). E_a values calculated using three different methods yield different results although difference was found to be in a narrow range. The calculated E_a for control sample P, C and PC, are 374.4 kJ/mol, 196.5 kJ/mol and 134.9/188.8 kJ/mol respectively when calculated using Briodo's method; 342.3 kJ/mol, 187.6 kJ/mol and 127.6/143.3 kJ/mol when calculated using C-R method; and 317.4 kJ/mol, 157.0 kJ/mol and 123.5/88.6 kJ/mol when calculated using H-M method (Table 2). Overall, E_a value calculated using Briodo's method is more than that calculated using other two methods. E_a value is observed reduced after the treatment. Reduction in E_a is due to the fact that less flammable products are formed or continuous burning of products is hindered. This is vindicated by drop in slope of TG curves[16]. The calculated E_a value using all the methods indicated the reduction and reductions are observed to be same extent. The drop in E_a values varies from 40-44% for P samples, 80-87% for C samples and 19-21%/60-78% for PC sample [17]. Overall thermal decomposition and E_a profile of sample under decomposition have been modified after application of flame retardant chemicals on them. It seems that thermal decomposition profile of different textile materials was completely regulated by FR chemical applied on them [18]. This view is substantiated in TG and DTA profile of treated samples when compared to the control samples.

CONCLUSION

Mass loss profile of the textile fabrics changed completely after they were treated with phosphorous containing FR compound. In initial stages of thermal degradation of treated samples, the system was working as heat sink; also there was also a drop in exothermic heat during the oxidative decomposition of fibre and char. Onset temperature of major mass curve shifted to lower temperature by 55°C, 75°C and 115°C for polyester, cotton and PC respectively. After application of FR compounds, the final step of mass loss was associated with a pair of closely spaced and broad exotherm. These two exothermic peaks were appeared prolonged duration when compared to their counterpart control samples. Also, the exothermic peak appeared at lower temperature (100°C) in treated samples. This suggests that the heat release is distributed between two broad peaks covering wider area, resulting in a major reduction in rate of heat release and also combustible gases supply fuel to further flaming. E_a values calculated using different method advocated by different researches yielded narrowly different values. The E_a treated fabrics reduced drastically when compared to control samples and the reduction was observed in all methods of calculation.

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