Volume : 4 | Issue : 10 | Special Issue Oct- 2015 • ISSN No 2277 - 8179

Thermal Degradation kinetic Study of Cotton and Coated Samples in Nitrogen Atmosphere

Chemistry

KEYWORDS: Cotton, Kinetics, Intumescent, thermal degradation.

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ABSTRACT

The thermal degradation kinetics study of intumescent coated cotton fabric has been carried out in nitrogen atmosphere using Modified Coats-Redfern (MCR), Ozawa-Flynn-Wall (OFW) and Kissinger methods to evaluate the kinetic parameters.The model free methods show that the activation energy values of intumenscent coated sample increases in the degradation range a=0.25 to 0.83. The increase in the value of activation energy of coated sample shows that the coating action does not support the decomposition of cotton fabric during thermal degradation. This is may be due to the growth of carbonaceous char layer on the cotton substrate, which act as the thermal barrier from burning phase to the middle side of the cotton surface.

Introduction:

In fire accidents, cotton cellulose mainly undergoes ignition, during ignition it forming highly combustible volatile compounds mainly leavoglucosan with propagation of fire causing injuries and fatalities[1]. Many flame retardants as coating formulations for cotton fabrics have been developed and commercialized successfully but without taking into account environmental effect of flame retardant especially of antimony-bromine system[2,3]. Cotton cellulose[4-6] thermally decomposes below 300°C under dehydration, depolymerisation and oxidation with release of CO, CO_2 and carbonaceous residue. At higher temperature (> 300°C), tar consisting leavoglucosan as a major flammable constituent is formed. Function of flame retardant is to increase char at the cost of flammable volatiles. Intumescent flame retardant system requires acid source, a swelling agent and a char forming agent[7-11]. This study presents improvement in flame retardant property with maintaining physio-mechanical properties of cotton fabric (CF) by selecting environment friendly phosphorus based intumescent system as coating formulations.

Experimental:

Materials

For intumescent flame retardant system, ammonium polyphosphate (APP) as an acid source, melamine as a swelling agent and pentaerythritol (PER) as a carbon source were obtained from Clariant Co., Germany. Cotton fabric (CF) was used for back coating and acrylic resin, Zytrol-7800 as binder (Zydex Industries, India) used as binder.

Preparation of Sample

Intumescent formulation was prepared containing components ammonium polyphosphate (APP), pentaerytritol, and melamine in ratio 3:1:1 wt/wt[7] of cotton fabric (total 30 % wt/wt of cotton fabric). Zydex – 7800, the acrylic resin (20 % wt/wt of cotton fabric) was used for coating the intumescent formulation on cotton fabric of area density, 140 g/m^2. The intumescent formulation was prepared by mixing evenly in pastel and mortar in the form of paste of desired consistency using water as a solvent. This formulation in the paste form was coated on cotton fabric with simple knife-blade technique, giving approximate 45 % add on weight on the cotton fabric substrate. Coated fabric was placed in an oven to dry at 80 ^{0}C at 3 h and then cured at 125 ^{0}C for 5 minutes in oven. The area density of coated fabric sample was found in the range 200-205 g/m^2. This coated sample coated with intumescent formulation is named as CF-Int-P.

3.5.4 Thermal Analysis

TG and DTA thermograms of cotton fabric sample and coated fabric sample were obtained using TG/DTA 6300 Seiko Instruments Inc from ambient temperature to 700 ^{0}C in nitrogen atmosphere (100mL/min) at different heating rated 8, 10 and 12 ^{0}C/min.

Kinetic study

TG data were analyzed for kinetic study using multi heating rate method like Ozawa [12,14] in Japan and Flynn and Wall[13] and Kissinger Method[15]. The single heating rate methods for determining the kinetic parameters have been subjected to criticism time and again because of two main reasons. The reasons are that (i) under these conditions any multi-step process or any change in the mechanism during the course of reaction cannot be dictated and (ii) the methods require a prior knowledge of mechanism which is not possible to obtain. All these aspects have been discussed in detail by Flynn[169]

OFW Method

This method was developed independently by Ozawa in Japan and Flynn and Wall in USA. According to this method, if the reaction mechanism does not undergo any change over a range of (or temperature) during the course of reaction then equation is valid at different heating rates. In the absence of any exact solution for p(x) we may use the following Doyle'sapproximation when 20<x<60 equation.

$$\log p(x) = -2.315 - 0.4567\frac{E_a}{RT}$$

Substituting in equation 8(12) and rearranging

$$\log \beta = \log\left[\frac{AE_a}{Rg(\alpha)}\right] - 2.315 - 0.4567\left(\frac{E_a}{RT}\right)$$

Therefore, plot of log β vs 1/T should yield a series of straight lines for different values of taken at suitable regular intervals. The E_a values obtained by this method are independent of any mechanistic model, if the decomposition takes place without any large variation in E_a value for a wide range of , then a uniformly similar mechanism is assumed to be operating. However, large change in E_a value with increasing degree of conversion indicates a complex reaction mechanism. Such large variation takes place when the overall reaction consists of several competitive or parallel reactions.

Kissinger's Method

Kissinger has shown that for a simple first order decomposition reaction the temperature at the maximum rate of decomposition (T_m) varies with the heating rate. Subsequently, it has been shown that the proposition is also valid when n1. The procedure followed by the author was double differentiation of generalized non-isothermal equation and set the condition $(d^2/dt^2) = 0$.

The relationships obtained are as follows:

When n=1

$$\log\left(\frac{\beta}{T_m^2}\right) = \log\frac{AR}{E_a} - \frac{E_a}{2.3RT_m^2}$$

And when n¹ 1 then

$$\log\left(\frac{\beta}{T^2{}_m}\right) = \log\left[\left(\frac{AR}{E_a}\right) - n\,(1-\alpha_m)^{n-1}\right] = \frac{E_a}{2.3RT}$$

Results and Discussion

Cotton fabric (CF)

TG curve of cotton fabric shows single stage of thermal degradation in temperature range 265-540 °C with weight loss 86.0 % in nitrogen atmosphere shown in table 1. The weight loss is due to dehydration and thermal decomposition releasing volatile and flammable compounds in inert atmosphere. In nitrogen atmosphere weight loss is due to pyrolysis and random chain scission. This stage is supported by single DTG peak at 370 °C in nitrogen atmosphere.

Coated Cotton fabric (CF-Int-P): Table 1 and fig 1 shows the different stage of intumescent coated sample explained as below.

First stage of thermal degradation: TG curves of the coated cotton fabric (CF-Int-P) show weight loss 14.8 % in the temperature range 175-287 °C in nitrogen atmosphere. The weight loss in this stage, dehydration, partial degradation of APP and fusion of pentaerythritol (PER) occurs. Other than these chemical/physical changes, APP also starts releasing phosphoric acid [7] at about 210 °C. This released acid results in phosphorylation of PER as well as cellulose thus favouring the catalysed dehydration of cellulose and char formation reactions. Melamine also starts sublimation in this stage of thermal degradation at about 250°C with the release of NH_3 gas.

Second stage of thermal degradation: TG curves of the coated cotton fabric (CF-Int-P) sample in the temperature range 287-340 °C show weight loss 22 % in nitrogen atmosphere. In this stage crosslinking of APP takes place forming a cross linked phosphate chain which further reacts with PER to form polyolphosphate with the release of water and ammonia. The decomposition of cellulose molecule also occurs to form char and volatile compounds [7,16,17]. Further decomposition of polylolphosphate and phosphoryleted cellulose occurs which releases out the phosphoric acid while in nitrogen atmosphere transformation of aliphatic char to aromatic char occurs. This phosphoric acid combines to form polyphosphoric acid [176] through crosslinking. Due to continuous release of NH_3 from melamine in the temperature range of this stage, intumescents also start to swell and form a layer on the substrate which acts as a thermal barrier and thus help to retard the combustion. The weight loss due to these processes is also supported by DTG peak in all the coated samples in range 272 °C in nitrogen atmosphere.

Third stage of thermal degradation: TG curves of the coated cotton fabric CF-Int-P sample in the temperature 340- 460°C show weight loss 16.7 % in nitrogen atmosphere. In this stage the process of swelling of intumescent continues upto the end of temperature of this stage. Melamine also reacts with polyphosphate and form complex structure of melamine/APP/PER. in nitrogen atmosphere deoxygenation, dehydrogenation and decomposition of char occurs.

Fourth stage of thermal degradation: TG curves of the coated cotton fabric CF-Int-P sample show weight loss 7.5 % in the temperature range 460-700 °C in nitrogen atmosphere. The crosslinking and aromatization of char occurs In nitrogen atmosphere. The decomposition of melamine complex produced in earlier stage also takes place at higher temperatures. No DTG peak is shown in this stage due to gradual loss of weight.

Kinetic study

Figures 2 and fig 3 show a group of lines obtained from the plot of log versus 1000/T using OFW equation (OFW method) at α = 0.2 to 0.83 for CF, CF-Int-P respectively. Activation energies obtained corresponding to the conversions, α = 0.2 to 0.83, for these samples are given in Table 2. Almost constant values of activation energies were found for all the samples in the conversion range under study. So an average value of activation energy was taken for each sample for comparison of all samples with each other. The average values of activation energy of CF, CF-Int-P, are 147, 218.5 kJ mol^{-1}, respectively in the conversion range as shown in Table 2

Kinetic parameters by Kissinger method (Figs. 4a & 4.b) were also calculated for cotton fabric coated with Int-P in nitrogen of second stage (E_a = 198.8 kJ mol^{-1}, ln A = 17.45 min^{-1}) and third stage (E_a = 266.8 kJ mol^{-1}, ln A = 21.04 min^{-1}). These values of kinetic parameters are found not far from the values obtained by other methods.

The activation energy is found increased on coating the cotton fabric in all samples. The increase in value of activation energy on coating with intumescent shows that the intumescent coating treatment does not activate the destabilization of the base cotton fabric during thermal degradation rather they form a layer of insulative char on the underlying material which not only protect the substrate from atmospheric air but also prevent transfer of heat from the combustion phase to the cotton surface, hence increase the of fame retardant property of cotton fabric. The improvement in thermal stability and the decline in degradation temperature confirm the flame retardancy of these formulations.

Conclusions:

TG curves of CF-Int-P show four stages of thermal degradation mainly due to dehydration, pyrolytic decomposition and deoxygenation and decomposition of char, respectively. For coated fabric, degradation gives a less amount of tar consisting flammable volatile products and correspondingly higher char yield. The increase in value of activation energy on coating with intumescent shows that the intumescent coating treatment does not activate the destabilization of the base cotton fabric during thermal degradation rather they form a layer of insulative char on the underlying material which not only protect the substrate from atmospheric air but also prevent transfer of heat from the combustion phase to the cotton surface, hence increase the of fame retardant property of cotton fabric. The improvement in thermal stability and the decline in degradation temperature confirm the flame retardancy of these formulations.

Table 1: TG data, DTG maxima and char yield of Cotton and coated cotton fabric with Int-P in nitrogen atmosphere

S. No	Name	Stage	Temp. range °C	Wt. loss %	DTG Peak °C	Char yield at 700 °C %
i	Uncoated cotton fabric (CF)	one	265-540	86	365	10/525 0/650
ii	Coated Cotton fabric (CF-Int-P)	1st 2nd 3rd 4th	175-287 287-340 340-460 460-700	14.8 22.0 16.7 7.5	 298 375 	37.8

Table 2. Activation energies obtained using OFW method of Samples

CF-Int-P			Cotton Fabric (CF)		
Conversion, α	Ea (kJ mol−1)	R2	Conversion, α	E^a (kJ mol^{-1})	R^2
0.25	201.3	0.9965	0.2	142.3	0.9752
0.33	207.1	0.9965	0.3	146.2	0.9996
0.41	210.0	0.9965	0.4	146.9	0.9945
0.50	210.2	0.9996	0.5	146.0	0.9901
0.59	211.7	0.9712	0.6	146.8	0.9946
0.66	217.0	0.9899	0.7	148.6	0.9861
0.75	239.4	0.9899	0.8	152.3	0.9861
0.83	252.6	0.9763			

Table 3 Activation energies obtained using Kisinger method for CF-int-P

Stages	Ea (kJ mol^{-1})	ln A, (min^{-1})	R^2
2^{nd} stage	198.8	17.45	0.9944
3^{rd} stage	266.8	21.04	0.9484

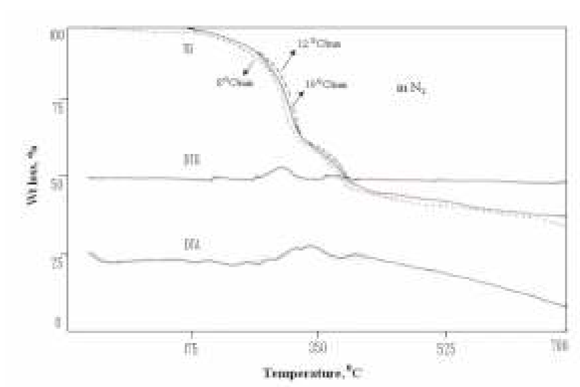

Fig. 1 TG, DTG and DTA of CF-Int-P in nitrogen at 8, 10 and 12 °C/min

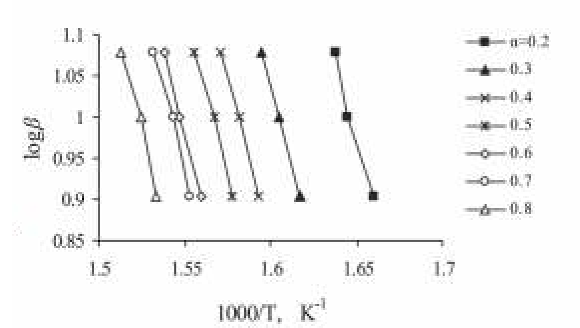

Fig. 2 OFW plot for plain cotton (CF) in nitrogen.

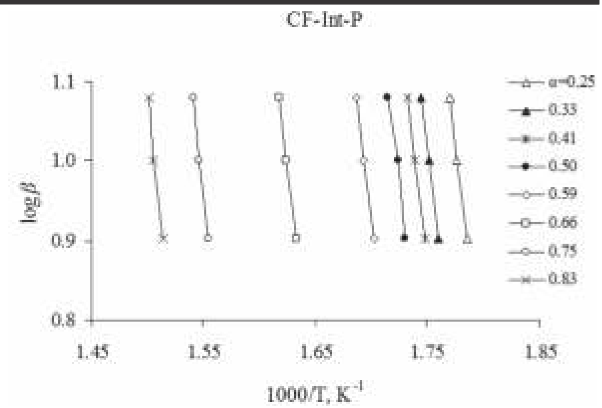

Fig. 3 OFW plot for CF-Int-P in nitrogen.

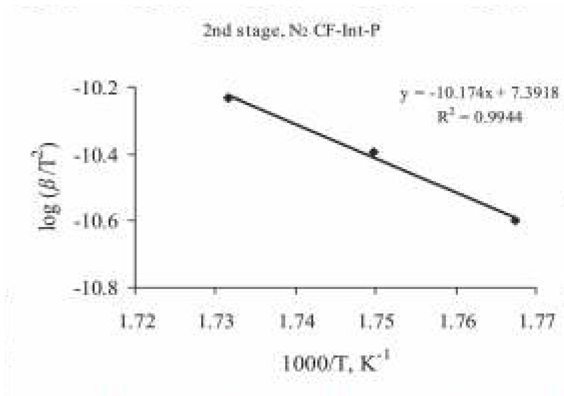

Fig. 4a) Kissinger plot for 2^{nd} stage of CF-Int-P in nitrogen.

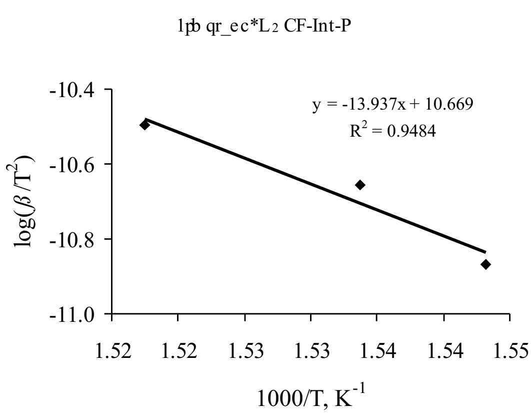

Fig.4b) Kissinger plot for 3^{rd} stage of CF-Int-P in nitrogen.

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