Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7254-7260

Kinetics of Thermal Degradation of Intumescent Coated Cotton Fabric

J.B. DAHIYA* and KRISHAN KUMAR
Department of Chemistry, Guru Jambheshwar University of
Science & Technology, Hisar-125 001, India
Fax: (91)(1662)276240; Tel: (91)(1662)263356; E-mail: jbdic@yahoo.com

The kinetics for thermal decomposition of coated cotton fabric sample coated with intumescent-nanoclay (CCF-Int-NC) formulation has been carried out to understand the flame retardant potential of the cotton sample. The Coats-Redfern method, Ozawa-Flynn-Wall (OFW) and modified Coats-Redfern methods have been applied on dynamic TG experiments at different heating rates. The random nucleation (F_3) type degradation mechanism is found most probable for CCF-Int-NC in inert atmosphere having activation energy (E_a) in range 143.5-168.6 kJ mol^{-1} and frequency factor in range ln A = 22-27 min^{-1} during decomposition process at different heating rates using Coats-Redfern method. The values of activation energy obtained in single heating rate and multi-heating rate methods are found not very far from each other in the conversion range $\alpha = 0.3$ to 0.5 indicating a similar mechanism operating in this range.

Key Words: Cotton, Thermal degradation, Kinetics, Isoconversional methods.

INTRODUCTION

The use of textile materials in industry and domestic purposes increases with the progress of society. Cotton is the most abundant used natural textile material. But it must be admitted that it bears fire risk, since most of the natural and synthetic polymers are flammable. From last twenty years, good research has taken place on flame retardancy of polymers[1-3]. Intumescent coating is one of the methods used to impart flame retardancy to textiles. The thermal degradation process of cellulosic material has been the focus of wide research[4,5] in the analysis of flame retardancy, release of harmful substances during waste ignition, recovering of chemical raw materials and optimizing the ignition processes to produce energy from fossil fuels. Many flame retardant systems have been developed and commercialized productively but without taking into account the toxic effect of flame retardant especially of antimony-bromine system[6,7]. The role of flame retardant intumescent coating is to protect the substrate from atmospheric oxygen and prevent flow of heat inward from flame as well as to shield the escape of low molecular weight volatile compounds into burning vapour phase. The main step in these processes is the thermal degradation through mass and energy transport which determines the rate of formation of various types of products from cellulosic materials. Therefore, study of degradation kinetics of cellulosic material is also important.

In view of the above, environmental friendly phosphorus based intumescent system as coating formulations containing the nanoclay has been selected as a flame retardant for cotton fabric. An intumescent system consists an acid source, a swelling agent and a char forming agent[8-12]. In this paper ammonium polyphosphate (APP) as an acid source, melamine as a swelling agent and pentaerythritol (PER) as a carbon source are used. The nanoclay (sodium bentonite) is also introduced in intumescent system. The thermal degradation kinetic study of coated cotton fabric samples is carried out using TG data. The Coats-Redfern[13], modified Coats-Redfern[14] and Ozawa[15], Flynn and Wall[16] methods were applied to evaluate kinetic parameters during thermal degradation of samples.

EXPERIMENTAL

Cotton fabric (CF) of area density (230.4 g/m^2) was used for back coating. The chemicals used to improve flame retardant property of cotton fabric were ammonium polyphosphate (APP), melamine, pentaerythritol (PER) (Clariant Co., Germany), sodium bentonite nanoclay (Sud-Chemical and acrylic based resin (Zytrol-7800) as binder (Zydex Industries, India).

Sample preparation: A formulation has been prepared containing intumescent components (ammonium polyphosphate, melamine and pentaerythritol) in ratio 3:1:1 *i.e.* (6:2:2 % w/w) plus 1 % nanoclay (NC) (sodium bentonite) weight by weight of pure cotton fabric. This formulation was coated on plane woven cotton fabric. The resin binder (30 % w/w of cotton fabric) used for coating the formulation was acrylic latex (Zytrol-7800). The fabric was coated with simple knife-blade technique, giving rise to approximate 30 % add on weight on the cotton fabric substrate. The coated cotton fabric sample in this study is abbreviated as CCF-Int-NC.

Thermal analysis: Thermal analysis (TG) for the sample was carried out using Perkin-Elmer (Pyris Diamond) thermobalance. Sample (about 10 mg) was contained in alumina crucibles and non-isothermal thermogravimetic measurements were carried out from ambient temperature to 700 ºC at heating rates of 10, 15 and 20 K/min. The nitrogen gas was used as purge gas with a flow rate of approximately 100 mL/min. The continuous records of samples temperature and mass loss were taken. DTG of the sample was also recorded.

RESULTS AND DISCUSSION

TG thermograms (Fig. 1) of coated cotton sample (CCF-Int-NC) were carried out at different heating rates 10, 15 and 20 K/min. TG thermograms show that the decomposition temperature increases with the increase of the heating rate. The kinetic parameters were determined using non-isothermal TG data by the following methods.

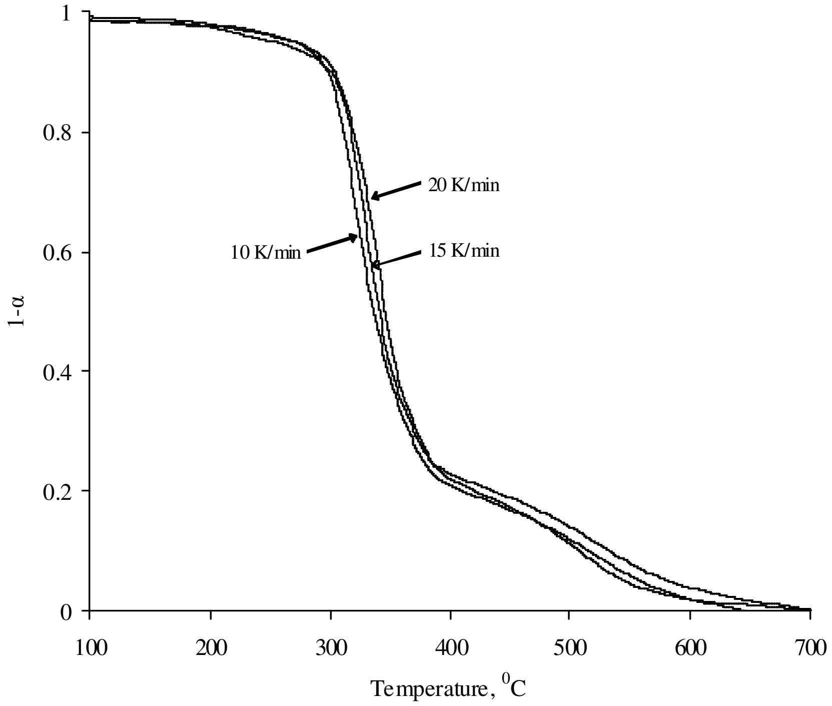

Fig. 1. TG curves of CCF-Int-NC at different heating rates

Integral method for single heating rate (Coats-Redfern method)[13]: This is an integral and model based method. This method is applicable for the non-iosthermal TG data of the materials. The equation of this method is as below:

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\frac{AR}{\beta E_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \qquad (1)$$

where $\beta = dT/dt$, $\alpha = (m_0\text{-}m_t)/(m_0\text{-}m_\infty)$, m_0 is the initial mass at t = 0, m_t is the mass at t time, m_∞ is the final mass. Other symbols have their usual meaning. Activation energy for every degradation process can be determined from a plot of log $(g(\alpha)/T^2)$ *versus* 1000/T.

The activation energy for thermal degradation of CCF-Int-NC was calculated using first order kinetics for every g(α) function listed in Table-1. The values of activation energy (E_a), pre-exponential factor (ln A) and correlation coefficient (R^2) (Table-2) were determined for different conversions (α) in the range of α = 0.30 to 0.70 at different constant single heating rates of 10, 15 and 20 K/min separately from the plots of $g(\alpha)/T^2$ *vs.* 1000/T. A plot of $\log\{(1\text{-}\alpha)^{-2}\text{-}1)/2T^2\}$ *versus* 1000/T as a representative is shown in Fig. 2. Arrhenius parameters calculated in this method are found highly variable indicating a strong dependence on the type of reaction mechanism selected. Based on high correlation coefficient, random nucleation type mechanism (F_3) appears the most probable mechanism for non-isothermal degradation

TABLE-1
COMMONLY USED MODELS FOR SOLID THERMAL DECOMPOSITION REACTIONS

Solid thermal decomposition reactions/model	Integral form $g(\alpha)$	Symbol of model
Nucleation and growth (Avrami equation-1)	$[-\ln(1-\alpha)]^{1/2}$	A_2
Nucleation and growth (Avrami equation-2)	$[-\ln(1-\alpha)]^{1/3}$	A_3
Nucleation and growth (Avrami equation-3)	$[-\ln(1-\alpha)]^{1/4}$	A_4
Phase boundary controlled reaction (1-dimensional movement)	α	R_1
Phase boundary controlled reaction (contraction area)	$[1-(1-\alpha)^{1/2}]$	R_2
Phase boundary controlled reaction (contraction volume)	$[1-(1-\alpha)^{1/3}]$	R_3
One dimensional diffusion	α^2	D_1
Two dimensional diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	D_2
Three dimensional diffusion (Jander's equation)	$[1-(1-\alpha)^{1/3}]^2$	D_3
Random nucleation with one nucleous on individual particle	$-\ln(1-\alpha)$	F_1
Random nucleation with two nuclei on individual particle	$[(1-\alpha)^{-1}-1]$	F_2
Random nucleation with three nuclei on individual particle	$[((1-\alpha)^{-2}-1)/2]$	F_3

TABLE-2
ACTIVATION ENERGIES OBTAINED USING COATS-REDFERN METHOD AT DIFFERENT HEATING RATES (MODEL BASED METHOD) FOR CCF-INT-NC

Model symbol	Heating rate (10 K/min)			Heating rate (15 K/min)			Heating rate (20 K/min)		
	E_a (kJ mol^{-1})	ln A (min^{-1})	R^2	E_a (kJ mol^{-1})	ln A (min^{-1})	R^2	E_a (kJ mol^{-1})	ln A (min^{-1})	R^2
A_2	30.1	-3.92	0.9266	32.4	-4.16	0.902	36.7	-4.19	0.9297
A_3	16.7	-6.96	0.8957	18.2	-6.22	0.8656	20.9	-5.28	0.9061
A_4	9.9	-8.69	0.8430	11.0	-8.00	0.8072	13.1	-7.17	0.8694
R_1	45.1	-0.69	0.8915	48.1	0.28	0.8658	54.1	1.77	0.8959
R_2	56.9	1.33	0.9231	60.6	2.42	0.9002	67.8	4.12	0.9246
R_3	61.2	1.91	0.9316	65.2	3.05	0.9097	72.9	4.82	0.9324
D_1	100.5	10.28	0.9112	106.5	11.76	0.8884	118.6	14.32	0.9123
D_2	115.1	12.79	0.9265	121.9	14.43	0.9051	135.6	16.96	0.9266
D_3	132.7	15.13	0.9415	140.7	16.96	0.9218	156.1	20.11	0.9409
F_1	70.5	4.26	0.9460	75.1	5.50	0.9260	83.7	7.44	0.9458
F_2	103.5	12.35	0.9739	110.2	13.96	0.9588	122.0	16.48	0.9721
F_3	143.5	22.36	0.9874	152.8	24.44	0.9760	168.6	27.64	0.9850

of CCF-Int-NC in this study with the activation energies 143.5, 152.8 and 168.6 kJ mol^{-1} at the heating rates 10, 15 and 20 K/min, respectively. The activation energies in F_3 mechanism are also found 17.5 % increased on increasing the heating rate twice. But as very high correlation coefficients (R^2) of linear regression are usually obtained for different form of $g(\alpha)$, one can not certain whether the lower values of R^2 are due to inappropriate choice of $g(\alpha)$ or experimental errors inherited to the measurements of TG curves[17]. Therefore, the correctness of mechanism may be considered on the basis of comparing kinetic parameters obtained from model-based as well as model-free non-isothermal methods.

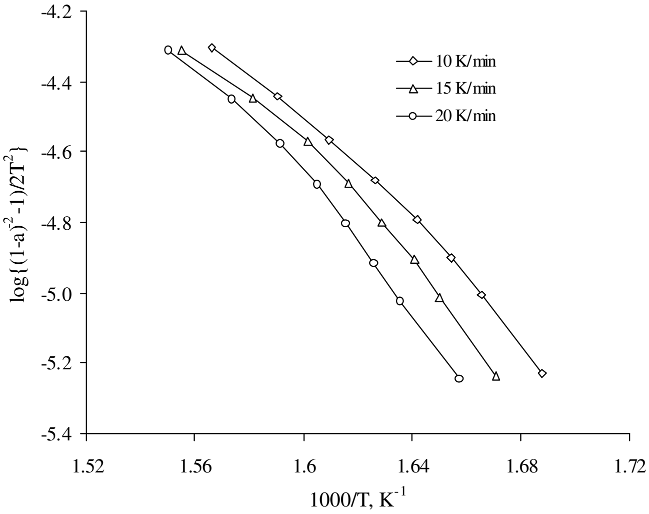

Fig. 2. Plots of log{$(1-\alpha)^{-2}$-1)/$2T^2$} *versus* 1000/T according to Coats-Redfern Method

Ozawa-Flynn-Wall (isoconversional method): This method was developed independently by Ozawa[15] and by Flynn and Wall[16]. The main equation of this method is as below:

$$\log\ \beta = \log\left[\frac{AE_a}{Rg(\alpha)}\right] - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \tag{2}$$

The activation energies for different conversion values (α = 0.2, 0.3, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65 and 0.7) were calculated (Table-3) from the slope of plots of log β *versus* 1000/T (Fig. 3) using eqn. 2. Almost constant values of activation energies (181.2 to 217.7 kJ mol^{-1}) were found in the conversion range from α = 0.3 to 0.5. But higher values of activation energy (253.1 and 331.9 kJ mol^{-1} at α = 0.55 and 0.70) were found at higher conversions, which indicates that different type of degradation mechanism takes place at higher conversions. The values of activation energy obtained by this method are found increasing with increase of conversion (Table-3).

Modified Coats-Redfern method: The following modified Coats-Redfern[13] method equation is was obtained after rearranging the eqn. 1.

$$\log\left[\frac{\beta * g(\alpha)}{T^2}\right] = \log\frac{AR}{E_a}\left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \tag{3}$$

From the plot of log (β*g(α)/T^2) *versus* 1000/T, the activation energy can be calculated from the slope. The kinetic parameters (Table-3) were calculated for conversions at α = 0.20, 0.30, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65 and 0.70 by plotting log{-β log(1-α)/T^2} *versus* 1000/T (Fig. 4) according to modified Coats-Redfern eqn. 3. Values of E_a are found near and in similar order as that of Ozawa-Flynn-Wall method[15,16].

TABLE-3
ACTIVATION ENERGIES OBTAINED USING MODEL INDEPENDENT OR ISOCONVERSONAL METHODS FOR CCF-INT-NC

Extent of conversion (α)	Ozawa-Flynn-Wall method		Modified Coats-Redfern method		
	E_a (kJ mol^{-1})	R^2	E_a (kJ mol^{-1})	ln A (min^{-1})	R^2
0.20	217.7	0.9783	219.4	36.32	0.9764
0.30	181.2	0.9992	181.2	28.23	0.9991
0.40	181.5	0.9956	180.9	28.03	0.9951
0.45	191.4	0.9843	191.3	30.07	0.9826
0.50	206.5	0.9914	207.2	33.12	0.9905
0.55	253.1	0.9732	256.1	42.65	0.9711
0.60	296.4	0.9666	301.5	51.22	0.9643
0.65	322.5	0.9881	328.9	55.94	0.9980
0.70	331.9	0.9836	338.7	56.92	0.9826

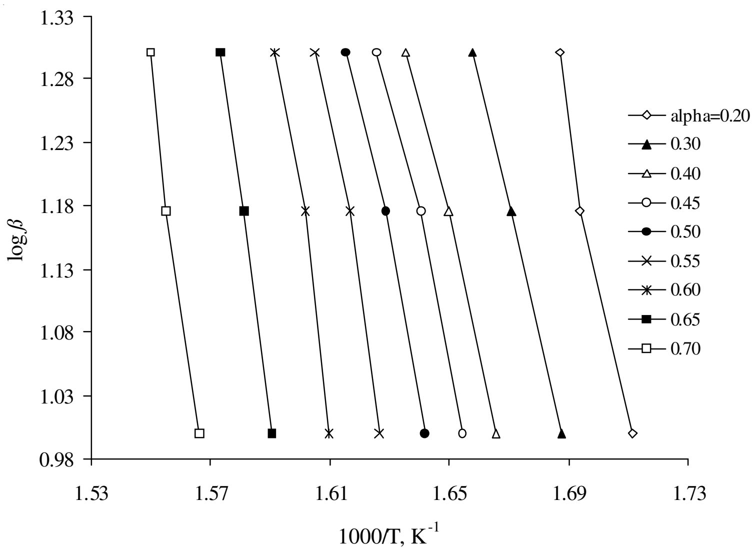

Fig. 3. Isoconversional plots of log β *vs.* 1000/T according to Ozawa-Flynn-Wall method

The activation energies obtained by isoconversional methods at lower conversion (α = 0.2-0.5) and higher conversion (α = 0.55-0.7) were found significantly different. The activation energies are also found almost constant in the range of α = 0.3 to 0.5. It predicts the different mechanisms of thermal degradation of coated cotton at the lower conversion (dehydration, depolymerization, disintegration of cellulose and competition between formation of volatile compounds and char) and at the higher conversion (cross-linking and aromatic cyclization of char residue). In the present study the values of activation energy obtained in single heating rate and multi-heating rate methods in the range of conversion (α = 0.3 to 0.5) are not found very far away from each other indicating a consistently similar mechanism operating in this range. Many workers have reported average value of E_a but because of

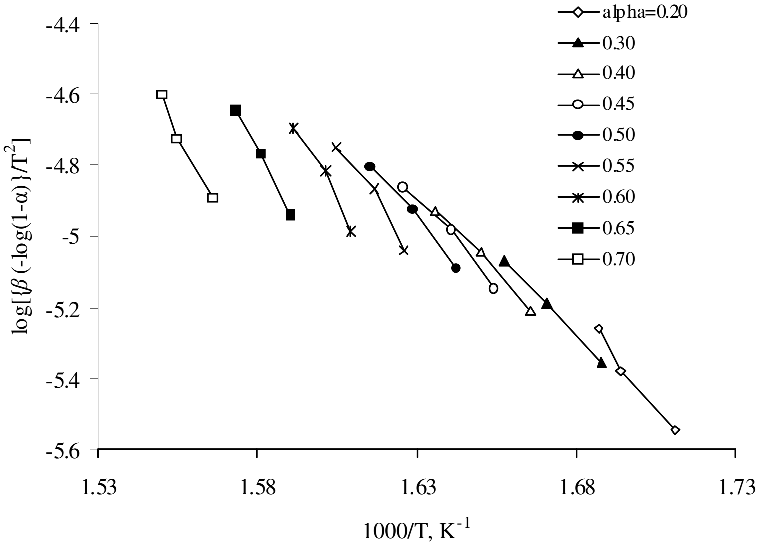

Fig. 4. Plots of log{-β log (1-α)/T^2} *vs.* 1000/T according to Modified Coats-Redfern method

occurrence of many different elementary steps and complex mechanism of thermal degradation of CCF-Int-NC it is not appropriate to give an average value of E_a. The variation in E_a is justified because of different elementary steps and complex mechanism of thermal degradation of coated cotton sample.

REFERENCES

1. A.R. Horrocks, *Rev. Prog. Color.*, **16**, 62 (1986).
2. P.G. Gordon, *Fire Safety J.*, **4**, 109 (1981).
3. B.K. Kandola, A.R. Horrocks, D. Price, G.V. Coleman and J.M.S. Rev, *Macromol. Chem. Phys.*, **C36**, 721 (1996).
4. J.B. Dahiya, K. Kumar, M.M. Hagedorn and H. Bockhorn, *Polym. Int.*, **57**, 722 (2008).
5. J.B. Dahiya, S. Rana and K. Kumar, *Asian. J. Chem.*, **20**, 1481 (2008).
6. S.M. lomakin, G.E. Zaikov and M.I. Artsis, *Int. J. Polym. Mater.*, **32**, 173 (1996).
7. G. Camino, in ed.: G. Nelson, Fire Retardant Polymeric Materials, ACS, Ch. 10, p. 461 (1995).
8. A.R. Horrocks, *Polym. Degrad. Stab.*, **54**, 143 (1996).
9. B.K. Kandola and A.R. Horrocks, *Text. Res. J.*, **69**, 374 (1999).
10. B.K. Kandola and A.R. Horrocks, *Fire Mater.*, **24**, 265 (2000).
11. A.R. Horrocks and D. Price, Fire Retardant Materials, Woodhead Publ. Ltd., England, p. 425 (2001).
12. B. Stein, J.S. Reynolds, W.T. Grondzik and A.G. Kwok, Mechanical and Electrical Equipment for Buildings, Wiley & Sons, Germany, edn. 10, p. 1724 (2005).
13. A.W. Coats and J.P. Redfern, *Nature (London)*, **201**, 68 (1964).
14. M.E. Brown, S. Vyazovkin, M. Maciejewski, R. Nomen, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseym, C.-R. Li, T.B. Tang, B. Roduit, J. Malek and T. Mitsuhashi, *Thermochim. Acta*, **355**, 125 (2000).
15. T. Ozawa, *Bull. Chem. Soc. (Japan)*, **38**, 1881 (1965).
16. J.H. Flynn and L.A. Wall, *J. Polym. Sci., Polym. Lett. Ed.*, **4**, 323 (1966).
17. P. Budrugeac, A.L. Petre and E. Segel, *J. Them. Anal.*, **47**, 123 (1996).

(*Received*: 22 February 2009; *Accepted*: 21 August 2009) AJC-7760