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Model Based and Model Free Methods for Kinetic Study of Thermal Degradation of Cellulose Thiophosphinite Derivative

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Cellulose diethylamino ammoniumthiophosphinite (CEAAT) has been chosen for a study of its degradation behaviour from ambient temperature to 700 ºC using thermogravimetry. Cellulose diethylamino ammoniumthiophosphinite when heated in helium atmosphere, gives rise to higher char yield (45 %) as compared to cellulose (9.1 %) at 700 ºC. Kinetics was studied using model based and model free methods for degradation of CEAAT up to 700 ºC. After taking into account the values of activation energy and pre-exponential factor both obtained by model free methods and comparing these values with the values obtained by model based method. The diffusion controlled and random nucleation type mechanisms are found the most probable during thermal degradation of CEAAT.

Key Words: Cellulose diethylamino ammoniumthiophosphinite, Thermal degradation, Kinetics, Char, Coats-Redfern method.

INTRODUCTION

Cotton textiles find many uses and add significantly to the quality of modern day life. A major problem arises because most of polymers are flammable and thus remains an obstacle to their still wider use and often plays a major role in the cause and growth of many destructive fires. Developments to control polymer flammability include intrinsically thermally stable polymers[1], fire retardant additives[2,3] and intumescent fire retardant systems[4-6] including our earlier chemical treatment study[7,8]. There are doubts about the general use of halogenated compounds as flame retardants (FR) because of likely environmental contamination from highly toxic combustion products released during fires and waste incineration, particularly brominated dioxins and dibenzofurans from halogenated flame retardants system[9]. Many fire retardant additives are available and found effective in reducing gross flammability but at the expense of increased smoke production. Therefore, there exists a need for new and more effective environmentally benign approaches with a permanent effect that reduces flammability with minimum change to the physico-mechanical properties.

In the present work, cellulose diethylamino ammoniumthiophosphinite (CEAAT) was synthesized for a study of their internal thermal degradative behaviour and hence potential flame retardancy. The compound has been subjected to thermal degradation from ambient temperature to 700 ºC at different heating rates using thermogravimetry (TG) in helium atmosphere. The thermal degradation process occurs through mass and energy transfer, which determines the rate of formation of various types of products from cellulosic materials. The thermal degradation kinetics of CEAAT was studied using TG data by employing non-isothermal methods such as Coats-Redfern[10], modified Coats-Redfern[11] and Flyann-Ozawa-Wall[12,13] methods were chosen and compared the result.

EXPERIMENTAL

The materials used for the study were (i) cellulose powder (CDH, India), (ii) diethylphosphoramidous dichloride and (iii) cellulose diethylamino ammoniumthiophosphinite (CEAAT). Diethylphosphoramidous dichloride was synthesized as per method given elsewhere[14].

Preparation of cellulose diethylamino ammoniumthiophosphinite (CEAAT): To 6.5 mL of diethylphosphoramidous dichloride (0.045 mol) added 4.85 g (0.03 mol) of an anhydroglucose unit of cellulose) of swallowed celluose and then 9.12 g of thiourea (0.12 mol) in 100 mL of pyridine. This mixture was heated for 4 h at 90 ºC under constant stirring. The product obtained was filtered, washed first with pyridine and then thoroughly by distilled water. Finally the product was dried at room temperature in air and then dried over P_2O_5.

Elemental analysis: Elemental analyses of phosphorus (1.1 %), sulphur (0.6 %) and nitrogen (1.7 %) were carried out by colorimetrically, gravimetrically and Kjeldahl method, respectively.

TG and DSC studies: TG thermograms of compound were obtained using DuPont 951 thermal analyzer at different heating rates of 2, 5 and 10 ºC min^{-1} from ambient temperature to 700 ºC. Pure helium was used as purge gas with a flow rate of approximately 100 mL/min. The samples with initial mass 7 to 9 mg were taken in open platinum pan. DSC thermogram of CEAAT was also obtained using DuPont 951 thermal analyzer at heating rates of 10 ºC min^{-1} from ambient temperature to 550 ºC in He atmosphere.

FTIR spectroscopy and characterization of compounds: FTIR spectra of compound were recorded by the KBr pellet technique using a Shimadzu FTIR-8001 PC, Kyoto, Japan. The CEAAT were characterized by FTIR spectra and elemental analysis. CEAAT, chlorodeoxycellulose and the pyridinium complex were formed when cellulose was reacted with dichlorodiethylphosphine. FTIR spectrum of CEAAT compared to spectrum of cellulose, shows additional infrared bands at 1900 (ammonium ion), 2422 ((P)-O-N), 810 (P-O-(C)), 750 (P-N-(C)), 669 ((P-S)-N) and 526 cm^{-1} (S-N band).

Kinetics of degradation

Flynn[15] gave review of innovative work in non-isothermal kinetics. The generalized kinetic expression for non-isothermal method is

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \tag{1}$$

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 is the mass at t time, m_∞ is the final mass. There are various methods for calculating kinetic parameters from eqn. 1 such as (i) differential method, (ii) integral method *i.e.* Coats-Redfern method[10] and (iii) model independent method based on heating rates such as Ozawa-Flynn-Wall method[12,13].

Integral method (model based method): The method is based on the integration of the basic differential eqn. 1 under non-isothermal condition as shown below.

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} e^{-E_a/RT}\,dT \tag{2}$$

or

$$g(\alpha) = \frac{AE_a}{\beta R}\int_0^\infty \frac{e^{-x}}{x^2}\,dx \tag{3}$$

where g(α) is the integrated forms of different kinetic model equations as given in Table-1 and $x = E_a/RT$. Integrating by various parts and introducing a new function p(x) for the negative exponential of temperature function under the condition that if T_0 is selected before the initiation of the reaction, then $p(x_0)$ is negligibly small. Hence eqn. 3 may be written as follows:

$$g(\alpha) = \frac{AE_a}{\beta R}\,p(x) \tag{4}$$

This is known as Doyle's equation[16].

TABLE-1
MODELS USED IN THE STUDY OF THE KINETICS OF THERMAL DEGRADATION

Model code	Name of model/ equations	Integral form, g(α)	Differential form, f(α)
	Diffusion controlled models		
D_1	One dimensional	α^2	$1/2\alpha$
D_2	Two dimensional	$(1-\alpha)\ln(1-\alpha)+\alpha$	$[-\ln(1-\alpha)]^{-1}$
D_3	Three dimensional. (Jander's equation)	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
	Nucleation and growth controlled models		
A_m	Avrami-Erofeev's eqn., with m=1.5, 2, 3, 4.	$[-\ln(1-\alpha)]^{1/m}$	$m(1-\alpha)[-\ln(1-\alpha)]^{(m-1)/m}$
F_1	First order reaction (random nucleation)	$-\ln(1-\alpha)$	$(1-\alpha)$
F_n	Second or third order reaction (random nucleation)	$[1/(1-\alpha)^{n-1}-1]/(n-1)$	$(1-\alpha)^n$
	Contracting phase boundary		
R_n	Plate (n=1), Cylinderical (n=2) and spherical geomatery (n=3)	$1-(1-\alpha)^{1/n}$	$n(1-\alpha)^{(n-1)/n}$

According to Coats and Redfern[10] approximation of the function p(x), becomes as given below:

$$p\,(x) = \frac{e^{-x}}{x^2}\left\{1 - \frac{2}{x}\right\} \tag{5}$$

Using this p(x) function the Coats and Redfern derived the following relation:

$$\log\left[\frac{g(\alpha)}{T^2}\right] = \log\ \frac{AR}{\beta E_a}\left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \tag{6}$$

Model independent methods: Ozawa, Flynn and Wall (OFW) method: This method was developed independently by Ozawa[12] in Japan and Flynn and Wall[13] in USA. Using Doyle's approximation, the eqn. 2 on taking integration and applying logaritham the result obtained as:

$$\log\ \beta = \log\left[\frac{AE_a}{Rg(\alpha)}\right] - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \tag{7}$$

In this method, plots of log β *vs.* 1/T give parallel lines for each α value. The slope of these lines gives the activation energy, Slope = -0.4567(E_a/R). The E_a values obtained by this method are independent of any mechanistic model.

Kissinger's method: Kissinger[17] 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. The relationship obtained when n = 1 is as follows:

$$\log\left(\frac{\beta}{T_m^2}\right) = \log\ \frac{AR}{E_a} - \frac{E_a}{2.3RT_m^2} \tag{8}$$

RESULTS AND DISCUSSION

Thermal degradation: TG thermograms of CEAAT compound were recorded from ambient temperature to 700 ºC in helium atmosphere at different heating rates 2, 5 and 10 ºC/min and are shown in Fig. 1. TG thermogram of cellulose shows one major area of weight loss and its details are given in our earlier publication[18] whereas its derivative (CEAAT) shows three significant areas of weight loss, termed as three stages of thermal degradation. CEAAT shows 13 % weight loss in first stage in the temperature range 80-225 ºC due to acid catalyzed dehydration and dephosphorylation. CEAAT shows 27 % weight loss in the temperature range 225-335 ºC due to its decomposition in second stage and 12 % weight loss in temperature range 335-580 ºC due to aromatization and cross-linking in the last stage of thermal degradation. Final char yield in weight per cent for CEAAT (45 %) was calculated at 700 ºC from TG thermograms in helium atmosphere and is found much higher than that of cellulose (9.1 %), indicating a reduction in the amount of low molecular weight volatiles formed during its pyrolysis.

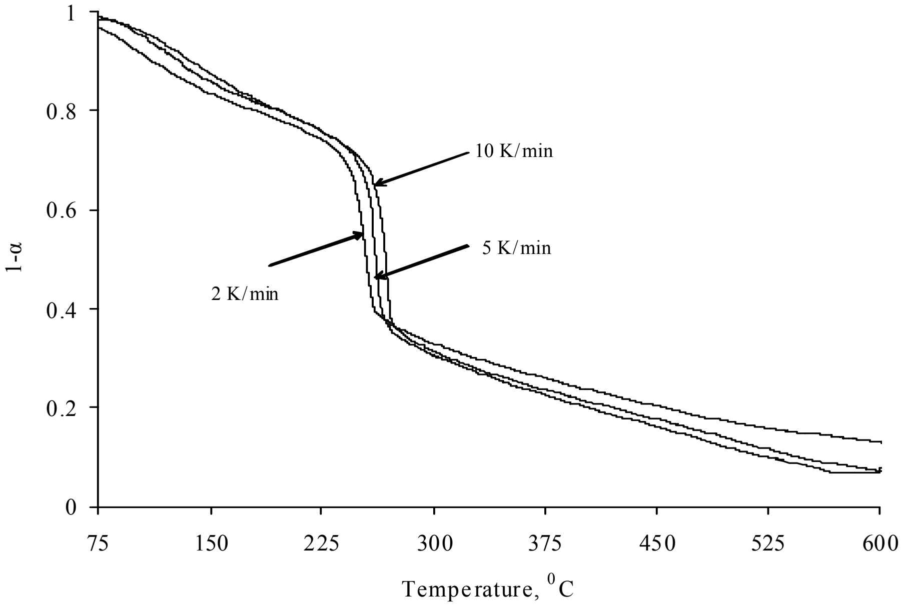

Fig. 1. TG curves of CEAAT compound at three different heating rates

DSC thermogram of CEAAT sample was obtained upto 550 ºC in helium atmosphere. DSC thermogram of CEAAT in helium shows endotherm with maxima at 135 ºC due to dephosphorylation and acid catalyzed dehydration reactions. The exotherms of CEAAT observed at 238 and 307 ºC are due to decomposition leading to the formation of char. Last exotherm of the sample at around 528 ºC may be considered due to aromatization and cross-linking of the char formed.

Kinetic parameters: Kinetics of thermal decomposition of CEAAT is of interest in the viewpoint of flame retardancy for safety. The kinetic parameters were determined using non-isothermal TG data of CEAAT up to 700 ºC in helium atmosphere by employing the following model based and model free methods.

Integral method for single heating rate (Coats-Redfern method): This is a model based method. The activation energy for thermal degradation of CEAAT was calculated using first order kinetics for every g(α) function listed in Table-1. The values of activation energy, pre-exponential factor and correlation coefficient were found for the degree of conversion in the range of $\alpha = 0.35$ to 0.6 at constant single heating rates of 2, 5 and 10 ºC/min, respectively, from fitting $g(\alpha)/T^2$ *vs.* 1000/T plots and the values are given in Table-2. A plot of log $\{-\log(1-\alpha)/T^2\}$ *vs.* 1000/T as a representative of model code F_1 type (random nucleation mechanism) is shown in Fig. 2. The Arrhenius parameters calculated using this method are highly variable, indicating a strong dependence on the reaction mechanism selected. The increase in the values of both E_a and A is observed with the increase of heating rates for each type of model. Based on high correlation coefficient D_3, F_1, F_2, F_3 seem equally the best mechanisms at 2 ºC/min, D_1, D_2, at 5 ºC/min and D_1, D_2 at 10 ºC/min

TABLE -2
ACTIVATION ENERGIES OBTAINED USING THE COATS-REDFERN METHOD AT DIFFERENT HEATING RATES (MODEL BASED METHOD) FOR CEAAT

Mechanism	Heating rate, 2 ºC/min			Heating rate, 5 ºC/min			Heating rate, 10 ºC/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	60.60	3.33	0.9768	83.20	9.46	0.9829	84.90	10.35	0.9588
A_3	37.50	2.21	0.9710	52.50	2.30	0.9810	53.70	3.13	0.9544
A_4	25.90	5.11	0.9661	37.20	1.40	0.9788	37.99	0.60	0.9492
R_1	90.20	10.38	0.9722	123.10	18.74	0.9888	126.10	19.80	0.9728
R_2	108.80	14.28	0.9758	147.60	23.90	0.9870	150.80	24.98	0.9678
R_3	115.60	15.52	0.9768	156.40	25.60	0.9862	159.90	26.68	0.9661
D_1	189.20	32.97	0.9747	255.10	48.47	0.9896	261.20	49.91	0.9746
D_2	212.50	37.91	0.9767	285.80	55.00	0.9885	292.30	56.46	0.9715
D_3	239.90	42.99	0.9784	321.70	61.93	0.9869	328.60	63.40	0.9678
F_1	129.90	19.28	0.9782	175.20	30.32	0.9846	178.90	31.41	0.9627
F_2	179.40	32.09	0.9804	240.10	46.45	0.9791	244.40	47.52	0.9526
F_3	238.30	46.22	0.9805	317.10	64.49	0.9736	322.20	65.50	0.9438

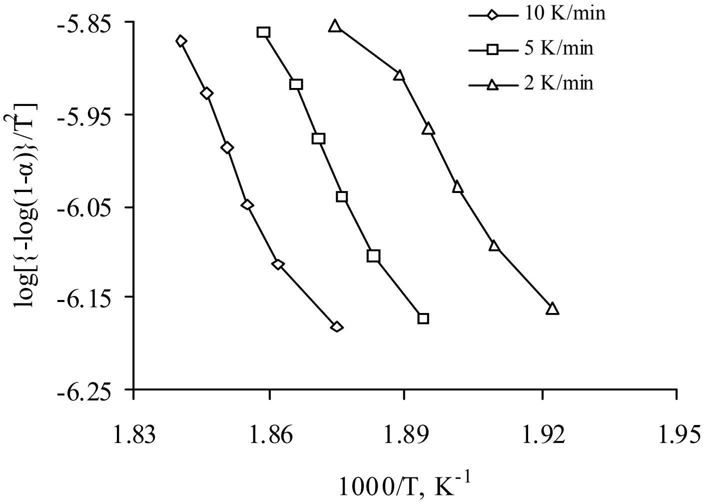

Fig. 2. Plots of CEAAT compound according to Coats-Redfern method

for non-isothermal degradation of CEAAT. But as very high correlation coefficients (R^2) of linear regression are usually obtained for different form g(α), one can not sure whether the little lower values of R^2 are due to improper choice of g(α) or experimental errors inborn to the measurements of TG curves. So the linear correlation coefficient has a drawback for verifying the exactness of a reaction mechanism in the study of decomposition kinetics. Therefore, the correctness of mechanism may be considered on the basis of comparing kinetic parameters obtained by model based as well as model free non-isothermal methods.

Ozawa-Flynn-Wall (Isoconversional method): Fig. 3 shows a collection of lines obtained from the plot of log β *vs.* 1000/T using eqn. 7 at α = 0.3, 0.4, 0.45, 0.5 and 0.55. Activation energies obtained, related to these conversions is given in Table-3. Almost constant values of activation energies were found in the range 265.3 to 299.7 kJ mol^{-1}.

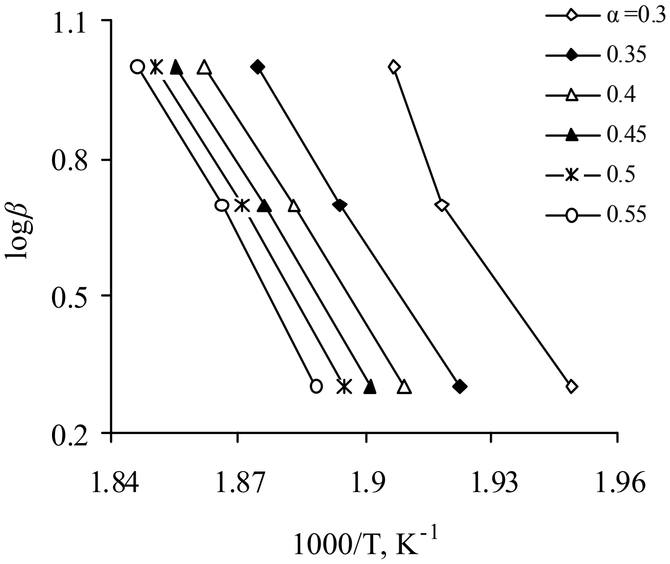

Fig. 3. Plots for CEAAT according to Ozawa-Flynn-Wall method

TABLE-3
ACTIVATION ENERGIES OBTAINED USING MODEL FREE METHODS FOR CEAAT

Conversion	Ozawa-Flynn-Wall method		Modified Coats-Redfern method		
(α)	E_a (kJ mol^{-1})	R^2	E_a (kJ mol^{-1})	ln A (min^{-1})	R^2
0.30	289.4	0.9688	295.9	66.98	0.9671
0.35	265.3	0.9993	270.4	60.26	0.9993
0.40	268.1	0.9992	273.3	60.68	0.9998
0.45	274.4	0.9992	279.9	62.09	0.9992
0.50	284.8	0.9990	290.8	64.56	0.9990
0.55	299.7	0.9980	306.5	68.07	0.9979

Modified Coats-Redfern method: The kinetic parameters (Table-3) were calculated for conversion at α = 0.3, 0.4, 0.45, 0.5 and 0.55 by a plot of log $\{-\beta \log (1-\alpha)/T^2\}$ *vs.* 1000/T according to Modified Coats-Redfern equation (Fig. 4). Values of E_a in the range 270-306 kJ mol^{-1} are found near and of similar order as in the case of OFW method. The values of ln A determined by this method were found in the range 60-68 min^{-1}.

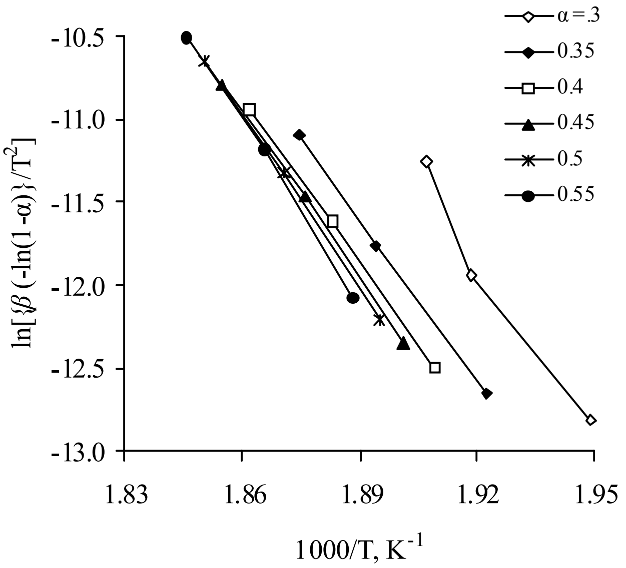

Fig. 4. Plots for CEAAT compound according to Modified Coats-Redfern method

Kissinger method: The activation energy 277.5 kJ mol^{-1} and pre-exponential factor ln A = 61.8 min^{-1} were calculated from the plot of ln (β/T_m^2) *vs.* $1000/T_m$ at different heating rates according to Kissinger method eqn. 8. Values were found close to the values obtained from other methods.

The activation energies obtained by all the model free methods *i.e.* isoconversional methods such as Ozawa-Flynn-Wall, Modified Coats-Redfern and Kissinger method are found in the range 265 to 306 kJ mol^{-1} and pre-exponential factor in the range 60-68 min^{-1}. The activation energies in the conversion range (α = 0.35 to 0.5) were not found significantly different predicting the same type of mechanism during thermal decomposition of CEAAT.

After taking into account the both values of E_a and A obtained by model free methods and comparing these values with the values E_a and A at very high correlation coefficients (R^2) obtained by model based method, the diffusion controlled and random nucleation type mechanisms are the most probable during thermal degradation of CEAAT.

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