Synthesis of Cellulose Diethylamino Ammoniumphosphonite and its Thermal Degradation Kinetics

Deepa Malhotra, Krishan Kumar and J.B. Dahiya*
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

Cellulose diethylamino ammoniumphosphonite (CEAP) has been synthesized and characterized. Flame retardancy potential of CEAP was investigated by the kinetics of thermal degradation using differential scanning calorimetery and thermogravimetery in air and He atmosphere. From the resulting data of thermogram curve using Broido method, the activation energy of CEAP (51.3 kJ mol^{-1}) for decomposition process is found lower than that of cellulose (155.3 kJ mol^{-1}) in air. The higher char yield of CEAP (28.3 %) as compared to cellulose (3.1 %) at 700 ºC in air and related observations lead to conclusion that such modification may give rise to novel flame retardant treatment for cellulosic materials.

Key Words: Cellulose, Cellulose diethylamino ammonium-phosphonite, Thermal degradation, Activation energy, Char yield.

INTRODUCTION

The consumption of textiles used in industry and civilian life increases swiftly with the development of society. Because fire disasters caused by textiles always cause huge losses, more and more people begin to think highly of studies on flame retardant textiles. Cotton cellulose is one of the most important natural textile materials that is intrinsically flammable, thus the emphasis on reducing combustibility has centered on the chemical modification by treating it with flame-retardants including reported studies[1-3]. The primary role of a flame retardant is to alter degradation process so that a lower percent of flammable volatiles is produced and a correspondingly larger amount of char is formed. The flame retardants, based on chlorine, bromine and antimony are increasingly regarded as environmentally unacceptable[4,5]. Therefore, there exists a need for new, more effective, with a permanent effect and environmentally benign approaches to obtain durable flame-retarding cotton cellulose.

In view of the above, cellulose diethylamino ammoniumphosphonite (CEAP) was synthesized for a study of thermal degradative behaviour and hence potential flame retardancy. The compounds have been subjected to thermal degradation from ambient temperature to 700 °C using thermogravimetry (TG) and differential scanning calorimetery (DSC) techniques in air and He atmosphere. Kinetic parameters were calculated for decomposition stage from TG data using Broido method[6] and thermodynamic quantities such as entropy, enthalpy and free energy of activation were calculated using transition state theory[7].

EXPERIMENTAL

Cellulose (CDH, India) and cellulose diethylamino ammoniumphosphonite compounds were used for the present study.

Preparation of cellulose diethylamino ammoniumphosphonite: Cellulose diethylamino ammoniumphosphonite (CEAT) was prepared by treating cellulose (0.03 mol of anhydroglucose unit of cellulose) in pyridine (100 mL) with diethylphosphoramidous dichloride (0.045 mol) and urea (0.12 mol) at 90 °C for 4 h with 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. Diethylphosphoramidous dichloride was prepared as per method given elsewhere[8].

Thermal analysis: DSC and TG thermograms of compounds were obtained using DuPont 951 thermal analyzer at a heating rate of 10 °C/min in both air and He atmosphere at flow rate of 100 mL/min. TG thermograms were recorded from ambient temperature to 700 °C while DSC thermograms were obtained upto 550 °C.

FTIR spectroscopy: FTIR spectra of compounds were recorded by the KBr pellet technique using a Shimadzu FTIR-8001 PC, Kyoto, Japan.

Elemental analysis: Elemental analyses of phosphorus, halogen and nitrogen were carried out by calorimetrically, gravimetrically and Kjeldahl method, respectively.

Characterization of CEAP: The cellulose diethylamino ammoniumphosphonite was characterized by FTIR spectra and elemental analysis. Owing to the method employed, the pyridinium complex was also formed in very small amount[9]. In IR spectrum of cellulose diethylamino ammoniumphosphonite, bands at 1900 (ammonium ion), 2422 ν[(P)-O-N], 810 ν[P-O-(C)], 750 ν[P-N-(C)] were observed in addition to cellulose.

RESULTS AND DISCUSSION

DSC and TG thermograms of cellulose and CEAP were recorded at a heating rate of 10 °C min^{-1} in both air and He atmosphere at flow rate of 100 mL/min.

DSC studies: DSC thermograms of samples were obtained upto 550 ºC in air and He atmosphere and are shown in Fig. 1. The peak temperatures (initial and maximum) for various endotherms and exotherms of DSC in air and He atmosphere were measured and are given in Table-1. The endotherm below 100 ºC due to evolution of moisture in each compound is not given in the Table-1. In air, cellulose shows first exotherm with maximum at 342 ºC, which is attributed to decomposition leading to the formation of laevo-glucosan, the major volatile product. After this, there is another sharp exotherm with maximum at 487 ºC, which may be attributed to the oxidation of volatile and charred products. The DSC thermogram of CEAP shows two major exotherms with maxima at 228 and 306 ºC due to acid catalyzation, decomposition and oxidation of released products in air atmosphere. DSC thermogram of CEAP indicates that the decomposition and oxidation process are found starting at lower temperature than that of pure cellulose. The last
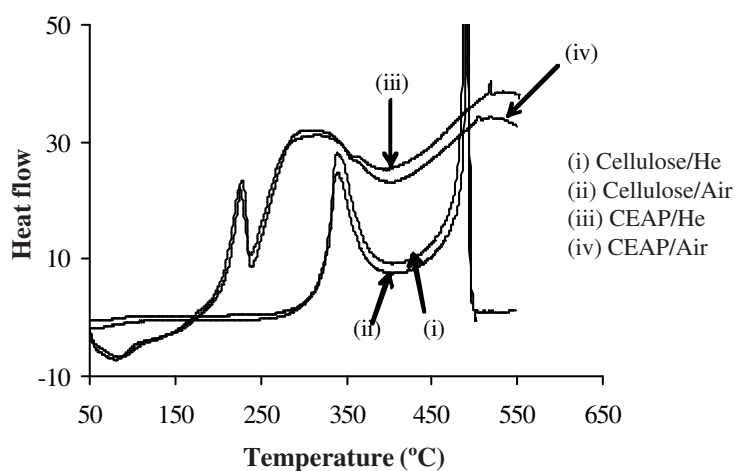

Fig. 1. DSC thermograms of cellulose and CEAP in air and He atmosphere

TABLE-1
ANALYTICAL DATA AND DESCRIPTION OF DSC
CURVES IN AIR AND He

| Compd. | Elemental data | Temperature (ºC) | | | | Nature of peak |
| | | Air | | Helium | | |
		Initiation	Maximum	Initiation	Maximum	
Cellulose	–	280	342	280	344	Exo, medium
		426	487	420	489	Exo, large
CEAP	P (1.2 %)	180	228	180	226	Exo, sharp
	N (1.7 %)	241	306	238	311	Exo, broad
	Cl (0.3 %)	396	510	395	528	Exo, large

CEAP = Cellulose diethylamino ammoniumphosphonite

exotherm with maximum at 510 ºC in case of CEAP indicates the possibility of occurrence of cross-linking and oxidation of residue. In He atmosphere no significant change in DSC peaks of the compounds is observed. This may be because of use of high flow rate of air and He gases which takes away the volatiles produces from the substrate.

TG studies and kinetics: TG thermograms of all samples were recorded from ambient temperature to 700 ºC in air and He atmosphere and are shown in Fig. 2. TG thermogram of cellulose shows one major area of weight loss whereas CEAP shows three significant areas of weight loss, termed as three stages of thermal degradation. The kinetic parameters are calculated for decomposition stage from TG data (Table-2) using Broido method[6]. The equation used in this method is given below:

$$\ln\left\{\ln\left(\frac{1}{y}\right)\right\} = -\frac{E_a}{R}\frac{1}{T} + \ln\left\{\frac{R}{E_a}\frac{Z}{\beta}T_m^2\right\}$$

where y is the fraction of number of initial molecules not yet decomposed, β is the heating rate, Z is the frequency factor and T_m is the temperature at maximum mass loss rate. In TG thermograms 1-α is equal to y, where α is defined as $(m_0-m)/(m_0-m_\infty)$. Using Broido equation, plots of $\ln[\ln(1/y)]$ *vs.* 1/T for decomposition stage of thermal degradation of cellulose and CEAP in air and He atmosphere are plotted. The activation energies and frequency factors are calculated from the slopes and intercepts, respectively and these values are given in Table-3. The thermodynamic quantities such as entropy, enthalpy and free energy of activation are also calculated using transition state theory at the respective T_m, for the decomposition stage of degradation of cellulose and CEAP and are given in Table-3.

TABLE-2
KINETIC PARAMETERS OBTAINED USING BROIDO
EQUATION IN AIR AND He ATMOSPHERE

Compd.	Stage	Temperature range (ºC)	Wt. loss (%)	Char yield at 700 ºC (%)
Cellulose	One	260-430 (270-420)	82 (84.5)	3.1 (9.1)
CEAP	First	80-231 (80-216)	16 (07)	28.3 (46.4)
	Second	231-305 (216-350)	24 (31)	
	Third	390-700 (350-565)	35 (12)	

CEAP = Cellulose diethylamino ammoniumphosphonite
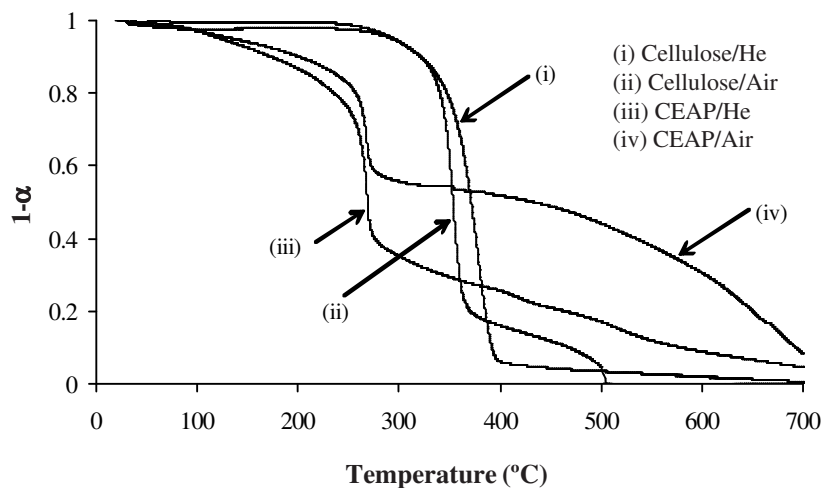Values in parenthesis were determined in He atmosphere

Fig. 2.   TG thermograms of cellulose and CEAP in air and He atmosphere

TABLE-3
KINETICS AND THERMODYNAMIC PARAMETERS OF
SECOND STAGE IN AIR AND He ATMOSPHERE

Compd.	T_m (°C)	E_a (kJ mol^{-1})	Z (s^{-1})	ΔS (JK^{-1} mol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})
Cellulose	354 (382)	155.3 (153.9)	9.6×10^{10} (2.0×10^{10})	-49.3 (-62.7)	150.1 (148.5)	181.0 (189.5)
CEAP	268 (267)	51.3 (49.4)	4.0×10^{2} (2.2×10^{2})	-208.6 (-213.5)	46.8 (44.9)	159.6 (160.3)

CEAP = Cellulose diethylamino ammoniumphosphonite
Values in parenthesis were determined in He atmosphere

Cellulose shows a weight loss of 82 % in the temperature range 260-430 ºC mainly due to oxidative decomposition with activation energy 155.3 kJ mol^{-1} in air atmosphere, which corresponds to first exotherm at 342 ºC in DSC. The modified cellulose, CEAP, during decomposition (second) stage of degradation shows 24 (31) % weight loss in the temperature range 231-305 (216-350) ºC with lower activation energy 51.3 (49.4) kJ mol^{-1} in comparison to cellulose in air (He) atmosphere. The major weight loss during decomposition and oxidation of CEAP in air corresponds to exotherms with maxima at 208 and 306 ºC in DSC leading to the formation of char.

Char yield: Final char yields in weight per cent for cellulose and CEAP were calculated at 700 ºC from TG themograms in air and He atmosphere and are given in Table-2. Char yields of CEAP (28 %) is found much higher than that of cellulose (3.1 %), indicating a reduction in the amount of low

molecular weight gases formed during oxidative degradation. Table-2 shows that char yields of samples are further increased in He atmosphere. The cellulose and CEAP show variation in the values of entropy of activation -49.3 to -208.6 (-62.7 to -213.5) J K^{-1} mol^{-1} but this variation is compensated by a change in values of enthalpy of activation 150.1 to 46.8 (148.5 to 44.9) kJ mol^{-1} leading to the almost constant values of free energy of activation 181.0 to 159.6 (189.5 to 160.3) kJ mol^{-1}. This indicates that basic step involved in decomposition stage does not change on chemical modification of cellulose.

REFERENCES

1. B.K. Kandola, A.R. Horrocks, D. Price and G.V. Coleman, *J. M S-Rev. Macromol. Chem. Phys.*, **C36**, 721 (1996).
2. J.B. Dahiya and S. Rana, *Indian J. Chem.*, **44A**, 2024 (2005).
3. J.B. Dahiya and S. Rana, *Polym. Int.*, **53**, 995 (2004).
4. D. Purser, in eds.: A.R. Horrocks and D. Price, Fire Retardant Materials, Woodhead Publ. Ltd., Cambridge, p. 69 (2001).
5. D. Purser, in eds.: A.F. Grand and C.A. Wilkie, Fire Retardancy of Polymeric Materials, Marcel Dekker, New York, p. 449 (2000).
6. A. Broido, *J. Polym. Sci. A-2*, **7**, 1761 (1969).
7. K.J. Laidler, Chemical Kinetics, Tata-McGraw-Hill, New York, p. 86 (1976).
8. J.G. Morse, K. Cohn, R.W. Rudolph and R.W. Parry, in ed.: E.L. Muetterties, Inorganic Syntheses, McGraw-Hill Inc, p. 147 (1967) (online 2007).
9. S.H. Zeronian, S. Adams, K. Alger and A.E. Lipska, *J. Appl. Polym. Sci.*, **25**, 519 (1980).

5TH INTERNATIONAL CONFERENCE ON COMBUSTION, INCINERATION/PYROLYSIS AND EMISSION CONYTROL

16 — 19 DECEMBER 2008

CHIANG MAI , THAILAND

Contact:
E-mail: srk@kmitnb.ac.th
Website: http://www.me.kmitnb.ac.th/~icipec