

Model free Multiple Heating Rate Degradation Kinetic Studies of Modified Celluloses

SATISH KUMAR¹, MAHESH KUMAR², SOHAN LAL³,
SANDEEP KUMAR⁴ and SANJIV ARORA^{3*}

¹Department of Chemistry, University College, Kurukshetra University,
Kurukshetra-136119, India

²Department of Chemistry, Mukand Lal National College, Yamuna Nagar-135001, India

³Department of Chemistry, Kurukshetra University, Kurukshetra-136119, India

⁴Department of Physics, Hindu College, Sonapat-131001, India
sanjivkuk@yahoo.co.in

Received 20 September 2014 / Accepted 17 October 2014

Abstract: The present paper depicts about the synthesis of cellulose ethyl ammonium thiophosphate (CEASP) and its metal complexes with Cd, Mo and Ce. CEASP and its metal complexes have been characterized by infrared (IR), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDXS) studies. The surface morphology of samples has been premeditated by means of scanning electron microscopy (SEM). The thermal studies of samples have been carried out at multiple heating rates 2, 5, 10 and 20 °C min⁻¹ from ambient to 700 °C in nitrogen atmosphere. Non-isothermal model free kinetic methods have been used to calculate activation energy of samples *i.e.* Friedman, Ozawa-Flynn-Wall (O-F-W) and modified Coats- Redfern. The activation energy of samples lie in range 72-282 kJ mol⁻¹. Thermal study shows that initial degradation temperature of CEASP and its metal complexes decreases and there is abrupt increase in char yield of synthesized samples as compared to pure cellulose. These and other related information suggest that such type of derivatisation could be proved a good flame retardant for cellulose.

Keywords: Cellulose, Model Free Kinetics, Flame Retardant, Activation energy

Introduction

Textile is very essential in modern living condition. It is not only essential for apparels but also for modern furnishing for grace and style. However, cheap element of textile is either cotton or polymer which is both flammable and combustible. It is therefore the need of our combat these characteristics of polymer either through chemical treatment or inventing new compound of fibre. The following paper is an attempt in that direction. Cellulose is the most abundant naturally occurring polymer that is used for apparels and also for modern furnishing to decorate interiors of buildings. Cellulose undergoes degradation on ignition, forming combustible volatile compounds mainly laevoglucosan that result in propagation of

fire causing injuries, fatalities and huge losses¹. So in order to reduce fire hazards the cellulose is modified that can be proved as good flame retardant^{2,3}. There is sturdy relation between flame retardancy of a substance with char yield as it acts as a protective barrier that seals the substrate from the surrounding heat that controls the flame spread. And also higher the char yield; the better will be the flame retardant character.

In this regard, Singh *et al.*⁴ and Dahiya *et al.*⁵ reported the thermal studies of cellulose modified with cresyldichlorothiophosphates, arylphosphorodichloridites, respectively. Dahiya *et al.*⁶ studied the thermal properties of cellulose benzylthiophosphate and its metal complexes and calculated the activation energy of samples using TG data. Consequently, thermal degradation of phosphorylated cellulose like cellulose 2-chlorophenylthiophosphates, cellulose arylphosphates and their metal complexes were studied⁷. However, authors have used single heating rate methods *e.g.* Broido for calculation of kinetic parameters. These methods are facing disapproval due to problematic procedures and unreliable results^{8,9}. Consequently the use of multiple heating rate methods *i.e.* Ozawa-Flynn-Wall (O-F-W)^{10,11}, Friedman¹² and modified Coats-Redfern¹³ are preferred and used in this paper.

In the present study, cellulose ethyl ammonium thiophosphate (CEASP) and its metal complexes with Cd, Mo and Ce have been synthesized. The samples have been characterized by IR, XRD, EDXS studies. The surface morphology of samples has been premeditated by means of SEM. Thermal properties of samples have been studied by TG, DTG techniques in nitrogen atmosphere with a view to calculate degradation activation energy (Ea) values at various degree of conversions using model-free methods.

Experimental

Cellulose was supplied by Acros Organics USA. Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diammonium molybdate tetrahydrate ($(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$) and ceric ammonium nitrate ($\text{Ce}(\text{NH}_4)(\text{NO}_3)_3$) were supplied by Himedia Lab (P) Ltd. Mumbai, India.

Synthesis of CEASP and its metal complexes

2 g of cellulose mercerized with 10% NaOH solution and pyridine (Py). The mercerized cellulose was taken in 250 mL two neck round bottom (RB) flask that was fitted with water condenser having guard tube containing solid CaCl_2 and its another end was fitted with septum. RB flask was cooled at ice salt mixture to 0 °C, 9.0 mL phosphorus oxychloride (POCl_3) (0.1 mol) has been injected through septum followed by addition of 6 mL ethyl alcohol (0.1 mol) with constant stirring at 0 °C for ½ h. Further 0.6 g thiourea (NH_2CSNH_2) (0.1 mol) was added to the reaction mixture and refluxed on oil bath at 125 °C for 24 h. The resulting product was filtered, washed with hot water and dried in vacuum over P_2O_5 . This resulting product was named as CEASP.

The metal complexes of CEASP were prepared via consistent shaking of 2 g of CEASP with 100 mL of 5% aqueous solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Mo}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{NH}_4)(\text{NO}_3)_3$ for 72 h at room temperature, separately. Subsequently the complexes were filtered, washed thoroughly with water and dried in vacuum over P_2O_5 . The synthesized complexes were named as CEASP-Cd, CEASP-Mo and CEASP-Ce depending upon the type of metal used.

Characterization Techniques

IR study

Cellulose and all prepared samples have been characterized by using ABB FTIR spectrophotometer over the frequency range of 4000-500 cm^{-1} . The samples were oven dried, mixed with KBr in a ratio of 1:200 (w/w) and pressed under vacuum to form pellets.

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS) analysis

The surface morphology of synthesized samples was studied by scanning electron microscopy (SEM, model: Zeiss EVO MA 10) and elements present in the matrix were confirmed by energy dispersive x-ray spectroscopy (EDXS, model: Oxford INCA 250).

X-ray diffraction study

The crystalline phase has been analyzed using a D-8 advance powder X-ray diffractometer (XRD, Bruker AXS, Karlsruhe, Germany), with 40kV and 30 mA, Cu-K α radiation and a step size rate of 0.002/s.

Thermal Analysis

Thermogravimetric (TG), derivative thermogravimetric (DTG) analysis of powdered samples was carried out using Perkin Elmer Diamond TG/DTA thermogravimetric analyzer. Thermograms of all samples were recorded at multiple heating rates of 2, 5, 10 and 20 °C min⁻¹ from ambient temperature to 700 °C under high purity nitrogen (99.999%) at a flow rate of 20 mL min⁻¹. The multiple heating rates were used in order to meet the requirement of activation energy calculation. Before starting each run, nitrogen was used to flush the furnace for 30 minute to create an inert atmosphere so as to avoid unwanted oxidation. Dried alumina powder was used as a reference material and ceramic sample holder was employed for taking thermograms. In order to ensure the uniformity of temperature of the sample and good reproducibility, small amounts (3-6 mg) were taken.

Data processing and activation energy calculation

TG curves were analyzed by using Pyris software from TG Analyzer and data was used in MS Excel and origin software to calculate activation energy (E_a) and correlation coefficient (R^2). The E_a values of samples were calculated by "model free" iso-conversional methods. The methods used in calculating activation energy at different conversions (α) were Ozawa-Flynn-Wall (O-F-W), Friedman and modified Coats-Redfern. The final equations used for calculation of E_a by different iso-conversional methods are given in Table 1. In these equations, β is the heating rate, R is the universal gas constant, A is the pre-exponential factor, α is the degree of conversion and $g(\alpha)$ is a function of α . Using the value of slope of each line, E_a was calculated at different conversions.

Table 1. Kinetic methods used in calculating activation energy

Method	Final Equation	Plots	References
O-F-W	$\log(g(\alpha)) = \log\left(\frac{AE_a}{R}\right) - \log(\beta) - 2.315 - 0.4567\left(\frac{E_a}{RT}\right)$	$\log \beta$ against $1/T$	Ozawa, Flynn and Wall ^{10,11}
Friedman	$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\left(\frac{d\alpha}{dT}\right)\right) = \ln A + n \ln(1 - \alpha) - \frac{E_a}{RT}$	$\ln(d\alpha/dT)$ against $1/T$	Friedman ¹²
Coats- Redfern (modified)	$\ln\left[\frac{\beta}{T^2\left(1 - \frac{2RT}{E_a}\right)}\right] = \ln\left[-\frac{AR}{E_a \ln(1 - \alpha)}\right] - \frac{E_a}{RT}$	$\ln(\beta/T^2)$ against $1/T$	Brown <i>et al.</i> ¹³

Results and Discussion

Characterization of samples

XRD curves of cellulose, CEASP and its metal complexes are shown in Figures 1-2. There are two sharp peaks at 2θ of 15° and 22° of intensity 1800 and 2500 a.u., respectively¹⁴. The patterns confirm the formation of the single phase glucose and no other extra phase peak is observed in the patterns. XRD studies of CEASP and its metal complexes shows sharp peak as 23° for CEASP, two broad peaks at 23° and 30° for CEASP-Cd complex, only one broad peak at 23° of CEASP-Mo complex and two peaks were observed for CEASP-Ce complex at 30° (sharp) & 48° (broad). The change in 2θ values *i.e.* in crystalline phase of cellulose point towards the chemical modification in cellulose.

Weight percentage of different elements present in samples as observed from EDXS study, there is increase in P% by a value 11% in CEASP sample as compared to cellulose that confirms the phosphorylation reaction. The weight % of metals present in complexes of CEASP lie in the range 27-31% that indicate about the synthesis of metal complex formation.

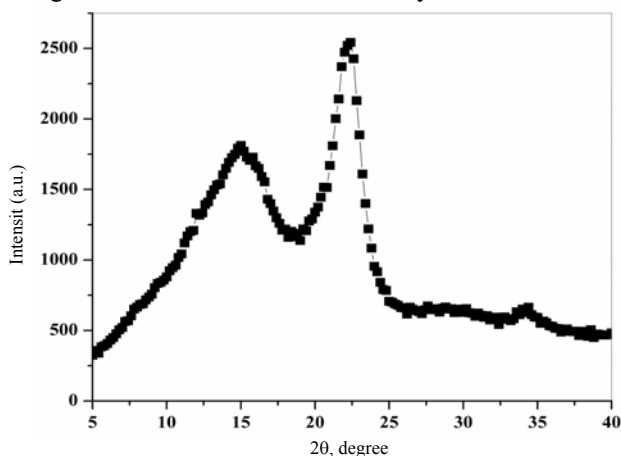


Figure 1. XRD of Cellulose

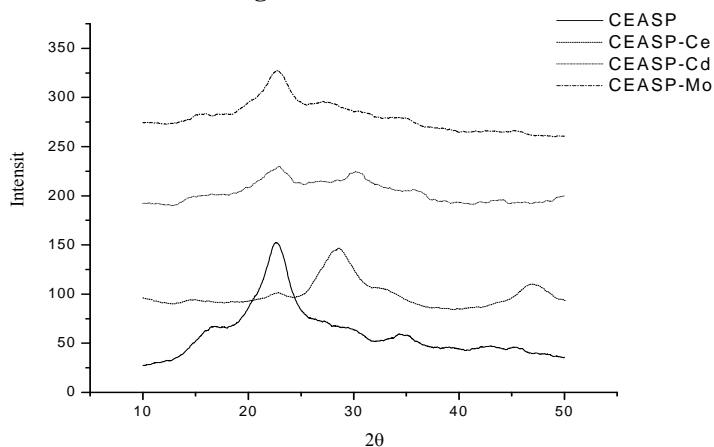


Figure 2. XRD of CEASP and its metal complexes

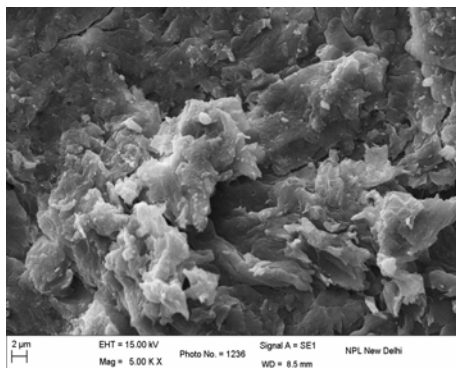


Figure 5. Micrograph of CEASP-Cd

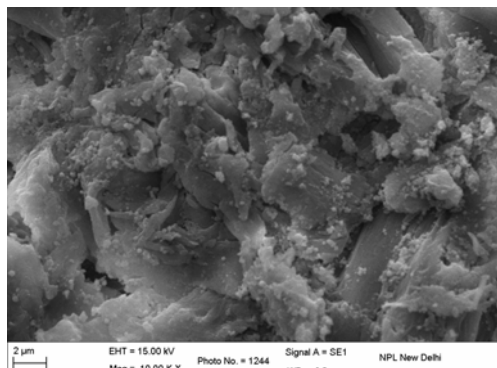


Figure 6. Micrographs of CEASP-Mo

Thermal analysis

TG curves profile of all samples at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere is shown in Figure 7. The TG curves of samples at multiple heating rates are given in Figures 8-11 and Figure 12 represents the DTG curves of samples. The data observed from TG and DTG curves of samples at $10\text{ }^{\circ}\text{C min}^{-1}$ is reported in Table 2. TG curves of all samples shift towards higher temperature with increase in heating rate. This shift is due to different heat transfers and kinetic rates that delay the sample decomposition and is similar to result reported by Williams *et al.*¹⁷. The onset degradation temperature (T_o) of pure cellulose is $\sim 310\text{ }^{\circ}\text{C}$ and for CEASP is $234.9\text{ }^{\circ}\text{C}$. This notable decrease in T_o value might be due to acids produced from the dephosphorylation reactions that catalyses the decomposition process⁹. The T_o values for CEASP metal complexes are greater than CEASP and found to be lie in range $246\text{-}276\text{ }^{\circ}\text{C}$. This might be due to presence of metal ions in the complex that increases the thermal stability of sample. Here it can be concluded that metals are increasing the thermal stability of CEASP. The mass loss (MLo) corresponds to onset degradation temperature for sample lie in the range 3-13% that is due to dehydration and decomposition process. The peak temperature (T_p) calculated from DTG curves of pure cellulose is $\sim 340\text{ }^{\circ}\text{C}$ and for CEASP it decreases to $247\text{ }^{\circ}\text{C}$. This decrease in T_p value might be due to acid catalysed reactions. The T_p for CEASP metal complexes is found to be in the range $277\text{-}313\text{ }^{\circ}\text{C}$ which is greater than for CEASP.

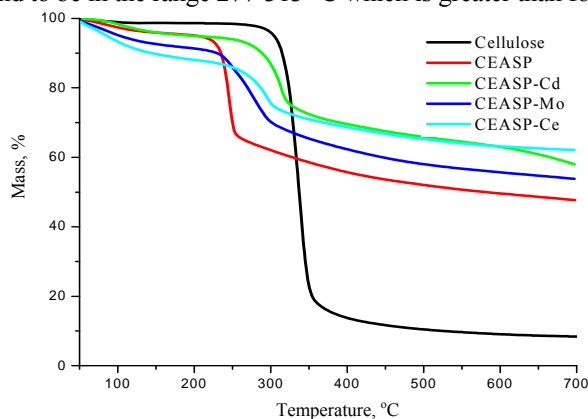


Figure 7. TG curves of Cellulose, CEASP and its metal complexes of Cd, Mo and Ce at heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2 atmosphere

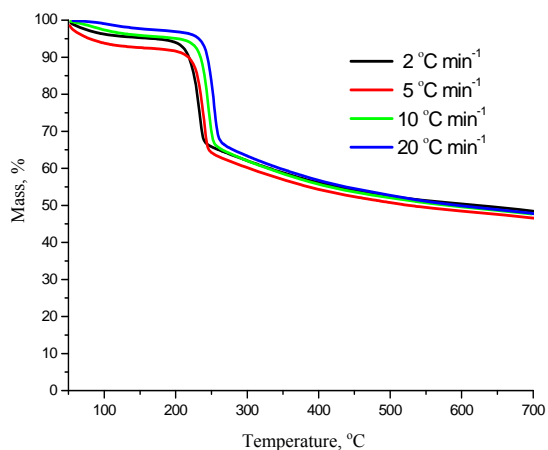


Figure 8. TG curves for CEASP at different heating rates of 2, 5, 10 and 20 °C min⁻¹ in N₂ atmosphere

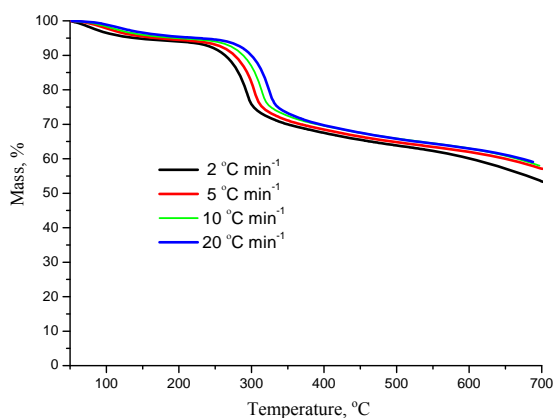


Figure 9. TG curve of CEASP-Cd complex at heating rates of 2, 5, 10 and 20 °C min⁻¹ in N₂ atmosphere

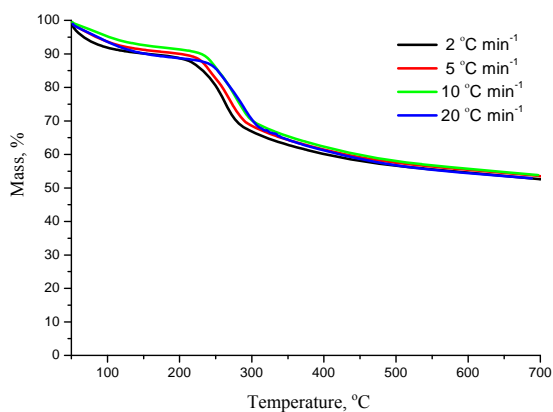


Figure 10. TG curve for CEASP-Mo complex at heating rates of 2, 5, 10 and 20 °C min⁻¹ in N₂ atmosphere

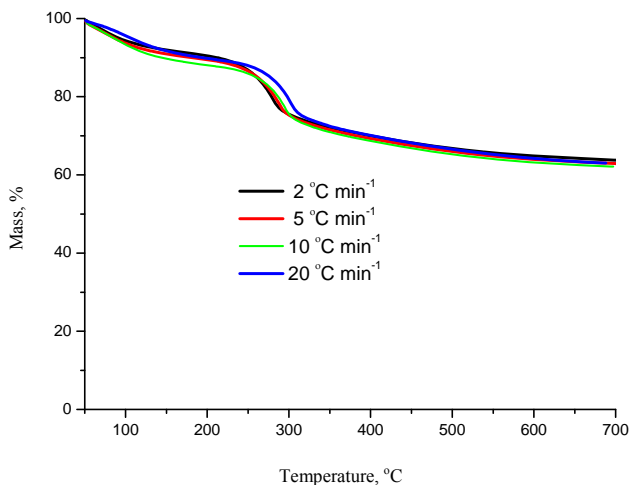


Figure 11. TG curve of CEASP-Ce complex at heating rates of 2, 5, 10 and 20 °C min⁻¹ in N₂ atmosphere

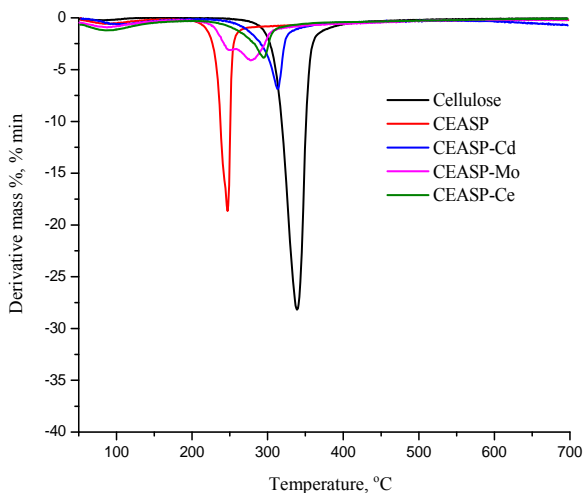


Figure 12. DTG curve of cellulose at heating rates of 2, 5, 10 and 20 °C min⁻¹ in N₂ atmosphere

The mass loss (MLp) corresponding to Tp for complexes is lower (range 19-23%) as compared to CEASP (25.5%) and cellulose (55.3%). Thus it is concluded from DTG study that metal complexes are thermally more stable than CEASP and pure cellulose which is also supported by T₀ data derived from TG curves.

TG, DTG data have great importance to evaluate the flame retardancy of samples¹⁸. The two parameters like maximum mass loss rate (MMLR) from DTG and char yield have premeditated from TG curves are used to evaluate flame retardancy character of samples. Higher value of char yield and lower value of MMLR point toward the improvement in the flame retardancy of sample. The parameter MMLR was calculated corresponding to peak maxima of DTG curves and char yield was calculated from TG curves at 650 °C. The MMLR and char yield data is prearranged in Table 2. The MMLR value for pure cellulose is

28 % min⁻¹ and for CEASP its value decreases up to 18.5 % min⁻¹ that further decreases to 3-7 % min⁻¹ for metal complexes. The char yield for cellulose is 8.7% and its value increases to 48.6% for CEASP. Char yield for metal complexes further increases and lie in the range 54-63%. The decrease in MMLR values and increase in char yield of CEASP and metal complexes as compared to cellulose show that depolymerization reaction in prepared samples are slower as compared to pure cellulose in nitrogen atmosphere. This might be due to formation of charred protective layer and incorporation of metal in the matrix of macromolecules that catalyses cross linking, leading to increased char yield and suppression of volatile products formed during combustion of polymers¹⁹. MMLR and char yield study led to a conclusion that all synthesized samples are showing good flame retardancy and among them CEASP-Ce sample is the best.

Table 2. Thermal decomposition parameters of cellulose and modified cellulose

Samples	T _o , °C	ML _o , %	T _S , °C	ML _S , %	T _P , °C	ML _P , %	Temperature Range, °C	MMLR % min ⁻¹	Char yield, %
Cellulose	310.4	3.1	355	82.9	339.1	55.3	289-388	28.0	8.7
CEASP	234.9	5.6	252.2	34.5	247.1	25.5	198-280	18.5	48.6
CEASP-Cd	275.5	6.7	321.2	24.7	313.2	19.8	248-378	6.8	60.9
CEASP-Mo	246.4	11.0	296.3	30.0	277.5	22.8	220-333	4.0	54.7
CEASP-Ce	240.9	13.0	303.1	25.7	294.6	22.6	236-354	3.8	62.5

Degradation Activation Energy

The degradation activation energy of samples have been calculated using model free O-F-W, Friedman and modified Coats-Redfern methods. For illustration, the iso-conversional plot of O-F-W for CEASP and modified Coats-Redfern for CEASP-Mo are shown in Figures 13-14. The iso-conversional plot of O-F-W and modified Coats-Redfern showed a general trend of activation energy. The Ea and R² values calculated by different methods at a particular conversion for all samples are summarized in Tables 3-5. The R² > 0.91 were selected to calculate Ea at a particular α value. The iso-conversional plot of activation energy shows the general trend of activation energy. The fitted lines in iso-conversional plots of samples are parallel pointing the possibility of single order of degradation mechanism^{20,21}.

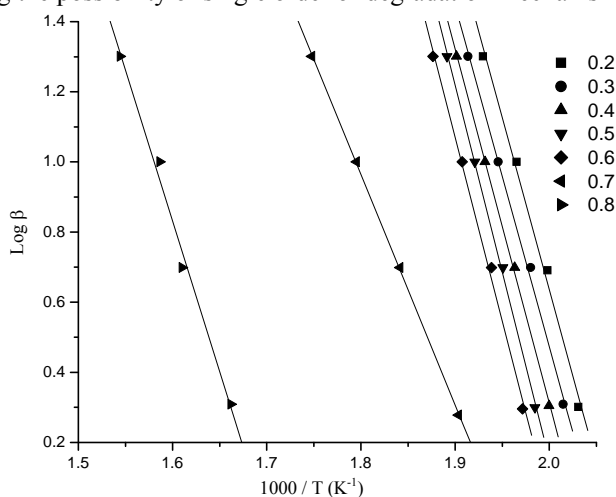


Figure 13. Iso-conversional plot of O-F-W method for CEASP at varying degree of conversion (α)

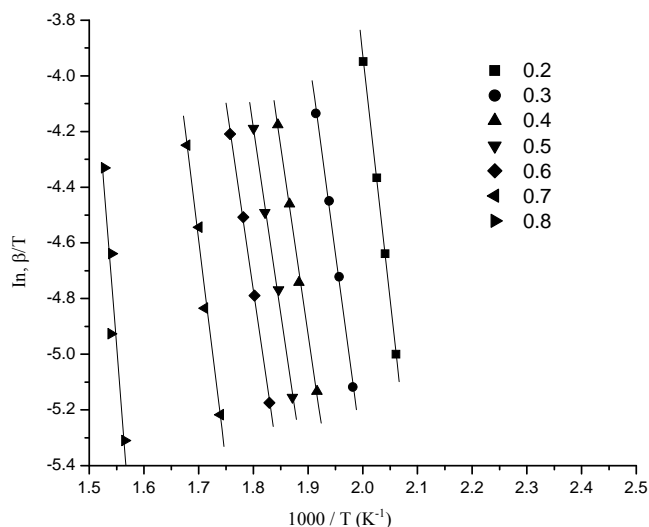


Figure 14. Plot of Coats-Redfern modified method for CEASP-Mo complex at varying degree of conversion

Table 3. Activation energy and correlation coefficient of samples calculated by Friedman method

α	Cellulose		CEASP		CEASP-Cd		CEASP-Mo		CEASP-Ce	
	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²
0.20	179.1	0.981	234.1	0.991	97.5	0.921	-	-	-	-
0.25	156.8	0.974	234.2	0.997	166.4	0.918	94.9	0.924	34.15	0.910
0.30	152.1	0.985	241.7	0.967	215.6	0.997	180	0.969	22.74	0.946
0.35	148.7	0.981	201.7	0.996	191.2	0.964	201.7	0.926	137.9	0.953
0.40	134.1	0.989	192.7	0.997	310.6	0.976	257.7	0.958	260.1	0.924
0.45	132.6	0.976	247.3	0.965	280.6	0.936	281.4	0.953	330.9	0.956
0.50	135.5	0.990	227.9	0.966	297.5	0.949	255	0.986	289.3	0.967
0.55	139.8	0.985	197.4	0.971	336.6	0.940	207.5	0.912	322.7	0.965
0.60	141.7	0.987	110.3	0.928	380.9	0.934	250	0.984	110.5	0.974
0.65	140.8	0.988	-	-	-	-	-	-	-	-
0.70	140.2	0.989	114.2	0.914	151	0.934	157.8	0.924	172.2	0.962

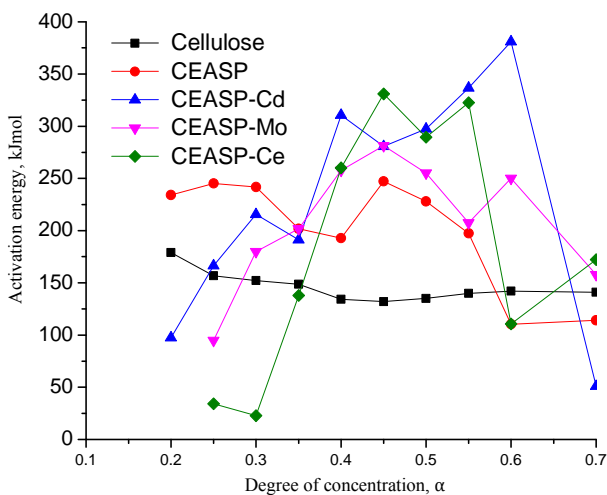
Table 4. Activation energy and correlation coefficient of samples calculated by O-F-W method

α	Cellulose		CEASP		CEASP-Cd		CEASP-Mo		CEASP-Ce	
	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²
0.20	161.3	0.981	160.4	0.986	175.9	0.986	90.7	0.951	80.4	0.906
0.25	160.9	0.974	184.3	0.968	191.5	0.990	91.5	0.920	95.2	0.977
0.30	158.0	0.985	197.6	0.975	201.6	0.990	195.2	0.910	100.4	0.936
0.35	157.6	0.981	204.0	0.977	209.4	0.991	227.9	0.936	123.7	0.972
0.40	156.5	0.989	209.2	0.978	214.4	0.992	246.7	0.935	248.7	0.966
0.45	155.5	0.976	213.6	0.978	218.2	0.992	244.9	0.960	273.4	0.902
0.50	154.3	0.990	218.9	0.977	228.1	0.986	238.6	0.977	275.1	0.951
0.55	152.9	0.985	218.8	0.978	271.9	0.933	238.0	0.983	277.1	0.976
0.60	151.9	0.987	213.2	0.970	295.1	0.917	238.9	0.983	284.6	0.977
0.65	150.8	0.988	200.0	0.900	-	-	-	-	-	-
0.70	150.6	0.989	156.6	0.951	190.2	0.988	252.7	0.921	323.3	0.902

Table 5. Activation energy and correlation coefficient of samples calculated by modified Coats-Redfern method

α	Cellulose		CEASP		CEASP-Cd		CEASP-Mo		CEASP-Ce	
	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²	Ea	R ²
0.20	165.0	0.986	160.3	0.922	175.9	0.984	72.7	0.904	92.3	0.900
0.25	162.9	0.989	185.3	0.965	192.1	0.989	87.9	0.982	105.2	0.946
0.30	156.7	0.989	199.4	0.972	202.7	0.990	196.9	0.903	116.4	0.975
0.35	156.6	0.987	206.1	0.975	210.8	0.992	231.1	0.931	120.6	0.945
0.40	152.6	0.985	211.5	0.977	215.9	0.991	250.7	0.931	252.7	0.953
0.45	155.3	0.984	216.1	0.976	219.9	0.985	248.7	0.957	278.4	0.901
0.50	158.4	0.988	221.7	0.987	230.3	0.928	241.9	0.975	280.2	0.948
0.55	154.8	0.983	221.5	0.978	276.3	0.901	245	0.981	282.2	0.974
0.60	152.6	0.985	215.6	0.968	300.5	0.973	242	0.982	289.9	0.975
0.65	151.2	0.985	173.6	0.962	119.5	0.973	250.3	0.972	300.3	0.918
0.70	150.1	0.988	154.3	0.924	130.2	0.901	256	0.915	330.3	0.982

The variation of activation energy with degree of conversion is shown in Figures 15-17. The activation energy of samples lie in range 72-282 kJ mol⁻¹. From the graphs it is clear that activation energy of synthesized samples is more as compared to Ea values of pure cellulose in the conversion range 4-5.5 and for metal complexes Ea values are more than CEASP. The increased value of Ea for CEASP and metal complexes than cellulose might be due to formation of protective layer that result in increase in Ea required for the depolymerization process. High values of Ea in this range indicate about the extended thermal stability of metal complexes and CEASP in comparison to cellulose. However the Ea for metal complexes is more than CEASP that means metal complexes are thermally more stable than CEASP. The outcomes from activation energy studies are in line with the results obtained from TG, DTG studies.

**Figure 15.** Variation of activation energy E vs. degree of conversion α for pyrolysis of all samples as calculated using Friedman method

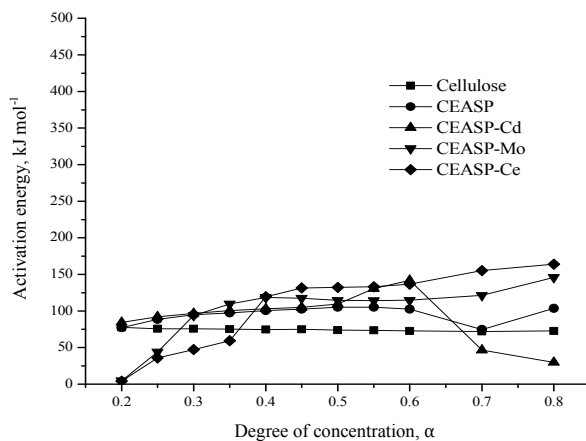


Figure 16. Relationship of activation energy E vs. α for pyrolysis of samples as calculated by O-F-W method

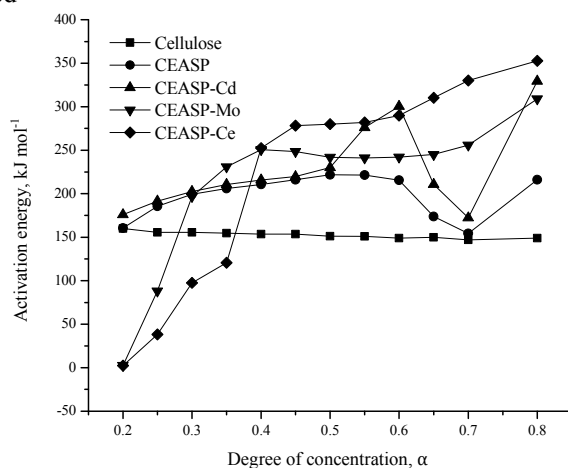


Figure 17. Relationship of activation energy E vs. α for pyrolysis of samples by Coats-Redfern modified method

Conclusion

The preparation of CEASP and its metal complexes have been characterized by IR, XRD, EDXS. The morphology of surface of sample by SEM shows that surface of synthesized sample is uneven as compared to pure cellulose that confirms the modification in cellulose chemically. The onset degradation temperature of CEASP is lower as compared to pure cellulose that might be due to release of acid that catalyses the decomposition process. The T_0 values for CEASP metal complexes is greater than CEASP and found to be lie in range 246-276 °C. This might be due to formation of protective layer of metal that increases the thermal stability of sample. The MMLR value for pure cellulose is 28% min⁻¹ and for CEASP its value decreases up to 18.5% min⁻¹ that further decreases to 3-7% min⁻¹ for metal complexes. The char yield for cellulose is 8.7% and its value increases to 48.6% for CEASP. Char yield for metal complexes further increases and lie in the range 54-63%. MMLR and char yield study led to a conclusion that all synthesized samples are showing good flame retardancy

and among them CEASP-Ce sample is the best. Thermal degradation activation energy deliberated using model free kinetic methods *viz* Friedman, Ozawa-Flynn-Wall (O-F-W) and modified Coats- Redfern lie in range 72-282 kJ mol⁻¹. Activation energy of synthesized samples is more as compared to Ea values of pure cellulose in the conversion range 4-5.5 and metal complexes Ea values are more than CEASP. The aforesaid study helps to conclude that metal complexes of CEASP are thermally more stable than CEASP and cellulose and such type of derivatization could be proved an good flame retardant for cellulose.

Acknowledgement

Authors are thankful to Chairman, Department of Chemistry, Kurukshetra University, Kurukshetra for providing necessary lab facilities. Authors are also thankful to authorities of National Physical Laboratory, New Delhi for carrying out EDXS, XRD and SEM analysis.

References

1. www.delhi.gov.in Delhi Fire Service, Accessed on 20 September 2014
2. Cabrales L and Abidi N, *J Therm Anal Calorim.*, 2010, **102**, 485-491.
3. Liu Y L, Hsiue G H, Lan C W and Chiu Y S, *Polym Degrad Stab.*, 1997, **56(0)**, 291-299; DOI:10.1016/S0141-3910(96)00177-2
4. Singh R, Arora S and Lal K, *Thermochim Acta*, 1996, **289(1)**, 9-21; DOI:10.1016/S0040-6031(96)03057-2
5. Dahiya J B and Rana S, *Polym Int.*, 2004, **53(7)**, 995-1002; DOI:10.1002/pi.1500
6. Dahiya J B and Sushila Rana, *Indian J Chem.*, 2005, **44A**, 2024-2029.
7. Bhagwan J, Arora S and Lal K, *J Polym Mater.*, 1990, **7**, 231-237.
8. Vyazovkin S and Wight C A, *Thermochim Acta*, 1999, **340/341**, 53-68; DOI:10.1016/S0040-6031(99)00253-1
9. Vyazovkin S, *Thermochim Acta*, 2000, **355(1-2)**, 155-163; DOI:10.1016/S0040-6031(00)00445-7
10. Ozawa T, *Bull Chem Soc Jpn.*, 1965, **38(11)**, 1881-1886; DOI:10.1246/bcsj.38.1881
11. Flynn J H and Wall L A, *J Res Nat Bur Stand.*, 1966, **70A**, 487-523.
12. Friedman H L, *J Polym Sci Part C-Polym Symp.*, 1964, **6**, 183-195.
13. Brown A L, Dayton D C and Daily J W, *Energy Fuels*, 2001, **15(5)**, 1286-1294; DOI:10.1021/ef010084c
14. Ardizzone S, Dioguardi F S, Mussini T, Mussini P R, Rondinini S, Verecelli B and Vertova A, *Cellulose*, 1999, **6**, 57-69; DOI:10.1023/A:1009204309120
15. Kumar A, Negi Y S, Choudhary V and Bhardwaj N K, *J Mater Phy Chem.*, 2014, **2(1)**, 1-8.
16. Zhao H, Kwak J H, Zhang Z C, Brown H M, Arey B W and Holladay J E, *Carbohydr Polym.*, 2007, **68(2)**, 235-241; DOI:10.1016/j.carbpol.2006.12.013
17. Williams P T and Besler S, *Renew Energy*, 1996, **7(3)**, 233-250; DOI:10.1016/0960-1481(96)00006-7
18. Arora S, Kumar M and Kumar M, *J Therm Anal Calorim.*, 2012, **107**, 1277-1286.
19. Arora S, Kumar M and Kumar M, *J Compos Mater.*, 2013, **47(16)**, 2027-2038; DOI:10.1177/0021998312453865
20. Arora S, Lal S, Kumar S, Kumar M and Kumar M, *Arch Appl Sci Res.*, 2011, **3(3)**, 188-201.
21. Shafizadeh F and Bradbury A G W, *J Appl Polym Sci.*, 1979, **23**, 1431-1442.