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# Thermal studies of Cellulose, Phosphorylated Cellulose and its metal complexes

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**Abstract**

The present paper deal with the phosphorylation of cellulose and preparation of its metal complexes with Cu, Ni, Fe and Co. Phosphorylated cellulose and its metal complexes have been characterized by infrared (IR) and elemental analysis techniques. The thermal studies of cellulose and modified celluloses have been carried out at a heating rate of 20 °C $min^{-1}$ from ambient to 700 °C in air atmosphere. Thermogravimetric (TG) analysis shows that initial degradation temperature of prepared samples is low as compared to pure cellulose. The char yield study calculated at 600 °C shows that metal complexes are more stable at higher temperatures as compared to phosphorylated and pure cellulose. The kinetic study of samples has premeditated using Broido method and it is found that activation energy lie in the ranges 82-149 kJ $mol^{-1}$. These and other related information suggest that such type of derivatization could be proved a good flame retardant for cellulose.

***Keywords:*** *Cellulose, Metal Complexes, Thermogravimetry, Kinetic Energy, IR.*

## 1. Introduction

Cellulose is basically very important material and has been subjected to great deal of investigation. It is main component of the cells of all the plants. Cellulose consists almost exclusively of specially purified wood pulp and chemical cotton which are produced in varieties of grade for specific use. For the year 2006, the estimate worldwide production of cellulose is $5x10^9$ tones (Kim et al., 2006). It can be transformed in to several important derivatives which are more useful because of their modified properties like hydrophobic nature (Theresa et al., 2007), greater flexibility, softness and solubility (Junshik et al., 2007) which is not possessed by cellulose itself One of the important property of cellulose is its high flammability. So, to impart flame retardancy to cellulose several chemical modifications have been applied to it. Consequently large numbers of cellulose derivatives like esters of organic and inorganic acids, ethers graft copolymers have been synthesized. Cellulose β-ketoester (Yoshida et al., 2007) and cellulose nitrate containing 10-11% nitrogen is used mainly for lacquers and plastic. Vigo and coworker (Vigo et al., 1965) have modified the cotton cellulose to form ester on cellulose. Phosphorus containing cellulose ester have been synthesized by Reid and Mazzeno (Reid et al., 1949). Various cellulose ester have been synthesized by Malm et al., 1961, Clarke et al., 1932,1935, Jain et al., 1986, 1987 and Ray et al., 1987. Certain transition metal ions and their metal oxides (Hastie et al., 1975 and Brouman et al., 1976) are known to impart flame retardency to cellulose because cellulose undergo degradation on ignition forming combustible volatile compound (Kumar et al., 2015) mainly laevoglucose that result in propagation of fire causing injuries, fatalities and huge loses. The main objective of the work reported is to investigate the effect of phosphorous containing flame retardant on the thermal degradation of cellulose. The thermal properties of coordinate complexes of phosphorylated (Swarn et al., 1990) cellulose with various transition metal ions were investigated by various thermal analysis technique such as TG, DTA, DTG which are widely used to measure the thermal stability and pyrolysis behaviour of polymers (Arora et al., 2011). The kinetic of thermal degradation of these transition metal complexes were studied from ambient temperature to 700°C using thermogravimetry and spectroscopic technique. IR was used with a view to evaluate the composition of charred product. Thermal degradation kinetic is helpful for understanding the mechanism of polymer degradation and the effect of the complex formation on its degradation The primary role of the flame retardant is to alter the decomposition process so that lower percentage of flammable volatile is produced and correspondingly larger amount of char is formed.

## 2. Experimental

**Materials**

**Chemical used**

Cellulose was supplied by M/s Schieicher and Schull, Dassal, Germany, was dried to a constant weight in vacuum over $P_2O_5$ at 60˚C before use. Phosphorus thiotrichloride (Fluke AG-CH- 9470 Buchs, d420 = 1.635), Pyridine by S.D. Fine-Chem, India, Amino Guanidine Bicarbonate by Aldrich, iron (II) sulphate heptahydrate by Analar, BDH, cobalt (II) sulphate monohydrate and phosphorus pentaoxide by Analar, E. Merck, India, copper (II) sulphate pentahydrate and nickel (II) sulphate hexahydrate were supplied by Analar, BDH.

**Preparation of cellulose derivatives**

**Mercerization of cellulose**

0.5g of cellulose was taken in a round bottom flask and 50 ml of pyridine was added to it. The flask was properly sealed in order to avoid the contact of moisture and kept flask undisturbed for mercerization for two days.

**Synthesis of phosphorylated cellulose**

4.9 ml of phosphorous thiotrichloride was taken in a round bottom flask and was placed in ice bath. 16.33g of amminoguanidine bicarbonate was added to it and further mercerized cellulose and 50 ml anhydrous pyridine was added to the reaction mixture. The reaction mixture was refluxed as oil bath at 115˚C for 12 hour. The product was filtered, washed repeatedly with water. Air dried the solid and finally dried in vacuum at 60˚C over $P_2O_5$.

**Metal complexes of phosphorylated cellulose**

Various metal complexes of phosphorylated cellulose were prepared by treating phosphorylated cellulose with aqueous solution of appropriate metal salt. In each case 1gm of phosphorylated cellulose was treated with 5% aqueous solution of nickel (II) sulphate hexahydrate, iron (II) sulphate heptahydrate, cobalt sulphate hexahydrate and copper (II) sulphate pentahydrate at ambient temperature for 72 hours with constant stirring. The product was filtered, washed repeatedly with warm water until the filtrate was free from the metal salt, air dried and finally dried in vacuum at 60˚C over $P_2O_5$.

**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.

**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 20°C $min^{-1}$ from ambient temperature to 700°C under flowing air at a flow rate of 20 ml $min^{-1}$. 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.

## 3. Results and Discussion

**Spectral study of the cellulose, phosphorylated cellulose and its metals complexes**

In case of cellulose, band observe at 3350.6$cm^{-1}$(O-H),2900.61 $cm^{-1}$(-C-H), 2127 $cm^{-1}$ (C-N).A band at 1429 $cm^{-1}$ (C=C) and C=N vibration of pyridine,1160 $cm^{-1}$ (C-O-C stretch.), 1162 $cm^{-1}$and both 1059.8 $cm^{-1}$ and 1033.2 $cm^{-1}$ (Skelton vibration involving C-O str. etc). In case of phosphorylated cellulose and its metals complexes same band are observed except one band which is observed at 1682 $cm^{-1}$

This band is due the ($CONH_2$) in phosphorylated cellulose.

But very small changes were observed in finger print region of phosphorylated cellulose and its metals complexes

**Elemental analysis**

Another important evidence for the reaction mechanism is to identify the product formed. All the solid products formed were identified by the elemental analysis. According to the result of elemental analysis, solid product formed contains 20% of nitrogen, 8.3% of phosphorus and 8.4% of sulphur. This data reveals that the product formed is according to probable mechanism used.

**Determination of kinetic parameters**

The kinetic parameters of thermal degradation of cellulose sample were determined from TG curves using Broido method. According to this method, the energy of activation ,Ea, and the frequency factor , Z

can be calculated using the equation

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

Where y is the fraction of number of initial molecules not yet decomposed and $T_m$ is the temperature of maximum reaction rate .A plot of ln(ln1/y) versus 1/T yield a straight line,whose slope and intercept give the value of Ea and z respectively.

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**Thermal study of the cellulose, phosphorylated cellulose and its metals complexes**

DTA and TG thermogram of cellulose, phosphorylated cellulose and its metals complexes were recorded in static air from ambient temperature to 700˚Cand are shown in Figs 1-6.

**Thermal analysis by DTA**

The peak temperature of various exotherm are measured and given in table 7.In DTA thermogram of cellulose, no endotherm is observed due the static air atmosphere. One exotherm peak at 347.9˚C may be due the oxidation of cellulose is observed .the last exotherm was observed at 517.4˚C temperature represent the oxidation of charred residue.

In the DTA thermogram of the phosphorylated cellulose and its ferrous and nikel complexes exotherms at 249˚C, 241 ˚C and 246˚C are observed. Another exotherm peak at 356˚C, 353˚C and 353˚C is observed due the oxidation decomposition of the samples. Last exotherm with peak maxima at 529˚C, 462˚C and 460˚C respectively is due to oxidation of charred residue.

In case of copper and cobalt complex of phosphorylated cellulose, exotherm at 357˚C and 235˚C respectively due to the oxidation of samples is observed. And another exotherm at 452 ˚C and 460˚C are observed due to the oxidation of charred product.

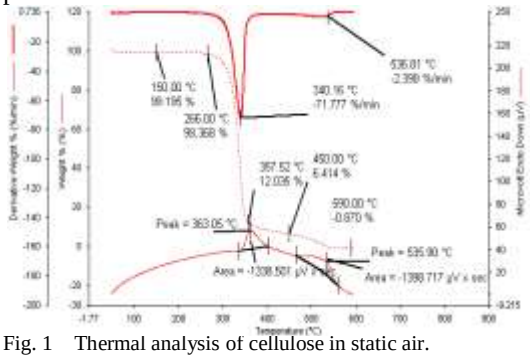

Fig. 1 Thermal analysis of cellulose in static air.

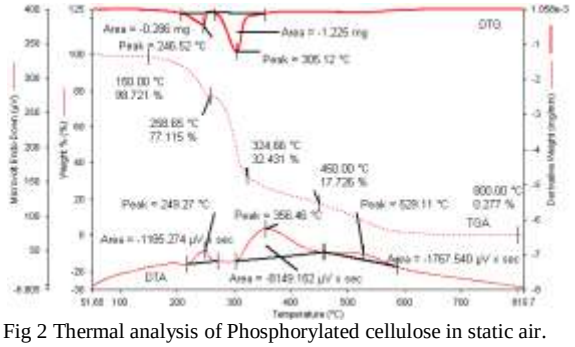

Fig 2 Thermal analysis of Phosphorylated cellulose in static air.

**TG studies**

TG thermograms of cellulose, phosphorylated cellulose, and its metal complex were recorded Figs 1-6.TG thermograms of cellulose and modified cellulose samples show three significant area of weight lose termed as three stage of thermal degradation .

The major lose in TG curves of all the treated sample occurs in the second stage due the decomposition process. So this stage is designated as decomposition stage of thermal degradation .For cellulose 60% weight lose occur in temperature range of 317-344˚C.Using the Broido method the activation energy for this stage is found to be 232.1kJmol$^{-1}$. The weight lose in the phosphorylated cellulose is 34% in the temperature range of 279-309˚C with activation energy 101.1kJ mol$^{-1}$. The corresponding weight lose, temperature range and activation energy, for the metal Complexes of cellulose vary from 21-31%, 213-307˚C and 82-149 kJ mol$^{-1}$. The activation energy for the entire phosphorylated cellulose samples for the decomposition stage decrease considerably as compared to that of cellulose, indicate their fairly effective flame retardant properties. But the activation energy of metal complexes is decrease in the order as given below Ni > Co > Cu > Fe. This order of decrease in activation energy indicates the increasing percentage of phosphorus in the above metal.

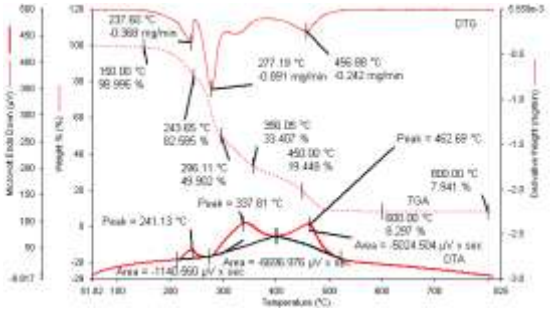

Fig. 3 Thermal analysis of ferrous complex of Phosphorylated cellulose.

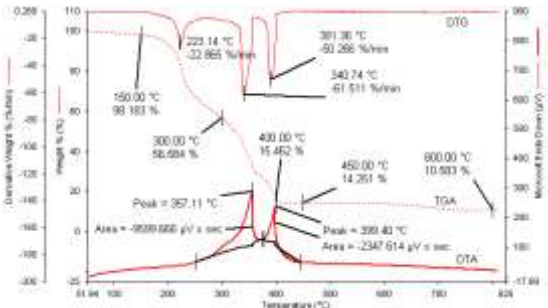

Fig. 4 Thermal analysis of copper complex of Phosphorylated cellulose.

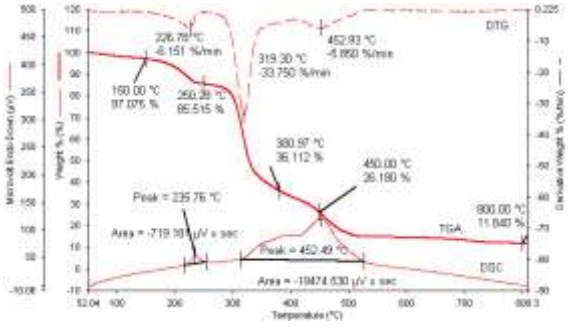

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Fig. 5 Thermal analysis of cobalt complex of Phosphorylated cellulose.

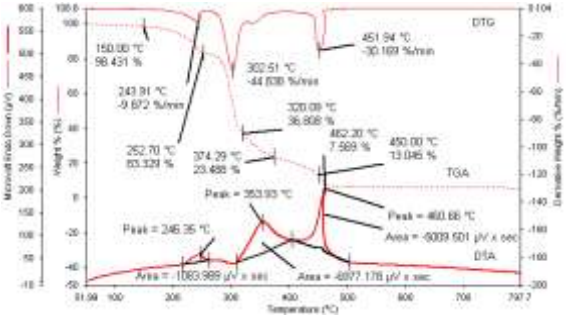


Fig. 6 Thermal analysis of nikel complex of Phosphorylated cellulose.

from phosphorylated cellulose at same temperatures is 17.72 % and 8.6 % .The char yield obtained from metal complexes of phosphorylated cellulose is in the range of 13-26% which is also more than cellulose. This indicates their effective flame retardant properties. This also show that transition metal has very important role in enhancing the char yield and thus diminished the smoke formation.

Table: 7 Temperature in the DTA thermograms of cellulose, Phasphorylated cellulose and its metal complexes in static air.

| Sr. No. | Compound | Initial Temperature (°C) | Peak Temperature (°C) | Termination Temperature (°C) | Nature of DTA peak |
|---|---|---|---|---|---|
| 1. | Cellulose | 330.4<br>492.0 | 347.9<br>517.4 | 394.4<br>535.4 | Exo(Large)<br>Exo(Small) |
| 2. | Phosphorylated Cellulose | 220.8<br>302.9<br>499.0 | 249.0<br>356.4<br>529.1 | 275.6<br>455.1<br>586.0 | Exo(small,sarp)<br>Exo(small,broad)<br>Exo(small,broad) |
| 3. | Fe complex of Phosphorylated Cellulose | 222.0<br>306.0<br>435.0 | 241.1<br>353.6<br>462.7 | 261.0<br>393.5<br>494.4 | Exo(small)<br>Exo(broad,large)<br>Exo(sharp,large) |
| 4. | Cu complex of Phosphorylated Cellulose | 315.0<br>377.0 | 357.1<br>400.4 | 365.0<br>434.2 | Exo(sharp)<br>Exo(sharp |
| 5. | Co complex of Phosphorylated Cellulose | 220.0<br>416.0 | 235.8<br>452.5 | 254.0<br>519.0 | Exo(small,sharp)<br>Exo(large,broad) |
| 6. | Ni complex of Phosphorylated Cellulose | 221.2<br>306.7<br>422.3 | 246.4<br>353.9<br>460.7 | 261.5<br>395.5<br>494.4 | Exo(small,broad)<br>Exo(sharp)<br>Exo(large, sharp) |

Table: 8 For activation energy and frequency factors for the second stage of thermal degradation of cellulose, cellulose complex and its metal complexes.

| **Compound** | **Temperature range (°C)** | **Ea(kJ/mole)** | **Z($S^{-1}$)** |
|---|---|---|---|
| Cellulose | 317-344 | 232.2 | $9.6 \times 10^{19}$ |
| Phosphorylated cellulose | 274-309 | 101.1 | $8.1 \times 10^{8}$ |
| Fe complex of phosphorylated cellulose | 255-290 | 82.7 | $2.4 \times 10^{8}$ |
| Cu complex of phosphorylated cellulose | 213-261 | 92.9 | $1.2 \times 10^{10}$ |
| Co complex of phosphorylated cellulose | 242-282 | 117.4 | $1.8 \times 10^{11}$ |
| Ni complex of phosphorylated cellulose | 237-303 | 148.7 | $2.1 \times 10^{13}$ |

## 4. Conclusion

The char yield of treated cellulose sample obtained from their TG curves at 723 K and 800 K temperature were calculated. The char yield of pure cellulose is 6.41 % at temperature 723K and2.30%at 800 K in static air medium. The char yield obtained

## 5. Acknowledgements

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