Innovative Developments in Coating for Making Flame Retardant Paper and their Kinetic Study

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ABSTRACT

Organic polymers and cellulose based papers are intrinsically flammable and therefore these materials need to be modified to prevent or delay fire propagation. This is usually carried out by means of incorporation of fire retardant material into the polymer/ cellulosic based materials. However, an alternative and innovative way to provide flame-retardant properties to such material may be carried out through application of flame-retardant coatings. Furthermore, this coating provides anti-fire properties without affecting the bulk properties or processing of the polymer substrate and can be applied easily to any substrates. In this study, attempts were made to develop a new approach based on an innovative coating. The coating composition includes compound based on phosphorus and nitrogen and char forming agents which trigger several fireproofing mode of actions in condensed and gas phases. This article investigates the preventive modification of cellulose paper to exhibit flame retardancy by application of intumescent coating through Pad-Dry- Cure conventional process. This study also explored the various parameter to achieve the goal like flammability and kinetic parameters of cellulosic paper and coated paper samples. Activation energy of thermal degradation of samples was determined using Coats-Redfern method. Result of the study revealed that paper samples coated with intumescent coating formulation were best as far as physical properties are concerned. The Limiting Oxygen Index (LOI) values of sample found increased from 18 to 31% on coating. Activation energy of coated paper is found to be lower than simple uncoated paper.

KeyWords: Cellulosic fibre, intumescent, coating, flame retardant, activation energy

1.0 Introduction

Cellulosic polymeric material like fabric, papers, wood etc. undergoes degradation on ignition, forming highly burnable volatile products mainly leavoglucosan with spread of fire causing injuries and losses in fire accidents [1]. Cellulose thermally decomposes below 300°C under dehydration, depolymerisation and oxidation with release of CO, CO2 and carbonaceous residue [2, 3]. At higher temperature (> 300°C), tar consisting leavoglucosana as major flammable constituent is formed [4, 5]. Function of flame retardant is to increase char at the cost of flammable volatiles. Many flame retardants available in the market such as chlorine-type flame retardant, bromine-type flame retardant, phosphorus-halogentype flameretardants and also inorganic flame retardantto make cellulosic papers as flame proof [6]. But halogen based flame retardant releases highly toxic and corrosive fumes during combustion. There has also been major interest in replacing halogenated flame retardants because of environmental and toxicity issues [7,8]. Also traditional phosphate-based flame-retarding papers meet the requirements of non-halogen, non-toxic, and low-fume characteristics. However, papers incorporating chemicals are liable to become wet when exposed to atmospheric moisture, leading to resist of their more-general acceptance.

In this study, attempts were made to develop a new approach based on an innovative coating. Intumescent flame retardant system requires acid source, a swelling agent and a char forming agent [9-13]. The coating composition includes compound based on phosphorus and nitrogen and char forming agents which trigger several fireproofing mode of actions in condensed and gas phases.

Experimental:

Materials

For intumescent flame retardant system, ammonium polyphosphate (APP) as an acid source, melamine as a swelling agent and pentaerythritol (PER) as a carbon source were obtained from Clariant Co., Germany. Normal Photocopy paper (purchased from market) was used for back coating, and acrylic resin, Zytrol-7800 as binder (Zydex Industries, India).

Preparation of intumescent formulation

Intumescent formulation was prepared containing intumescent components (APP, pentaerythritol and melamine) in ratio 3:1:1. The acrylic resin was used for coating the intumescent formulation on ordinary paper. The intumescent formulation was prepared by mixing evenly in pastel and mortar.

Intumescent formulation application and curing process

The intumescent formulations solution was prepared with desired proportions of M : L (material to liquor) ratio that incorporated into sample by using pad- dry- cure technique. The solution was placed in the trough of padding mangle for giving treatment. After dipping the samples into the solution for approximately 2 minutes, the sample was passed through the rolls at 2.5kPa pressure.

Two dip two nip were given to get desired chemical level of weight add on. The paper sample was taken for this study was basis weight of 75g/m2. Initial weight of sample taken for this proposes was 3.32 gram. The coating amount was adjusted using bars of different numbers and coat weight was maintained to 20-22 g/m2.Then the coated sample was dried in oven and cured at 110- 1200C for 2 minutes.

Thermal Analysis

Thermal degradation of samples was carried out by thermogravimetry (TG) (TA instruments SDT Q600). Samples in platinum crucibles were analyzed from ambient temperature to 600°C (heating rate, 10°C/min). Nitrogen was used as carrier gas (flow rate, 100 ml/min).

Limiting Oxygen Index (LOI)

LOI values that measure performance of flame retardancy were measured using a Stanford Redcroft FTA flammability unit BS-2782 instrument. Samples were tested according to standard method ASTM D2863, ISO-4589.

Kinetics Study

TG data were analyzed for kinetic study using Coats-Redfern method [14, 15]. It is assumed that only a single reaction occurs while a sample undergoes a certain temperature rise at a steady heating rate, β. Thus, Coats-Redfern equation when n≠1 is given below:

$$ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = ln\frac{AR}{\beta E} + ln\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \qquad ………Equation\ (1)$$

Where n=order of reaction, E is Activation Energy, A is Pre-exponential Factor, R is gas constant,

β is heating rate i.e, 10 0C/Min,

α is degree of conversion= (W0-WT)/(W0-Wf) where W0 is initial weight of sample, WT is residual weight of sample at temperature, T 0C, Wf is the final weight of sample.

when order of reaction, n=1 then Coats-Redfern equation become as below:

$$ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = ln\frac{AR}{\beta E} + ln\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \qquad ………Equation\ (2)$$

Result and Discussion:

Thermal analysis

The untreated paper sample shows one stage of thermal degradation in range of 295-400 0C with weight loss of 79.2%

and with DTG peak at 375 °C as given in Table 1 and shown in Fig 1-2. The sample degraded almost completely up to 400 °C leaving no char yield at 600 °C. The thermal degradation of sample was due to pyrolytic decomposition of reactions.
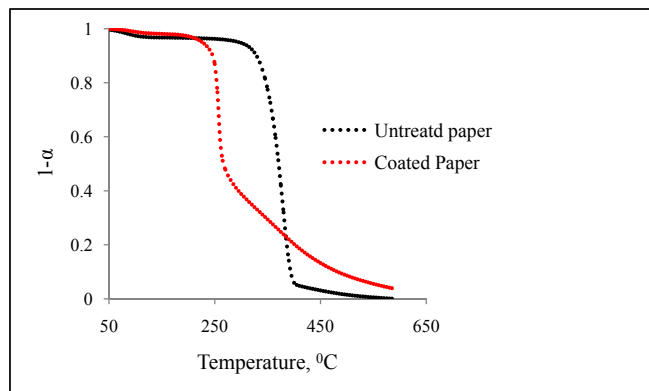

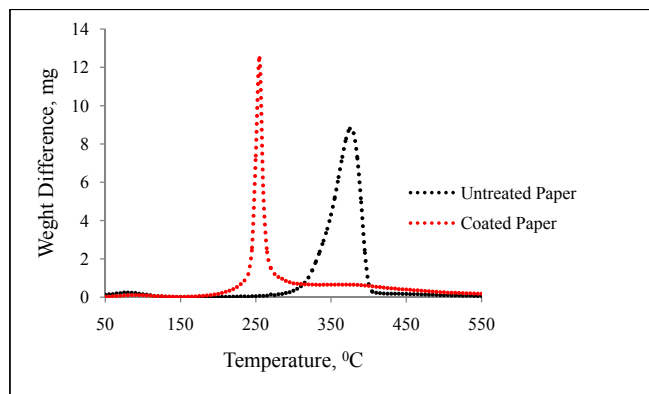**Fig 1:** *curves in Nitrogen at heating rate of 10°C/min of untreated paper and Coated Paper*

Fig 2: *DTG curves in Nitrogen at heating rate of 10°C/min of untreated paper and Coated Paper*
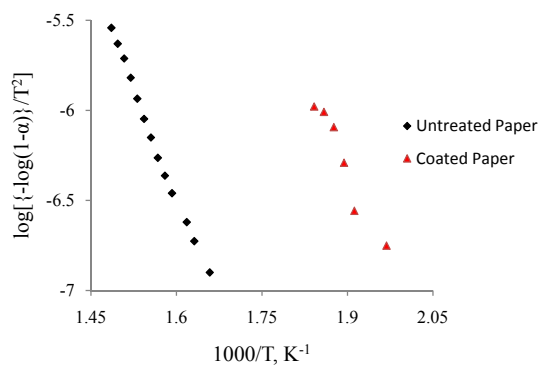

Fig 3: *Coats-Redfern plot for first stage of thermal degradation of untreated paper and Coated Paper*

Table 1: DTG peaks, LOI and Char Yield and Kinetic Parameters of untreated paper and its coated sample

Sample	TG Stages	Temperature Range (^{0}C)	Weight Loss (%)	DTG Peak (^{0}C)	1-α range	Activation Energy, (kJmol^{-1})	ln A (min^{-1})	Char Yield (%) at 600 ^{0}C	LOI (%)
Untreated Paper	Single	295-400	79.2	375	0.9-0.05	154.7	20.07	Nil	18
Coated Paper	First Stage	240-270	31.5	255	09-0.49	129.8	20.12	28.7	30.2
	Second Stage	270-600	31.2	-	-	-	-	-	-

First stage of thermal degradation:

Firststage of thermal degradation of intumescent coated paper in temperature range 240- 270 °C shows 31.5 % (Fig 1) weight loss. The first stage thermal degradation of sample is mainly due to pyrolyticdecomposition reactions corresponds to release of phosphoric acid from intumescent.This released phosphoric acid startsphosphorylate the cellulose as well as thepentaerythritol at about 200 °C. In themeantime the melamine (the third componentof intumescent formulation as swelling agent) sublimes at about 240 °C and start releasingNH3 at about 260 °C and continues up to 380 °Cand weight is less in nitrogen atmosphere.This way, a cover of swelled material startsbuilding on the polymer substrate as a thermalbarrier. The dispersion of combustible volatilesfrom the burning substrate to combustion phaseis also prevented. The DTG peak at 255 °C (Fig 2) for coated paper also predicts the changes indecomposition stage of paper sample.

Second stage of thermal degradation:

Secondstageofthermaldegradationofintumescentcoatedpaperin temperature range 270-600 °C shows 31.2 % weight loss as in Fig 2.This may be due to pyrolytic decomposition,deoxygenation, dehydrogenation, andaromatization of char. At the same timecomplex formation takes place of intumescentcomponent with the substrate and solidification throughcross-linking reaction of residual char occurs inthis stage. No DTG peak is shown in this stagebecause of gradual weight loss.

Kinetics Study of Thermal Degradation

The kinetic parameters of thermal degradation of untreated and its coated samples were determined using first order Coats-Redfern method as in equation (2) on data obtained from TG and is given in Table 1 using Coats Redfern Plot (Fig 3). Activation energies of coated sample and untreated sample was calculated in range of degree of conversion ($1-\alpha=0.9-0.49$) and ($1-\alpha=0.9-0.05$) respectively, which falls in first stage of thermal degradation of maximum mass loss. Activation energy of coated paper (129.8 kJ mol–1) is found lower than that of untreated paper (154.7 kJ mol–1). Decrease in activation energy is due to catalyzing effect of phosphoric acid and metals, which show that dehydration path during thermal degradation of cotton is chosen resulting in more char formation at the expense of tar.

LOI and Char Yield

Char yield at 600°C and LOI values of untreated paper and its coated sample were obtained. Higher the valueof LOI and char yield, better is the flame resistance ofthe material. LOI value for pure untreated sample (18%) was found toincrease for intumescent coated sample (30.2%).No char yield was obtained for pure untreated paper sample at 600°C. Char yield for intumescent coated sample increased from zero to 28.7%.

Conclusions

TGcurvesofcoatedpapershowstwostagesofthermaldegradation which are mainly due to dehydration,pyrolytic decomposition and aromatization of char,respectively. For coated sample, pyrolytic degradationgives a less amount of tar consisting flammable volatileproducts and correspondingly higher char yield. Decrease in activation energy is due to catalyzing effectof released phosphoric acid, and support thatdehydration path during thermal degradation of polymeric substrateispreferred in which more char is formed at the expenseof tar. LOI value for pure untreated fabric (18%) increased for coated fabric(30.2%) again supports the flame retardant behaviour of coated sample.

Hence the thermogravimetric analysis, LOI and char yield results has demonstrated that coatings decompose, absorb heat, swell and form the protective char layers at the different temperature ranges, and, therefore, these cooperated reactions provide a good fire protection for the polymeric substrate in a fire.

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