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Comparative degradation kinetic studies of three biopolymers: Chitin, chitosan and cellulose

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ABSTRACT

Cellulose, chitin and chitosan are the most abundant biopolymer on earth and constitute an important class of biodegradable materials. The decomposition of three major biopolymers viz. chitin, chitosan and cellulose are studied using simultaneous thermal analysis i.e. thermogravimetry/differential thermal analyzer (TG/DTA). Thermal analysis is performed from ambient temperature to 700 °C in a flowing nitrogen medium at four different linear heating rates i.e. 2.5, 5, 10 and 20 °C min^{-1}. Thermal stability order of the three biopolymers based on TG followed the order: cellulose > chitin > chitosan. Non-isothermal multiple heating rate model free methods Ozawa-Flynn-Wall (O-F-W), Kissinger, Friedman and modified Coats-Redfern methods are used to calculate degradation activation energy of the biopolymers. The reaction mechanism based on activation energy calculation at different conversions has been proposed.

Keywords: Biopolymers, TG, DTG, DTA, Kinetics.

INTRODUCTION

Chitin (β-(1,4)-2-acetamido-2-deoxy-D-glucopyrnaose) is the second most abundant polysaccharide on the earth next to cellulose. It is nontoxic biodegradable polymer and present in marine invertebrates, insects, fungi and yeasts. When chitin is deacetylated with alkali to about 50-85%, it becomes soluble in dilute acids and referred to as chitosan (β-(1,4)-2-amino-2-deoxy-D-glucopyranose) [1-2].

In fact, chitosan is preferred form of this polymer as it can be dissolved very easily in different solvents to form solution. Chitosan is mainly used in pharmaceutical and biomedical industries along with photographic production, cements and waste water treatment [2]. The most attractive application of chitosan is to make either antibacterial finishes for cotton (cellulose) or blends with polymers like cellulose, starch, poly (vinyl alcohol) etc. [3-4]. Further these processes may involve heating chitosan solution at high temperatures and subsequent curing with cotton [5]. This treatment may cause thermal degradation of cotton as well as chitosan. Moreover, it is always desirable and beneficial to study the thermal profiles of the blending materials to optimize the processing. Pyrolysis kinetics of these polymers will also help to get in depth knowledge of their pyrolysis mechanism.

Thermal analysis techniques such as thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) are widely used to measure the thermal stability and pyrolysis behavior of polymers in different conditions. It is worth to state here that higher heating rates cannot give good results as at higher heating rates results into large thermal lag and improper heat transfer which in turn would invalidate the kinetic data. In this regard, Gronli et al. [6] had reported that the thermal decomposition should be carried out at low or moderate heating rates to keep possible heat/mass–transfer intrusions to a minimum level.

It is already known from previous experience that kinetic analysis based on single heating rate methods is not dependable and encountered with many problems [7-8]. Therefore, the multiple-heating rate methods like Kissinger [9], Friedman [10], Coats-Redfern (modified) [11-12] and Ozawa-Flynn-Wall (O-F-W) [13-14] etc. are preferred for the same reason.

Wanjun et al. [15] had applied model-free method on the TG data to evaluate the pyrolysis kinetic parameters of chitin and chitosan. Lopez et al. [16] had used differential scanning calorimeter (DSC) to determine the degradation kinetic parameters of chitosan using model-free methods. Hong et al. [17] described the degradation profile of chitosan at different heating rates under nitrogen atmosphere. Recently, Stawski et al. explained the TG behavior of chitins of different origins [18]. From our best of knowledge there is no report which compare the thermal profile of these three biopolymers i.e. cellulose, chitin and chitosan in nitrogen atmosphere by using four ‘model free’ iso-conversional methods.

The present paper deals with the comparative thermal and pyrolysis kinetic study of chitin, chitosan and cellulose using simultaneous thermal analysis (TG/DTA) and four model-free methods. The thermal and kinetic data presented in this study would help to find out new applications of these biopolymers either as binary or ternary blends.

MATERIALS AND METHODS

Materials

Chitin (Mol. wt. ~ 400000) supplied by Himedia Lab. India, chitosan (Mol. wt. 100000-300000) and microcrystalline cellulose by Acros Organics USA were used as such. The degree of deacetylation of chitosan was 85%.

Thermal analysis

Thermogravimetric (TG) analysis was carried out using Perkin Elmer Diamond TG/DTA thermogravimetric analyzer instrument. The resolution of this instrument is 0.02 µg as a function of temperature. Runs were carried out at linear multiple heating rates (β) 2.5, 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}. 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. The TG/DTA analyzer was calibrated before recording thermograms. 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 [19]. Three runs of same sample were conducted under same set of experimental conditions.

Data processing and activation energy calculation

TG curves were analyzed by using Pyris software from TG Analyzer and data was used in MS Excel software to calculate activation energy (E) by the method of least squares. Activation energy of samples was calculated by "model free" iso-conversional methods. The methods used in calculating activation energy at different conversions (α) were Kissinger [9], Friedman [10], Coats-Redfern (modified) [11-12] and Ozawa-Flynn-Wall (O-F-W) [13-14] as given in Table 1.

Table 1 Kinetic methods used in calculating activation energy in this study

Methods	Final equation	Plots
O-F-W	$\log(\beta) = \log(\frac{AE}{R}) - \log(g(\alpha)) - 2.315 - 0.4567\frac{E}{RT}$	$\log \beta$ against $1/T$
Kissinger	$\frac{d(\ln(\beta/T_m^2))}{d(1/T_m)} = -\frac{E}{R}$	$\ln(\beta/T_m^2)$ against $1/T_m$
Friedman	$\ln(\frac{d\alpha}{dt}) = \ln(\beta(\frac{d\alpha}{dT})) = \ln A + n\ln(1-\alpha) - \frac{E}{RT}$	$\ln(\beta(d\alpha/dT))$ against $1/T$
Coats-Redfern (modified)	$\ln\left[\frac{\beta}{T^2(1-\frac{2RT}{E})}\right] = \ln\left[-\frac{AR}{E\ln(1-\alpha)}\right] - \frac{E}{RT}$	$\ln(\beta/T^2)$ against $1/T$

The Friedman method is the iso-conversional method, which directly leads to (-E/R) for a given value of α by plotting ln(β(dα/dT)) against 1/T. The O-F-W method is also iso-conversional method but has integral equation unlike Friedman which is a differential method, which leads to -(0.4567 E/R) from the slope of line determined by plotting log β against 1/T at any degree of conversion. The modified Coats–Redfern method is a multiple-heating rate application of the Coats–Redfern equation. In this method $\ln(\beta/T^2)$ is plotted against 1/T, which gives slope $-E_a/R$ of line at different conversion. The E values can be calculated using slopes obtained from each plot for every degree of conversion. In the Kissinger method, the activation energy, E, can be obtained from a plot of $\ln(\beta/T_m^2)$ against $1/T_m$ for particular stage of decomposition since the slope of such line is given by (-E/R).

RESULTS AND DISCUSSION

Comparative TG, DTG and DTA studies

TG curves for chitin, chitosan and cellulose at different heating rates in nitrogen atmosphere are shown in Fig. 1-3. The shapes of TG curves are quite similar shifting toward higher temperatures at higher heating rates [20]. This is due to the heat transfer lag with increased heating rate. The parameters calculated from TG, DTG and DTA thermograms of samples at a heating rate of 10 °C min^{-1} in nitrogen atmosphere are reported in Table 2.

The initial decomposition temperature of chitin, chitosan and cellulose are 276.4, 254.6 and 312.9 °C and char yield are 20.4, 38.4 and 9.1 % at 600 °C, respectively. On the basis of T_i, the thermal stability of samples follows the order: cellulose > chitin > chitosan (Fig. 4). The decomposition of chitin, chitosan and cellulose occurs in single step as confirmed by DTG curves (Fig. 5). The main decomposition of chitosan occurs around 296.3 °C which is assigned to depolymerisation reaction. On the other hand, the DTG maxima temperature in case of chitin occurs at 375.7 °C, which quite higher than that of chitosan. This clearly indicates that the amino polymer is less thermally stable than the N-acetyl one [33].

Since, parameter MWLR for cellulose is highest (28 % min^{-1}) and least for chitosan (9.6 % min^{-1}). Also, MWLR for chitin lies in between those of cellulose and chitosan i.e. 16.1 % min^{-1}. It means the depolymerisation reactions are fastest in cellulose and lowest in case of chitosan in nitrogen atmosphere (Table 2). This results in lowest percentage char residue for cellulose while highest in case of chitosan.

The DTA curves of samples at a heating rate of 10 °C min^{-1} under nitrogen atmosphere are given in Fig. 6. The decomposition of chitosan is an exothermic event with peak maxima at 303 °C and occurs in the temperature range 270-337 °C. It can be assigned to the thermal decomposition of amino and N-acetyl (GlcNAc) residues; respectively [21]. In contrast, decomposition of chitin and cellulose is endothermic process which takes place in the temperature range 341-406 °C and 296-365 °C with peak maxima at 380.4 and 335.5 °C, respectively. The main endothermic effect in case of chitin is primarily due to the depolymerisation of polymeric chains with the formation of volatile low molecular products and the formation of char [15]. The endothermic peak is due to pyrolysis and random chain scission of cellulose molecule [22]. It can be noted here that the DTA maxima temperature order is same as found in case of DTG.

Table 2 Data calculated from TG, DTG and DTA thermograms of samples at a heating rate of 10 °C min^{-1} in nitrogen atmosphere

Samples	T_i (°C)	Char yield at 600 °C (%)	DTG peak maxima temperature (°C)	MWLR (% min^{-1})	DTA maxima (°C)	Nature of DTA peak	DTA peak range (°C)
Chitin	276.4	20.4	375.7	16.1	380.4	Endo	341-406
Chitosan	254.6	38.4	296.3	9.6	303.0	Exo	270-337
Cellulose	312.9	9.1	339.2	28.0	335.5	Endo	296-365

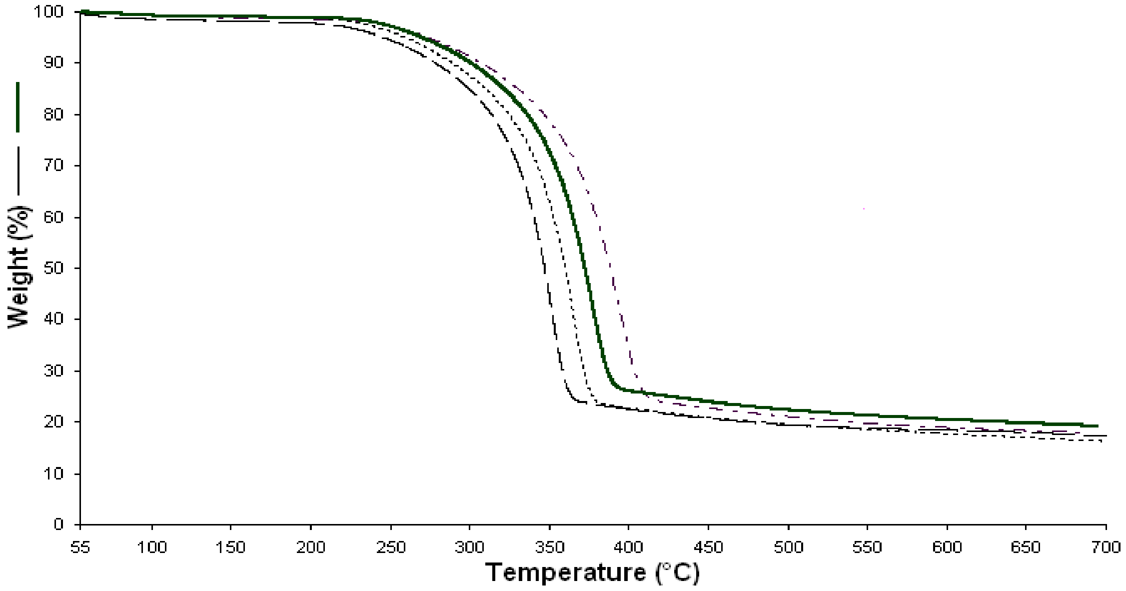

Fig.1 TG curves of chitin at heating rates of (-----) 2.5, (……) 5, (———) 10 and (-·-·-) 20 °C min^{-1}

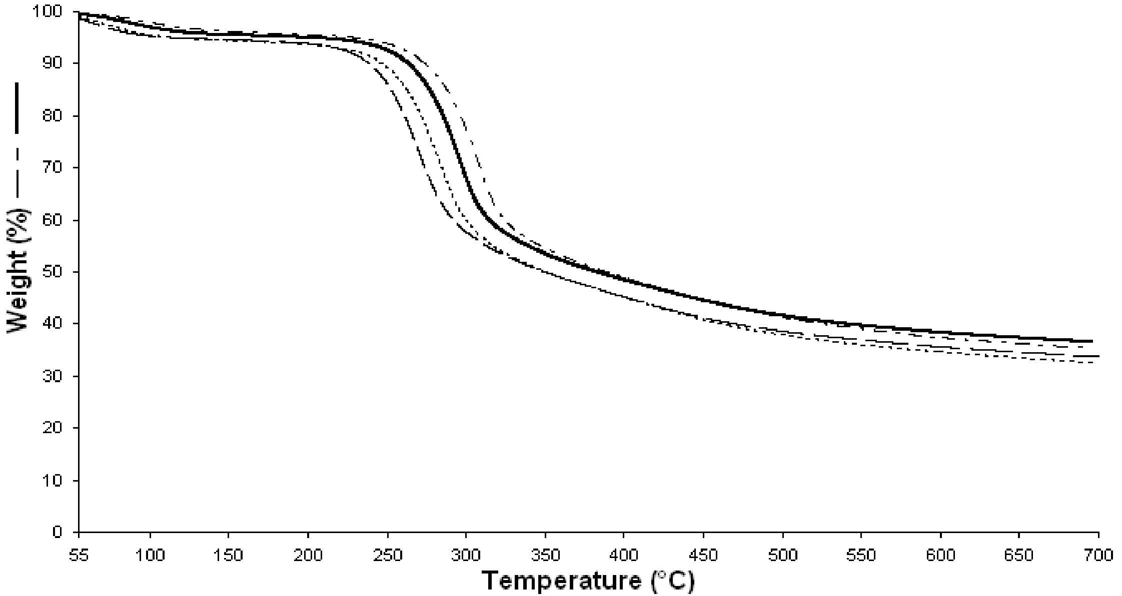

Fig. 2 TG curves of chitosan at heating rates of (-----) 2.5, (……) 5, (———) 10 and (-·-·-) 20 °Cmin^{-1}

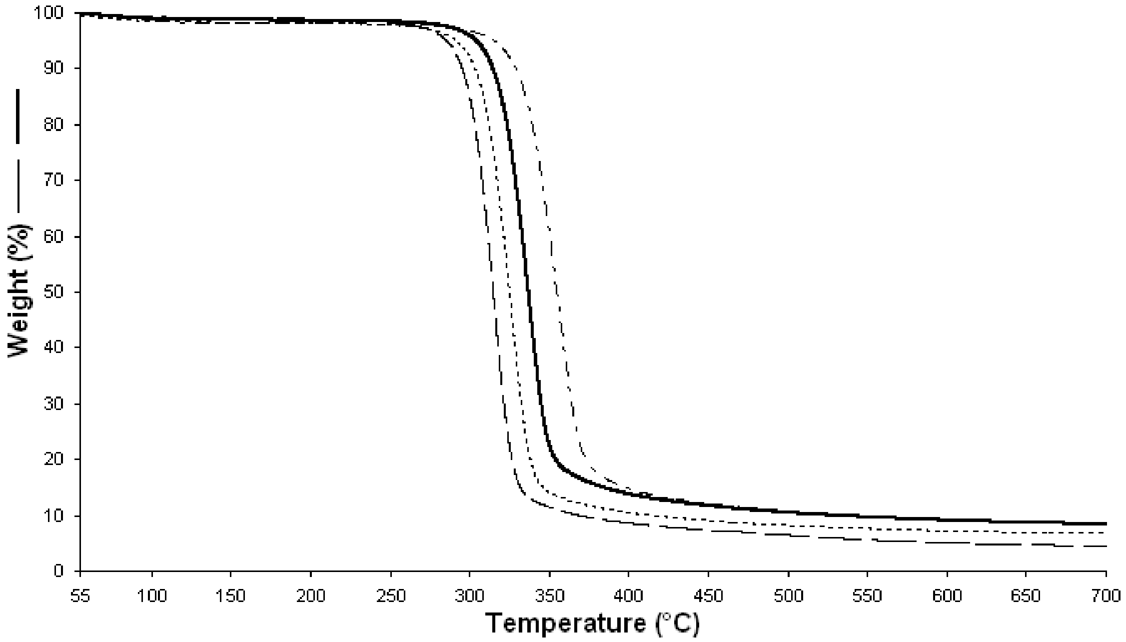

Fig. 3 TG curves of cellulose at heating rates of (-----) 2.5, (……) 5, (———) 10 and (-·-·-·-) 20 °C min^{-1}

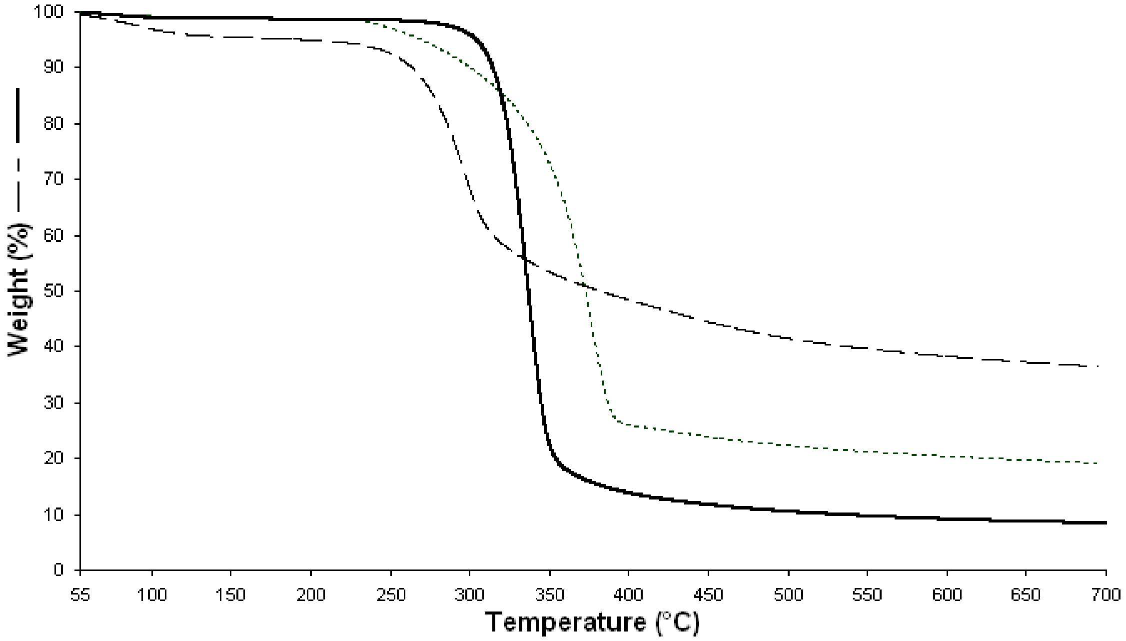

Fig. 4 TG curves of cellulose (———), chitosan (-----) and chitin (……) at heating rate of 10 °C min^{-1}

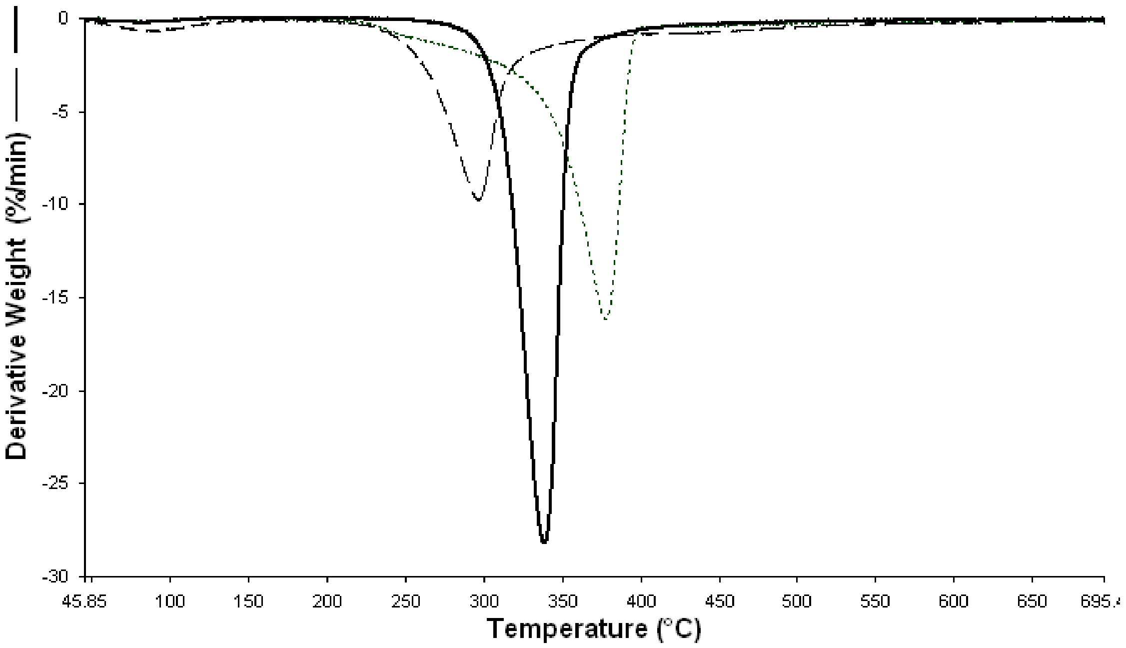

Fig. 5 DTG curves of cellulose (———), chitosan (-----) and chitin (……) at heating rate of 10 °C min^{-1}

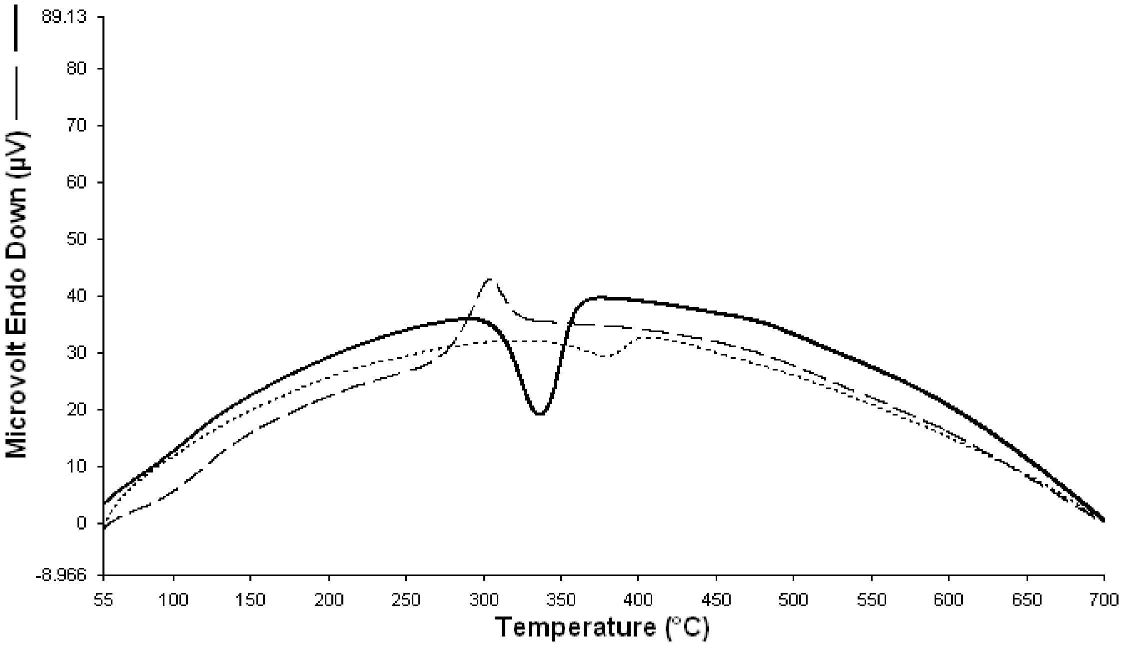

Fig. 6 DTA curves of cellulose (———), chitosan (-----) and chitin (……) at heating rate of 10 °C min^{-1}

Comparison of degradation activation energies of three biopolymers

Activation energies for chitin, chitosan and cellulose were calculated using O-F-W, Friedman and Coats-Redfern modified procedures at varying degree of conversions and are given in Table

3. The iso-conversional plot of O-F-W and modified Coats-Redfern show a general trend of activation energy. For illustration iso-conversional plot of O-F-W for chitin and modified Coats-Redfern for chitosan are shown in Fig. 7-8. The linear plots of Kissinger method for chitin, chitosan and cellulose is given in Fig. 9. The iso-conversional plots which are shown show the same trend as shown in Fig 7-8. It is clear that fitted lines (regression coefficient > 0.9776) for chitin and cellulose are almost parallel which indicates the activation energy at different conversions and consequently, implying the possibility of single reaction mechanism. However, in case of chitosan slopes of fitted lines (regression coefficient > 0.9856) are not parallel (Fig. 8) thereby showing the complexity of the mechanism.

Table 3 Activation energies for chitin, chitosan and cellulose calculated by O-F-W, Friedman and Coats-Redfern modified methods at varying degree of conversion

α	chitin			chitosan			cellulose		
	O-F-W	Friedman	Coats-Redfern modified	O-F-W	Friedman	Coats-Redfern modified	O-F-W	Friedman	Coats-Redfern modified
0.06	160.9	154.6	161.2	-----	----	----	175.6	224.6	175.0
0.07	167.8	161.5	166.0	-----	----	----	174.1	212.4	174.1
0.08	172.7	166.4	172.6	38.0	51.2	32.3	170.7	177.4	166.9
0.09	177.5	171.3	176.1	72.4	85.3	69.7	170.6	178.2	168.3
0.1	180.1	173.9	178.6	95.7	122.6	94.2	167.8	148.1	167.2
0.15	186.3	180.7	186.4	112.6	114.9	108.8	162.5	168.5	161.2
0.2	185.6	180.6	187.2	138.1	131.8	135.9	161.3	179.1	165.0
0.25	183.4	178.5	183.8	140.6	142.8	140.1	160.9	156.8	162.9
0.3	179.8	175.1	180.0	142.9	156.2	141.8	158.0	152.1	156.7
0.35	177.1	172.6	175.6	145.8	161.2	142.6	157.6	148.7	156.6
0.4	174.0	169.6	172.7	148.6	162.1	147.1	156.5	134.1	152.6
0.45	171.6	166.7	168.8	152.8	170.5	153.0	155.5	132.6	155.3
0.5	169.6	164.5	170.2	159.2	194.0	155.8	154.3	135.5	158.4
0.55	167.4	162.3	167.1	170.2	188.8	170.1	152.9	139.8	154.8
0.6	166.1	162.8	166.1	185.4	192.3	185.4	151.9	141.7	152.6
0.65	163.8	160.5	162.2	199.6	235.8	196.3	150.8	140.8	151.2
0.7	162.7	160.1	162.5	223.5	301.1	220.7	150.6	140.2	150.1
0.75	160.8	158.2	156.8	256.8	356.9	253.4	156.3	146.6	152.8
0.8	160.0	158.6	157.5	282.1	------	286.7	149.0	147.9	148.9
0.85	158.6	156.9	159.6	222.6	325.4	220.9	134.2	100.2	132.5
0.9	158.3	156.7	155.8	350.9	428.6	356.6	132.8	69.7	133.4

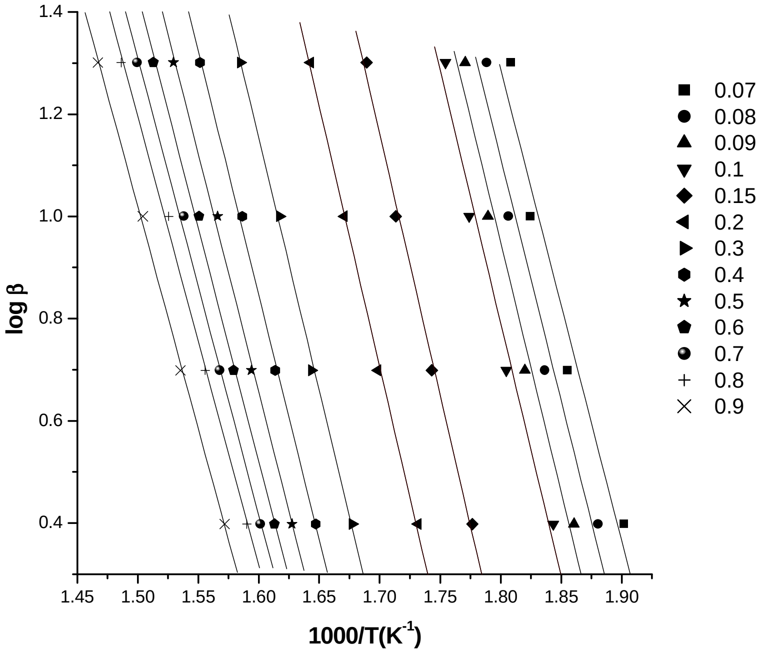

Fig. 7 Iso-conversion plot of O-F-W method for chitin at varying degree of conversions

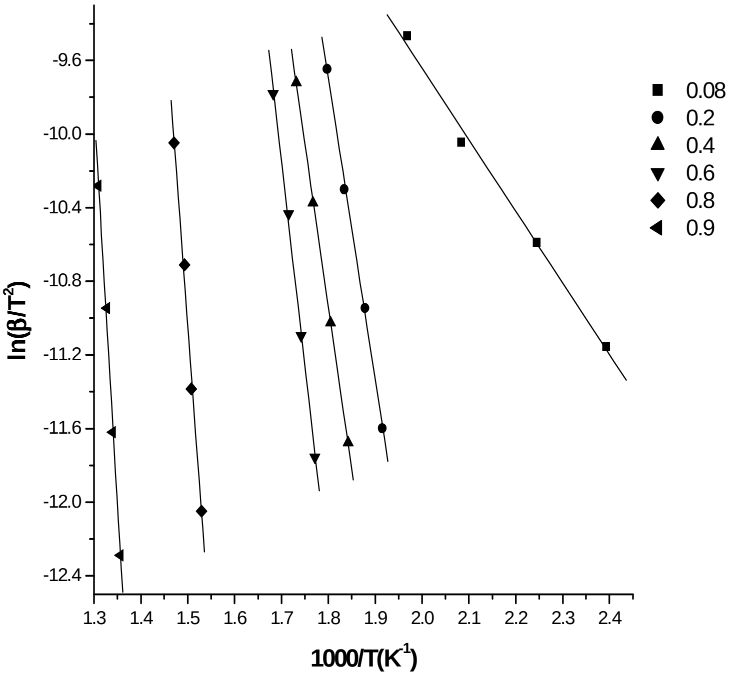

Fig. 8 Plot of Coats-Redfern modified method for chitosan at varying degree of conversions

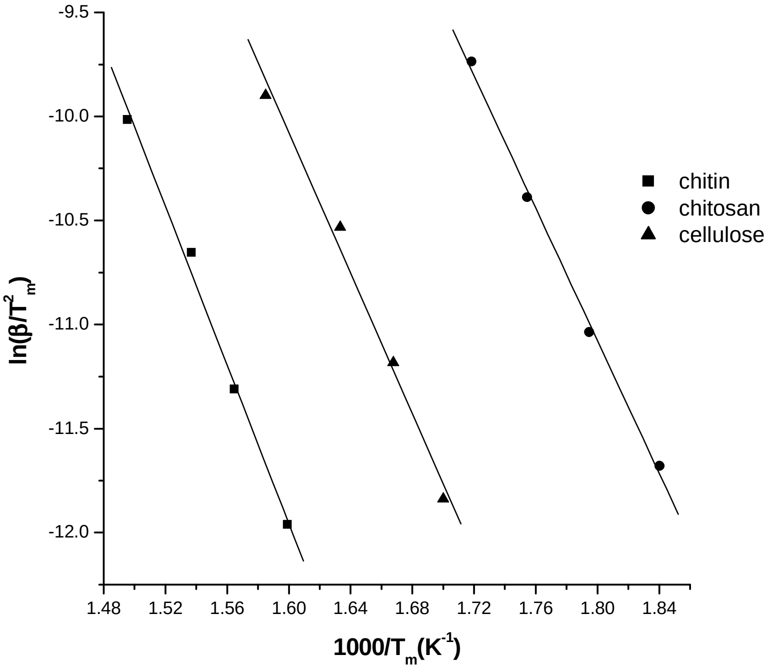

Fig. 9 Plot of Kissinger method for biopolymers at varying degree of conversions

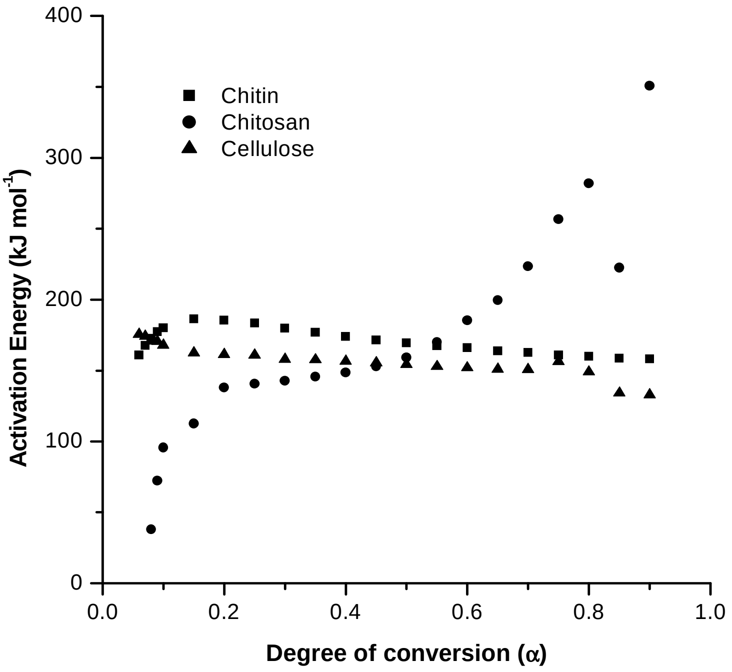

Fig. 10 Relationship of activation energy E vs α for pyrolysis of chitin (■), chitosan (●) and cellulose (▲) as calculated by O-F-W method

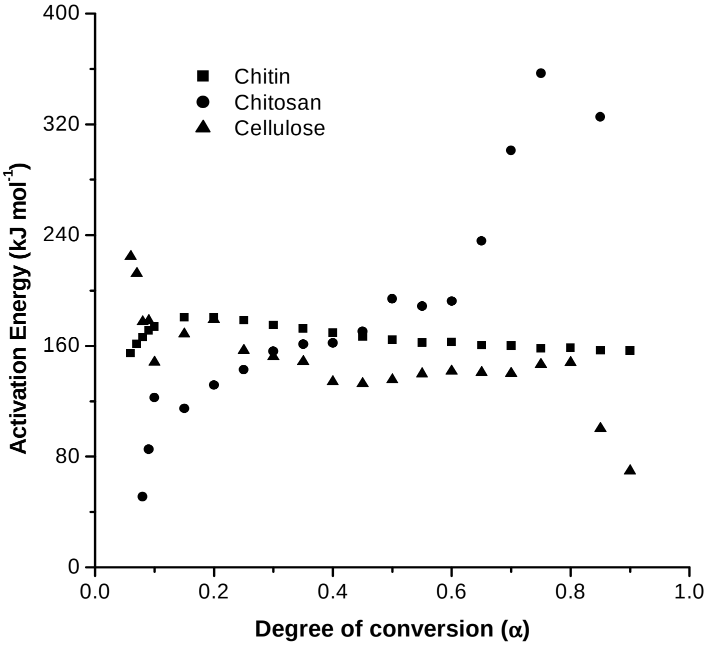

Fig. 11 Relationship of activation energy E vs α for pyrolysis of chitin (■), chitosan (●) and cellulose (▲) as calculated by Friedman method

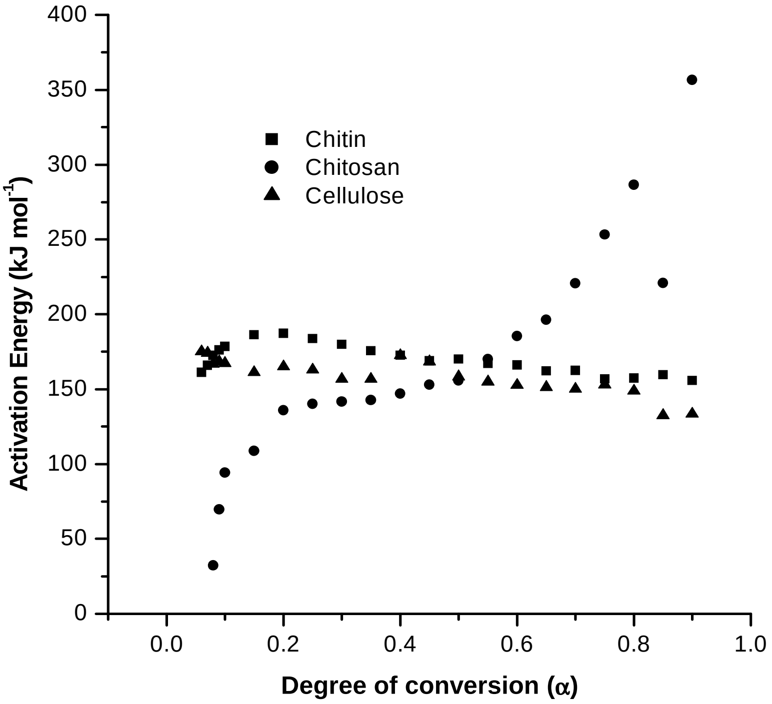

Fig. 12 Relationship of activation energy E vs α for pyrolysis of chitin (■), chitosan (●) and cellulose (▲) as calculated by Coats-Redfern (modified) method

It can be seen from the Table 3 that the activation energies calculated by all the iso-conversional methods are following a general trend and are in good agreement with each other. For initial degree of conversions i.e. at 0.06 and 0.07 the E values for cellulose are greater than those of chitin. This means that the initial thermal stability of cellulose is comparatively higher than others, which also matches well with the T_i order observed for TG curves.

The variations of E values with degree of conversion are shown in Fig. 10-12. The E values for chitin changes by small magnitude through the progress of the decomposition. This implies the possibility of single reaction mechanism for the decomposition [15]. On the other hand, degradation E values for cellulose decreases in three steps i.e. 1st α =0.06 to 0.2, 2nd 0.25 to 0.8 and 3rd starts above 0.8. These steps correspond to dehydration and depolymerization (lower conversion), decomposition of cellulose and formation of volatile compounds and char (moderate conversion) and cross-linking and aromatic cyclization of char residue (higher conversion) [23]. Also, the E values calculated using iso-conversional methods are independent of degree of conversion in the range α=0.25–0.8 indicating that single mechanism is working during this range.

The E values for chitosan are much dependent on the degree of conversion and increase in three steps i.e. 0.08-0.1, 0.15-0.5 and 0.55-0.9 (Fig. 10-12) which is entirely different behavior from other two. Though, the decomposition in chitosan starts from scission from weak C-O-C link like chitin but it is the presence of N-acetylated units in chitin which makes all the differences. The initial (1st step) E values for chitosan are comparatively lesser than chitin thus indicating lower thermal stability of chitosan. This behavior matches well with the previous report [21] i.e. the N-acetylated units have increased the thermal stability of the chitin molecular chains compared to amino units of chitosan. The second step degradation E values correspond to cross-linking reactions during thermal degradation of amino polymer. The huge increase in the E values during the third step can be assigned to the decomposition and charring reactions of more stable cross-linked structures formed in second step [15].

The E values calculated by Kissinger method for cellulose, chitin and chitosan are 160.2, 158.5 and 132.3 kJ mol^{-1}, respectively. The order of E values calculated by Kissinger method is same as evaluated by initial thermal degradation order i.e. cellulose > chitin > chitosan.

CONCLUSIONS

Simultaneous thermal analysis (TG/DTA) technique was used to understand the basic theory and kinetics of thermal degradation of chitin, chitosan and cellulose. On the basis of initial thermal decomposition temperature calculated from TG curves, the thermal stability of samples follows the order: cellulose > chitin > chitosan. The DTA study shows that the decomposition of chitin and cellulose is endothermic process whereas chitosan decomposition is exothermic process. The iso-conversion methods have been used to calculate the degradation activation energy using non-isothermal TG data. The activation energy calculated at 0.06 and 0.07 conversions for chitin and cellulose, followed same thermal stability order as determined by initial degradation temperature. The activation energy values calculated for chitin methods are independent of degree of conversion indicating that single mechanism. However, the activation energy values for chitosan are much dependent on the degree of conversion. The degradation E values of cellulose falls in three steps i.e. dehydration and depolymerization (lower conversion), decomposition of cellulose and formation of volatile compounds and char (moderate conversion) and cross-linking and aromatic cyclization of char residue (higher conversion). The thermal and kinetic data presented in this study would help to find out new applications of these biopolymers either as binary or ternary blends.

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Nomenclature

A	pre-exponential factor or frequency factor, (min^{-1})
E	activation energy of degradation reaction, (kJ mol^{-1})
R	universal gas constant, (J K^{-1} mol^{-1})
n	Order of reaction
t	time, (min)
T	absolute temperature, (°C)
T_m	temperature value at the maxima of the first derivative mass loss curve, (°C)
T_i	initial onset degradation temperature, (°C)
MWLR	maximum weight loss rate corresponding to DTG peak maxima, (% min^{-1})

Greek

α	degree of conversion or degree of decomposition or the fraction reacted
β	linear heating rate, (°C min^{-1})