Thermal Degradation Kinetics of Biopolymers and their Composites: Estimation of Appropriate Kinetic Parameters

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ABSTRACT

Renewable resource based polymers are biodegradable, biocompatible and eco-friendly in nature. Starch, Cellulose, Chitin, Chitosan, Poly (3-hydroxybutyrate) (PHB), Poly (lactic acid) (PLA) and poly (ϵ -caprolactone) (PCL) are used in biomedical field and for food packaging purposes. Due to limited thermal stability, these polymers undergo significant degradation when exposed for long time during industrial processing. Understanding of thermal behaviour of these polymers and their composites need to be investigated towards their applications. In the current research work, thermal degradation kinetics of pure PLA, PHB, PCL and chitosan along with various bio-fillers and inorganic fillers are studied. Thermal gravimetric analysis (TGA) data reported in literature for non-isothermal experiments were used to determine the thermal degradation behaviour and associated kinetics. Efforts were made on understanding the applicability of various models. Reconstruction of the conversion profiles for different thermal history were performed and compared with experimental data. A choice of a model for a specific material was investigated based on root mean square (RMS) values.

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Abbreviations:

A: Pre-exponential Factor (min^{-1})
AAC: Aliphatic Aromatic Copolyesters
A&B: Augis & Bennett
AIC: Advanced Isoconversional Model
CR: Coats-Redfern
CA: Cellulose Acetate
DTG: Differential Thermogravimetric Analysis
E: Activation Energy (kJ/mole)
FR: Friedman
KGR: Kissinger
KAS: Kissinger Akahira Sunose
K(T): Rate Constant
MWCNT's: Multiwalled Carbon Nanotubes
MCC: Microcrystalline Cellulose
 M_n : Number Average Molecular Weight
OMMT: Organomodified Montmorillonite

OFW: Ozawa-Flynn-Wall
PLA: Poly(lactic acid)
PHB: Poly(3-hydroxybutyrate)
PHBV: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PCL: Poly(ϵ -caprolactone)
R: Universal Gas Constant
RMSE: Root Mean Square Error
TGA: Thermogravimetric Analysis
 TiO_2 : Titanium Dioxide
T: Temperature ($^{\circ}\text{C}$ or K)
 T_m or T_p : Maximum or Peak Temperature ($^{\circ}\text{C}$)
 T_o : Onset Temperature ($^{\circ}\text{C}$)
 α : Degree of Conversion
 β : Heating Rate ($^{\circ}\text{C/min}$)
 $f(\alpha)$: Reaction Model Function
 $g(\alpha)$: Integral Reaction Model
n: Order of Degradation

1. Introduction

In recent years, significant efforts have been made towards the development of biopolymers and their composites for specific applications due to their biodegradability, non-toxicity & biocompatibility nature. Biopolymer based technologies may play a vital role in substituting significant uses of conventional polymers produced from petroleum resources [Reddy et al., 2013]. Biopolymers such as cellulose, chitosan, starch and biodegradable polymers poly (lactic acid) (PLA), poly (3-hydroxybutyrate) (PHB), and poly (ϵ -caprolactone) (PCL) etc., are used in food packaging, commodity & biomedical fields [Arora et al., 2011].

Degradation of polymers includes all changes related to chemical structure and physical properties due to external chemical or physical stresses [Carrasco et al., 2013]. Certain organic (including biopolymers) and/or inorganic fillers (TiO_2 , SiO_2 and montmorillonite clay) are added to biopolymers to yield biopolymers based composites. The addition of the fillers to biopolymers enhances mechanical, electrical and thermal strength. For example, incorporation of cellulose nanofibres or nanocrystals into PLA increases tensile strength and modulus [Fortunati et al., 2010]. However, these soft materials when exposed to heat, thermal degradation occur which results in undesirable changes to the properties. It is

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noteworthy to mention that bio-fillers may also catalyse (auto) the thermal degradation process, depending on its chemical interaction with polymer chains [Zheng et al., 2009; Carrasco et al., 2010; Arifin et al., 2008].

The mechanism of thermal degradation of polymers is complex in nature. Thermal degradation involves the occurrence of molecular scission which leads to the changes in molecular weight distribution of the polymers. This phenomenon is decisive for recycled polymers because they suffer continuous change with temperatures [Erceg et al., 2005]. Thermal degradation of PLA follows different pathways via random chain scissions of the ester groups, intra- and inter- molecular transesterification [Carrasco et al., 2013; Carrasco et al., 2010]. While, thermal degradation of PHB mainly occurs via a random chain scission by β -elimination [Arifin et al., 2008]. Thermal degradation of starch is a multistage process; liberation of water and small molecules at lower temperatures (below 120°C) followed by depolymerisation through competitive reactions, and the last stage is due to the oxidation of organic matter [Petinakis et al., 2010].

The biodegradable polymers & various filler combinations chosen for this study have been tabulated in Table 1. These are most common biodegradable polymers, widely used for food-packing purposes and in bio-medical field. Experimental data for each material at different heating rates were extracted from TGA curves reported by several researchers [Carrasco et al., 2013; Fortunati et al., 2010; Arifin et al., 2008; Petinakis et al., 2010; Su et al., 2008; Britto and Campana-Filho, 2007; Li et al., 2011; Chrissafis, 2010; Achilias et al., 2011; Srithep et al., 2013; Buzarovska et al., 2009]. Non-isothermal TGA curves show that the onset temperatures (start and end) and peak temperatures (T_m) shift to high temperatures with increasing heating rate for all the materials. This shift is mainly due to the time and temperature history a material is subjected. A variety of kinetic models based on single heating rate and multiple heating rates have been reported in literature to determine the kinetic triplets and behaviour of thermal degradation process. A series of the papers were published by Carrasco et al. [Carrasco et al., 2013; Fortunati et al., 2010; Zheng et al., 2009; Carrasco et al., 2010] on kinetics of thermal degradation of PLA. They reported that the thermal degradation of PLA follows the random scission mechanism and the kinetics parameters obtained from modified Sestak-Berggren model are more accurate than n^{th} order reaction model. Arora et al. [Arora et al., 2011] reported the comparative thermal degradation kinetic studies of chitin, chitosan and cellulose using OFW, Kissinger, Friedman and modified Coats-Redfern methods. It was reported that cellulose is more thermally stable than other two materials and, chitosan is least thermally stable. de Britto et al. [Britto and Campana-Filho, 2007] studied thermal degradation behaviour of chitosan (with 12% degree of deacetylation) by using isothermal and non-isothermal TGA experiments under nitrogen atmosphere. The values of E (kJ/mole) by Kissinger and OFW methods were obtained as 138.5 and 149.6 (average value), respectively. Su et al.

[Su et al., 2008] studied thermal degradation behaviour of PCL using an iterative procedure based on Senum Yang function. They reported the activation energy values ranging between 64-160 kJ/mole and degradation of PCL follows two mechanisms, diffusion mechanism when $\alpha = 0.1-0.2$ and limiting surface reaction (phase controlled models) when $\alpha = 0.25-0.8$. Activation energy values reported by researchers for pure biodegradable polymers using various kinetic expressions are listed in Table 2 [Carrasco et al., 2013; Arrifin et al., 2008; Erceg et al., 2005; Petinakis et al., 2010; Su et al., 2008; Britto and Campana-Filho, 2007; Chrissafis, 2010; Achilias et al., 2011; Marquez et al., 2012; Al-Mulla and Al-Sagheer, 2012; Faria and Prado, 2007].

The thermal stability, onset temperature and temperature at maximum rate of biodegradable polymers with blending/fillers (biocomposites) depend on the characteristic of filler used. Petinakis et al. [Petinakis et al., 2010] studied the effect of hydrophilic fillers (starch and cellulose) on the biodegradation and thermal decomposition of PLA based materials. It was reported that the thermal degradation of starch proceeds in a three step instead of two steps for pure PLA and the decomposition temperature of PLA decreases gradually with increasing amount of starch. Li et al. [Li et al., 2011] synthesized bionanocomposite of PLA and TiO_2 nanowires by insitu polymerisation. They reported that the addition of TiO_2 nanowires of 0.25 & 2% wt. increased M_n of PLA-g- TiO_2 nanocomposites by 12% and 65% respectively. The degradation temperature increases with the amount of TiO_2 loading thereby enhances the thermal stability. Similar trend was observed for PLA/MWCNT (2.5%) nanocomposite [Chrissafis, 2010], PHBV/ TiO_2 nanocomposites [Buzarovska et al., 2009] and PCL/MCC [Zhou and Xanthos, 2009]. The increase in thermal stability of PCL/MCC composite is due to the interaction (formation of hydrogen bonds) between the polymer matrix and the MCC. A reverse trend was reported for PHB/AAC [Erceg et al., 2005] and PHB/ Ag_2S [Faria and Prado, 2007] composites. The presence of AAC or Ag_2S filler in PHB decreases the onset degradation temperature of composites than pure PHB. The catalytic effect of Ag_2S nanoparticles on PHB decreases. TGA-FTIR studies suggested that the thermal degradation of PHB in the presence of Ag_2S nanoparticles occur according to the random chain scission mechanism [Faria and Prado, 2007]. Srithep et al. [Srithep et al., 2013] synthesized biodegradable nanocomposites of PHBV and nanofibrillated cellulose (NFC) as reinforcement, and it was reported that the presence of cellulose nanofibres reduces onset temperatures and enhances degradation rate.

This article focuses on the determination of accurate kinetics parameters for the biodegradable polymers and their composites using organic and inorganic fillers at various experimental conditions (Table 1). Four isoconversional and three model fitting methods were applied on the TGA data (Table 3) [Friedman, 1964; Kissinger, 1956; Kissinger, 1957; Akaheira and Sunose, 1971; Flynn and Wall, 1966; Ozawa, 1956; Vyazovkin et al., 2011; Coats and Redfern, 1964; Augis and Bennett,

Table 1: List of biodegradable polymers and biocomposites along with heating rate & onset and end temperatures considered for kinetic analyses.

Pure	Material	Heating rates ($^{\circ}\text{C}/\text{min}$)	$[T_{\text{onset}}-T_{\text{end}}]$ ($^{\circ}\text{C}$)	Reference
Pure	PLA	1[271-326]	2[283-338]	4[291-344]
	PHB	3[254-278]	5[260-287]	7[266-292]
	PCL	5[277-418]	10[312-433]	15[326-441]
	Chitosan	2.5[249-350]	5[264-354]	10[279-362]
Biocomposites	PLA	Starch	15[309-360]	20[335-368]
			20[335-442]	[Petinakis et al., 2010]
			20[332-448]	
			20[326-456]	
			20[318-463]	
	PLA	Cellulose	20[312-472]	
			10[310-360]	[Fortunati et al., 2010]
			20[249-304]	[Li et al., 2011]
			20[256-312]	
			20[252-315]	
	PLA	TiO_2	20[265-324]	
			5[309-365]	10[319-377]
			15[328-386]	20[335-392]
				[Chrissafis, 2010]
				[Achilias et al., 2011]
	PHB	OMMT	5[217-255]	
			5[225-264]	
			5[231-267]	
			5[234-261]	
	PHBV	CNF	10[273-304]	[Srithep et al., 2013]
			10[270-302]	
			10[265-294]	
			10[270-290]	[Buzarovska et al., 2009]
	PHBV	TiO_2	10[272-292]	

Table 2: Kinetic parameters for various biodegradable polymers reported in literature

Material	Reference	Model	E
PLA	[Carrasco et al., 2013]	FR	168±4
		KGR	171
		OFW	162±6
	[Li et al., 2009]	OFW	166±6.3
		Invariant Kinetic	174.7±16.5
	[Chrissafis, 2010]	FR	118-169
		OFW	111-149
		n th order	134.9
		Prout-Tompkins	135.2
		n th order with Autocatalysis	135.3
PHB	[Arriffin et al., 2008]	1 st Order	118
		OFW	137
	[Achillas et al., 2011]	KAS	104.3±2.6
		KGR	99.4
		IKP	100.4±1.8
	[Erceg et al., 2005]	Sestak-Berggren	100.3
		OFW	135
		KGR	131
PCL	[Su et al., 2008]	KAS	64-158
		OFW	70-163
	[Marquez et al., 2012]	KGR	171
		KAS	179
		FR	177
		CR	170
Chitosan	[de Britto et al., 2007]	OFW	149.6
		KGR	138.5
		Broido's	143
		MacCallum	153
		First order kinetics	73-101
	[Al-Mulla and Al-Sagheer, 2012]	CR	87.84
		Modified CR	32.3-356.6
	[Faria and Prado 2007]	FR	51.2-428.6
		OFW	38-350.9
		OFW	38-350.9

1978]. Thermal degradation process was assumed to follow first order reaction model (wherever it is required) due to its simplicity. Kinetic models such as Friedman, Ozawa-Flynn-Wall (OFW), Kissinger AkahiraSunose (KAS) and advanced isoconversional (AIC) are based on isoconversional concept. Isoconversional models involve measuring temperatures corresponding to fixed values of 'α' at several heating rates and generate an array of kinetic parameters, E and A, and/or Af (α). On the other hand model fitting methods estimate a single set of E and A which represents entire process based on reaction model chosen. Different models predict different kinetic triplets for various polymeric material/composites. This creates confusion on the choice of the model for a specific material. This article critically reviews the applicability and suitability of kinetic models available in open literature for biopolymer and their composite.

2. Methods

Thermal degradation behaviour of polymers can be well studied by using TGA. TGA records change in mass of the sample with temperature (or time) at specified gas environment and heating rate. Globally, for any chemical reaction the kinetic analysis is generally composed of two functions; one depends on the temperature and the other depends on the fraction transformed 'α'.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

The temperature dependence of the rate constant can be described by Arrhenius equation. Thus, the rate equation can be written as

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (2)$$

Different kinetic models based on isothermal & non-isothermal TGA measurements can be derived using equation (2) to determine kinetic triplet, pre-exponential factor A, activation energy E and reaction model f (α). Broadly, these models are classified as isoconversional and model fitting models.

Table 3: List of the isoconversional and model fitting kinetic models considered to study the kinetics of the materials mentioned in Table-1

	Model	Expression	Comments
Isoconversional Models	Friedman (FR) [26]	$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT}$	Differential isoconversional method applicable for multiple heating rate data. Very sensitive to small changes in rate data.
	Kissinger AkahiraSunose (KAS) [27-29]	$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT}$	Integral isoconversional expression depends on the Arrhenius integral approximations.
	Ozawa Flynn Wall (OFW) [30-31]	$\log \beta = \log \frac{AE}{g(\alpha)R} - 2.315 - 0.4567 \frac{E}{RT}$	Integral isoconversional method uses Doyle's approximation.
	Advanced Isoconversional Model (AIC) [32]	$\phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i}$	Distributed activation energy with respect to degree of conversion is determined by minimizing the function $\phi(E_\alpha)$.
Model Fitting methods	Coats Redfern (CR) [33]	$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\left(\frac{AR}{\beta E}\right)\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$	It depends on the integral reaction model and use single heating rate non-isothermal data.
	Kissinger [28]	$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m}$	Maximum rate method. Depends on the heating rates and peak temperatures.
	Augis& Bennett [34]	$\ln\left(\frac{\beta}{(T_p - T_0)}\right) = -\frac{E}{RT_p} + \ln A$	Integral method based on the heating rates and peak & onset temperatures.

2.1. Friedman (FR) method:

The fundamental isoconversional model was developed by Friedman [Friedman, 1964]. It is a differential isoconversional method, directly derived from the degradation rate expression with no assumptions. Later, Friedman method had been modified with certain assumptions to various isoconversional kinetic expressions for different applications. The rate expression (equation (2)) can be arranged using heating rate, β

$$dt = \frac{dT}{\beta} \text{ (or) } \beta = \frac{dT}{dt} \quad (3)$$

$$\text{Then equation (2) becomes, } d\alpha = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \frac{dT}{\beta} \quad (4)$$

Applying logarithms on both sides results,

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A + \ln f(\alpha) - \frac{E}{RT} \quad (5)$$

For a constant α , the plot of $\ln\left(\beta \frac{d\alpha}{dT}\right)$ vs. $1/T$ yields a straight line.

The value of E & A can be calculated from its slope and intercept for a known reaction model. This method is more sensitive to the rate data obtained from DTG curves and may results erroneous values of E and A , if the small deviations in rate data encounters.

2.2. Ozawa-Flynn-Wall (OFW) model:

Ozawa, Flynn & Wall [Flynn and Wall, 1966; Ozawa, 1956] developed kinetic rate equation based on the Arrhenius temperature integral $p(x)$. Integrating equation (4) on both sides yield

$$\beta \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{T_0}^T A \exp\left(\frac{-E}{RT}\right) dT \quad (6)$$

$$\text{Let } g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (7)$$

The rate equation can be written as,

$$g(\alpha) = \frac{AE}{\beta R} p(x) \quad (8)$$

$$\text{Where } (x) = \int_0^\alpha \frac{\exp(-x)}{x^2} dx, \text{ and } x = E/RT$$

The determination of analytical solution for $p(x)$ is difficult. It can be solved by using some numerical approximations. The final form of the expression can be derived by using Doyle's approximation [Doyle, 1961].

$$\log \beta = \log \frac{AE}{g(\alpha)R} - 2.315 - 0.4567 \frac{E}{RT} \quad (9)$$

The plot of $\log \beta$ vs. $1/T$ for non-isothermal data results a straight line. The values of E and A can be calculated from its slope and intercept. The advantage of this method is the easy applicability to any kind of system uses multiple heating rates without prior knowledge of reaction model. The evaluation of A depends on the reaction model. For single heating rate data, equation (9) can be written as

$$\log g(\alpha) = \log \frac{AE}{\beta R} - 2.315 - 0.4567 \frac{E}{RT} \quad (10)$$

2.3. Kissinger-Akahira-Sunose (KAS) model:

Kissinger-Akahira-Sunose (KAS) derived kinetic expression from the integral approximation of the degradation rate expression assuming constant value of α [Kissinger, 1956; Kissinger, 1957; Akahira and Sunose, 1971]. It is an integral isoconversional model based on the following expression

$$\log g(\alpha) = \log \frac{AE}{\beta R} - 2.315 - 0.4567 \frac{E}{RT} \quad (11)$$

2.4. Advanced isoconversional (AIC) model:

Vyazovkin et al [Vyazovkin et al., 2011] suggested an advanced isoconversional method (AIC), for the better evaluation of Arrhenius temperature integral to determine the accurate value of activation energy by minimizing the following function

$$\phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \quad (12)$$

At a particular α , the value of E_α can be calculated by minimizing the function ' ϕ '. Where the temperature integral

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT \quad (13)$$

The dependence of E_α on α can be evaluated by repetitive minimization of the function ϕ at each value of α . this equation is mostly applicable for the linear change in temperature with time. For varying temperature programs $T_i(t)$, the above expression can be written as

$$\phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_i(t_\alpha))}{I(E_\alpha, T_j(t_\alpha))} \quad (14)$$

Where the Arrhenius integral in terms of time domain is

$$I(E_\alpha, T(t_\alpha)) = \int_0^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right) dt \quad (15)$$

The fundamental assumptions made in developing the integral isoconversional methods i.e. E_α is constant with α over the whole integration step yields large deviations in the kinetic parameters. The variation of E_α with α can be identified by modified the temperature integral as

$$I(E_\alpha, T_\alpha) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(\frac{-E_\alpha}{RT}\right) dT \quad (16)$$

Here E_α is assumed to be constant for a small interval of α . Like differential method of Friedman, the application of integration by segments generates the value of E_α . A detailed AIC method and its application in kinetic analysis can be found elsewhere [Vyazovkin, 1996; Burnham, 2000; Tiwari and Deo, 2012].

2.5. Augis & Bennett (A&B) model:

Augis & Bennett [Augis and Bennett, 1978] developed a kinetic expression to determine kinetic parameters for crystallization processes. It is a model fitting method based on the expression

$$\ln\left(\frac{\beta}{(T_p - T_0)}\right) = -\frac{E}{RT_p} + \ln A \quad (17)$$

A plot of $\ln\left(\frac{\beta}{(T_p - T_0)}\right)$ vs. $1/T$ gives a straight line whose slope is

equal to E/R , and pre-exponential factor is calculated from its intercept

2.6. Coats-Redfern (CR) model:

According to the general analytical solution developed by Carrasco [Carrasco et al., 2013; Carrasco et al., 2010], the temperature integral can be solved using numerical approximation [Doyle, 1961].

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{\beta R} \left[\exp\left(\frac{-E}{RT}\right) \right] \sum_{i=1}^\infty (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i+1} \quad (18)$$

It can be rearranged in the form of integral function

$$\frac{g(\alpha)}{\sum_{i=1}^\infty (-1)^{i+1} i! \left(\frac{RT}{E}\right)^{i+1}} = \frac{AE}{\beta R} \left[\exp\left(\frac{-E}{RT}\right) \right]$$

For $i = 1$,

$$\begin{aligned} & \frac{g(\alpha)}{\{(RT/E)^2 - 2!(RT/E)^3 + 3!(RT/E)^4 - 4!(RT/E)^5 + 5!(RT/E)^6 - \dots\}} \\ &= \frac{AE}{\beta R} \left[\exp\left(\frac{-E}{RT}\right) \right] \end{aligned}$$

or

$$\frac{g(\alpha)}{\{1 - 2(RT/E)^2 + 6(RT/E)^3 - 24(RT/E)^4 + 120(RT/E)^5 - \dots\}} = \frac{AE}{\beta R} \left[\exp\left(\frac{-E}{RT}\right) \right] (RT/E)^2$$

Applying logarithms on both sides, and truncate the expression up to 2nd term by neglecting the higher order terms other than 1st above expression becomes [Coats and Redfern, 1964]

$$\ln \left[\frac{g(\alpha)}{\left(1 - 2 \left(\frac{RT}{E}\right)\right)} \right] = \ln \left(\frac{ART^2}{\beta E} \right) - \frac{E}{RT}$$

This expression can be rearranged as

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\left(\frac{AR}{\beta E} \right) \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (19)$$

A plot of $\ln \left(\frac{g(\alpha)}{T^2} \right)$ vs. $1/T$ gives a straight line; the values of E & A can be calculated from its slope and intercept. This model is applicable to both, single & multiple heating rate experimental data and depends on the integral reaction model.

2.7. Kissinger (KGR) model:

The model assumes that the rate reaches its maximum at temperature T_m . The mathematical expression is obtained by setting $\frac{d^2\alpha}{dT^2} = 0$ & $T = T_m$ [Kissinger, 1957].

$$0 = \frac{-AE}{\beta R} \exp \left(\frac{-E}{RT_m} \right) \frac{1}{T_m^2} (1-\alpha)^n + \frac{A}{\beta} \exp \left(\frac{-E}{RT_m} \right) n(1-\alpha)^{n-1} \frac{d\alpha}{dT} \quad (20)$$

Substituting value of $\frac{d\alpha}{dT}$ in equation (20) and after subsequent arrangements, the equation becomes

$$\frac{E\beta}{RT_m^2(1-\alpha)^{n-1}} = A \exp \left(\frac{-E}{RT_m} \right) \quad (21)$$

For first order degradation ($n = 1$) the final logarithm form of the kinetic expression becomes

$$\ln \left(\frac{\beta}{T_m^2} \right) = \ln \left(\frac{AR}{E} \right) - \frac{E}{RT_m} \quad (22)$$

Activation energy and pre-exponential factor can be calculated from the slope and intercept of plot of $\left(\frac{\beta}{T_m^2} \right)$ vs. $1/T$ at different heating rates.

3. Results and Discussion:

Mode of TGA measurements plays a vital role in studying the degradation behaviour of complex materials. Pure biodegradable polymers and their composites (Table 1) were subject to kinetic analyses using kinetic expressions mentioned in Table 3 and discussed in section (2). The TGA data (either weight loss or conversion) were extracted carefully considering the onset points mentioned in respective articles. Multiple heating rates data were available only for a few materials, pure biodegradable polymers and one composite (Table 1) and, accordingly all the kinetic methods (Table 3) were applied on these material. For other materials, considered in this study the data were reported for single heating rate only, thus the kinetic analyses was conducted using OFW and CR methods.

3.1. Pure Biodegradable polymers:

Four pure biodegradable materials, PLA, PHB, PCL and Chitosan were considered for kinetic analysis. The TGA curves at different heating rates for PLA [Carrasco et al., 2013] and PHB [Arrifin et al., 2008] are depicted in Figures 1a and 1b respectively. Similar set of the TGA data were used for Chitosan [Britto and Campana-Filho, 2007] and PCL [Su et al., 2008]. The pyrolysis data were used in different kinetic expressions to evaluate the kinetic parameters. The distributions of activation energy obtained from the isoconversional models, using linear curve fittings approaches such as FR, KAS and OFW are tabulated in Table 4 with regression coefficients. The activation energies were estimated for nine equal interval conversion points. The distributions of kinetic parameters over entire conversion range obtained for pure biodegradable polymers using advanced isoconversional method (AIC) is shown in Figure 2. The values of activation energies were observed to be strictly dependent on the extent of conversion. The values vary for different materials due to the different mechanism involved at different temperature and/or heating rate. For a same material (data set) different kinetic expressions also produced different set of kinetic parameters. The change in E values for PLA & PHB followed a similar trend, that the gradual increase of E for pure PHB whereas for PLA, it increased up to $\alpha = 0.37$ and thereafter remains constant. For chitosan, an arbitrary change in E values was observed at $\alpha = 0.5 - 0.9$ with a maximum value at $\alpha = 0.88$. The model fitting methods such as CR, KGR and A&B were also applied on these materials. The resulted straight lines by applying Augis & Bennett and Kissinger methods on TGA data are shown in Figure 3(a) and 3(b) respectively. The kinetic parameters, single values obtained from model fitting methods are summarized in Table 5. PHB has a broad range of activation energy values ranging from 110-375 kJ/mole with single and multiple heating rates. During the pyrolysis of PHB, the occurrence of multiple degradation reactions makes kinetic analysis difficulty. For PCL, a continuous increase in E values, from $\alpha = 0.2$ to 0.9 using all isoconversional was observed, which indicates variation of degradation mechanism of PCL. A sudden change in E value at early stage (~68 to ~118 kJ/mole) is due to the degradation of volatile components, occurrence of random chain scissions at low conversions. Chitosan shown a large variation in the kinetic parameters, this may be due to complex multistep mechanism (so kinetics) involved during chitosan degradation.

Figure 1: TGA curves, conversion vs. temperature data for pure (a) PLA [Zheng et al., 2009] (b) PHB [Carrasco et al., 2010] at multiple heating rates.

Table 4: Distribution of activation energies (with regression coefficients) obtained from isoconversational models for pure biodegradable polymers.

Material	Model	E/R ²	$\alpha=0.1$	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Avg
PLA	FR	E	151	157	162	164	169	172	175	180	183	168.1
		R ²	0.97	0.97	0.97	0.98	0.98	0.98	0.99	0.99	0.99	0.98
	KAS	E	130.7	142.4	150.5	153.4	160	161.9	158.5	165.1	168.4	154.5
		R ²	0.96	0.95	0.96	0.96	0.97	0.98	0.98	0.97	0.98	0.96
	OFW	E	141.6	152.8	160.5	163.5	169.5	171.3	168.2	175.2	177.7	164.4
		R ²	0.97	0.96	0.96	0.96	0.97	0.98	0.98	0.97	0.98	0.97
PHB	FR	E	78.3	94.3	96.7	101.4	103.3	101.8	121.6	125.8	130	105.9
		R ²	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	KAS	E	123.6	130.8	125.4	131.4	132.5	128.7	129.7	130	130	129.1
		R ²	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	1	0.99
	OFW	E	134.8	141.6	136.6	142.2	143.3	139.6	140	141.7	141	140
		R ²	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	1	0.99
PCL	FR	E	71	108.8	146.7	157	169.6	171.9	178.3	185.5	199.5	154.2
		R ²	0.98	0.98	0.99	0.99	0.99	1	0.99	0.99	1	0.99
	KAS	E	65.1	111.7	132.8	140.7	147.5	151.0	153.5	159.5	161.7	135.9
		R ²	0.99	0.99	0.99	0.99	1	0.99	0.99	0.99	0.99	0.99
	OFW	E	68.6	118.9	137.4	149.3	150.2	151.6	156.5	156	168.9	139.7
		R ²	0.99	0.99	0.99	1	1	0.99	1	1	0.99	0.99
Chitosan	FR	E	128.8	135.7	136.9	132.9	143.5	157.6	158.4	162.3	157.5	145.9
		R ²	0.99	0.99	0.99	1	0.98	1	0.99	0.98	0.98	0.99
	KAS	E	143	140.7	148.2	162.6	164.7	167	168	170	175	160.1
		R ²	0.98	0.98	0.98	0.98	0.99	0.99	0.99	0.99	0.99	0.99
	OFW	E	153.2	151.1	158.3	172	174.4	176	178.6	178	179.4	169
		R ²	0.98	0.98	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99

Figure 2: Distribution of activation energies for pure biodegradable polymers obtained using advanced isoconversational method. **Figure 3:** Comparison of experimental and simulated conversion profiles generated using various kinetic models for (a) PLA at 8K/min and (b) PHB at 7K/min.

The CR model did not follow the linear line for chitosan; at later stage the deviation was large. For the material like chitosan, the kinetic can be evaluated with the methods use multiple heating rates with attention on the data sampling. The activation energy values calculated from KAS model were found lower than OFW model at all conversions for all the materials. KAS model considers both heating rate and temperature at each instant while OFW model depends only on heating rates applied. The values of activation energy obtained for these materials are well within the range of values reported in literature (Table 2). However, the combination of kinetic parameters (triplet) should be considered for analysis as the variation in activation energies may be reflected in pre-exponential factor values for a reaction model assumed.

3.2. Biocomposites:

Single heating rate data from TGA curves for various biocomposites, except for PLA/MWCNT's (multiple heating rates TGA curves) were considered kinetic analysis. Kinetic parameters were calculated for all biocomposites methods using single heating rate methods, CR and OFW. The kinetic parameters obtained for all the biocomposites, containing various amounts of filler content are summarized in Table 6. The activation

Table 5: Activation energy values (with regression coefficients) for pure biodegradable polymers obtained from model fitting methods.

Material	Model	E	A	R ²
PLA	CR	215	18.27×10^{17}	0.97
	KGR	172	15.86×10^{13}	0.99
	A&B	165	1.660×10^{13}	0.98
PHB	CR	260	11.9410^{19}	0.95
	KGR	116	3.206×10^{10}	0.99
	A&B	153.9	1.031×10^{14}	0.99
PCL	CR	85.8	9.095×10^5	0.95
	KGR	152.2	5.677×10^{11}	1
	A&B	169.7	2.417×10^{12}	1
Chitosan	CR	---	-----	-----
	KGR	139	1.0624×10^{12}	0.99
	A&B	157.9	2.3475×10^{13}	0.99

Table 6: Activation energy values (with regression coefficients) for biocomposites generated from model fitting methods.

Material		Models								
		OFW			CR					
		E	A	R ²	E	A	R ²			
Biocomposites	PLA	Starch	PLA/starch(5%)	199.2	8.85×10 ¹⁴	1	190.9	9.76×10 ¹⁴	1	
			PLA/starch(10%)	199	7.31×10 ¹⁴	1	190.7	8.20×10 ¹⁴	1	
			PLA/starch(20%)	177.9	7.13×10 ¹³	0.99	168.6	6.12×10 ¹²	0.99	
			PLA/starch(30%)	167.8	7.01×10 ¹²	0.97	158	5.01×10 ¹¹	0.97	
			PLA/starch(40%)	148.7	4.21×10 ¹⁰	0.99	137.9	2.87×10 ¹⁰	0.98	
		Cellulose	PLA/Cellulose(5%)	111.5	1.20×10 ⁹	0.98	99	2.19×10 ⁸	0.97	
			TiO ₂	PLA/TiO ₂ (0.25%)	174	2.58×10 ¹⁶	1	165.7	1.29×10 ¹⁶	1
				PLA/TiO ₂ (0.5%)	176.8	2.59×10 ¹⁶	1	167.8	1.32×10 ¹⁶	1
				PLA/TiO ₂ (1%)	161	9.60×10 ¹⁴	1	151.3	4.02×10 ¹⁴	1
				PLA/TiO ₂ (2%)	175.1	9.88×10 ¹⁵	1	166	4.91×10 ¹⁵	1
		MWCNTs	PLA/MWCNTs(2.5%)	175.6	2.26×10 ¹⁴	0.99	171	1.24×10 ¹⁴	0.99	
	PHB	OMMT	PHB/OMMT(1%)	102	4.6×10 ⁹	0.99	107	6.43×10 ¹⁰	0.99	
			PHB/OMMT(3%)	103	7.85×10 ⁹	0.99	99	3.85×10 ⁹	0.99	
			PHB/OMMT(5%)	105.4	4.113×10 ⁹	0.99	104	8.23×10 ⁹	0.99	
			PHB/OMMT(10%)	106	6.071×10 ⁹	0.99	110	2.89×10 ¹¹	1	
			CNF	PHBV/CNF(2.5%)	291.9	1.15×10 ²⁷	1	288	1.67×10 ²⁷	1
PHBV/CNF(5%)	275.6	5.63×10 ²⁵		0.99	271.7	7.24×10 ²⁵	0.98			
PHBV/CNF(10%)	286.2	1.31×10 ²⁷		1	282.8	1.83×10 ²⁷	1			
PHBV	TiO ₂	PHBV/TiO ₂ (1%)	221	1.69×10 ¹⁶	0.99	219	1.31×10 ¹⁶	1		
		PHBV/TiO ₂ (2%)	227	2.149×10 ¹⁷	1	229	4.51×10 ¹⁷	1		

energies were found be decreased with increase in starch content in PLA/ Starch composites. For other biocomposites the percent of filler (s) did not show a large deviation in the activation energies; however the values of A changed to one order magnitude. The kinetic parameters evaluated by OFW & CR methods for pure PLA are higher than the values obtained for PLA/MCC(5%) indicating the decrease in thermal stability of PLA/MCC(5%) than that of PLA. The deviation in the kinetic parameters obtained may be due to the assumption of first order reaction model considered. Other possibility is the modification of OFW to the application of single heating rate processes. The onset degradation temperature of PLA/chitosan composites was observed approximately same as that of pure PLA. This indicates a very poor interaction (less miscibility) between polymer & filler [Bonilla et al., 2013]. At higher heating rates thermal stability of PLA/MWCNT's improves compared to pure PLA. It is also in good agreement with observed in the kinetic parameters calculated from kinetic models. The presence of TiO₂ nanoparticles enhances the thermal stability of PHBV nanocomposites. Kinetic parameters also revealed that the increase in thermal stability of bionanocomposite at moderate percentages of TiO₂ content. The incorporation of TiO₂ nanoparticles showed enhancement of thermal stability of PHBV.

3.3. Model Selection:

The application of single heating rate methods to degradation kinetic study of complex material cause undesirable changes in the activation energy values due to the occurrence of complex set of reactions. A good regression coefficient (~1) may not necessary that the model captures the

actual decomposition behaviour. Choice of a particular model can be assured based on the deviation from the original path by evaluating statistical parameter like root mean square error (RMSE). The kinetic parameters obtained from different models were subjected to reconstruct the conversion profiles. The E (or E_a) and A (or A_f(α)) obtained from different models were used to reconstruct the α - T data. A MATLAB code using the function *ode45* was used to solve the ordinary differential equation, rate expression. The initial temperature was fixed at 180°C. The experimental and model simulated conversion profiles for PLA at 8°C/min and for PHB at 7°C/min are shown in Figure 4(a) and 4(b) respectively. Similar methodology was used for constructing the data for all the material at experimental heating rates and also at extrapolated heating rates. The RMSE were calculated between reconstructed and experimental conversion points for common experimental temperature values. The errors were calculated for 25 data points for each heating rates. The RSME values for pure biodegradable polymers calculated for each heating rate using kinetic models are shown in Figure 5. Advanced isoconversional method (AIC) produces simulated conversional profiles with less RMSE values for pure biodegradable polymers compared to other models. Pure PLA exhibits comparable RMSE values to AIC from Kissinger model. This is attributed from the minimal variation of with α throughout the process observed from AIC model as also described by Vyazovkin et al [Vyazovkin and Sbirarazuoli, 2006]. For the other materials Kissinger produces high RMSE values due to large variation in with α. In general at lower heating rates RMSE produced are nominally less than that at higher heating rates.

Figure 4: Sum of RMS values between experimental and simulated conversion data (various heating rates) from various models for (a) PLA (b) PHB (c) PCL and (d) chitosan.

Figure 5: RMS values (a, b) for PLA biocomposites and (c,d) for PHB and PHBV bio composites using single heating rate methods (OFW and CR models)

In case of biocomposites, the kinetic models based on single heating rates were compared. The generated RMSE values for CR and OFW methods are shown in Figure 6. For PLA/Starch composites CR produced lesser RSME and OFW. The RMSE values obtained from OFW model for PLA/TiO₂ nanocomposites were lower compared to other composites. It was also observed that PHBV/TiO₂ nanocomposites produce more RMSE values than other composites. The RSME shown in Figure 6 is for a single heating rate data only; use of multiple heating rates will increase these values. For complex material, like polymer and their composites, the single heating rate methods may not be appropriate. For examples, the CR method is based on curve fitting, requires linear regression to predict the kinetics. In case of Chitosan, the CR method is not able to fit the experimental data because of multiple stage degradation involved.

Figure 6 : Simulated conversion profiles for PLA degradation using advanced isoconversional method. The heating rates vary from very slow pyrolysis (0.05°C/min) to flash pyrolysis (500°C/min).

A model selected for kinetic analysis should be able to reproduce the data and extrapolate the profile to the conditions, experiments not performed. Overall, the RMSE analysis suggests that the AIC method is more appropriate to capture the complexity of thermal degradation process of a material. This may be due to the regress data sampling for small temperature interval adopted in the analysis for each heating rate considered. Due to the optimization by minimization of the function (equation (12)) the model is more accurate for a large pool of data collected at wide range and as well as more number of heating rates. Extrapolated TGA curves generated for degradation of pure PLA at several heating rates ranging from 0.01°C/min to 500°C/min are shown in Figure 7. The degradation step (α -T) varies with varying heating rates lead to low onset & end degradation temperatures at lower heating rates whereas the degradation temperatures are shifted to higher temperatures at high rates. The shape of the extrapolated simulated conversion profiles followed the experimental conversion profiles.

4. Conclusions:

Within variety of kinetic models available for thermal degradation, it is difficult to choose one model. The fundamental difference in all the methods is the way measurable data (mass loss, conversion, and rate) are imported. Several models are based on single heating rate and others use multiple heating rates data. The deviation in the kinetic parameters is attributed to the fact the equation is solved using differential, integral and/or approximation approaches. The continuous change in E values with α explains the change in mechanism of degradation and it is important in the early and end stages of the degradation. Overall, isoconversional models are able to capture the reaction mechanism as kinetics followed the reaction progress. Advanced isoconversional model uses optimization and produces fewer errors. The exact mechanism can be determined using different reaction models. However, the kinetic analysis is also very subjective to the reaction configuration and data sampling.

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