Thermal degradation study of waste polyethylene terephthalate (PET) under inert and oxidative environments

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ABSTRACT

Thermogravimetric analysis (TGA) of polyethylene terephthalate obtained from waste soft drink bottles (PET-SDB) was carried out under inert (nitrogen) as well as reactive (synthetic air) environments to evaluate the degradation behaviour and degradation kinetics. Non-isothermal TGA experiments at heating rates of 5, 10, 20, 40 and 50 °C/min were performed and the kinetic parameters such as activation energy (E_α) and pre-exponential factor (A_α) were determined at various extent of conversions using advance isoconversional (AIC) method. Criados' master plot technique established F1 (first order) as possible reaction model ($f(\alpha)$) for both inert and oxygenated non-isothermal TGA data. Under inert (N_2) environment a residue accumulation of around 20% was observed whereas complete conversion of PET-SDB occurred in oxygenated environment. The activation energy values were found in the range of 203–355 kJ/mol and 145–218 kJ/mol for inert and oxygenated environment respectively. Isothermal TGA data at various temperatures were analysed for the estimation of kinetic parameters. In the considered range of conversions, the range of activation energy obtained for multiple isothermal TGA data was found in the range of 196–217 kJ/mol.

1. Introduction

Polyethylene terephthalate (PET) is one of the most common thermoplastic polymer resin of polyester family with multidimensional applications as one-dimensional fiber, two-dimensional films to three-dimensional bottles or containers including various composites with other polymers, glass and ceramics etc. Two third of the PET produced is utilized for fiber and staple filaments [1–4]. Films and bottles are mainly used as packaging materials in the food and shipping industry. Most products from PET are mechanically recyclable and can be recycled back to its pure form by cleaning the contamination and foreign substances [5,6]. However, the PET recyclate cannot be used directly in food packaging, because of hygiene concerns. Other recycling processes like solvolysis, glycolysis, methanolysis, bio-degradation [7] etc. can produce terepathalic acid (TPA), dimethylterephthalate (DMT), ethylene glycol (EG) bis-2-hydroxyethylene terephthalate (BHET), monomers and oligomers etc. [2–4]. Plastic waste including post-consumer PET has become a worldwide concern due to the huge generation and the complexity involved in the recycle and disposal processes. The PET waste can also be treated in high temperature processes like combustion and pyrolysis. These processes are conducted at high temperature (300 °C – 1000 °C) and at low pressure (1 atm).

Bednas et al. [8] carried out extensive study on the pyrolysis of commercial PET applied in textile industry and analysed the volatile products with the help of gas chromatography. At 700 °C, pyrolysis of PET produced CO, CO_2, ethylene-acetylene, acetaldehyde, benzene, benzoic acid, vinyl benzoate, divinyl terephthalate, acetophenone and p-acetyl vinyl benzoate. Martín-Gullón et al. [9] carried out the pyrolysis of PET waste at the temperature of 200, 300, 400, 500, 600 and 700 °C for 20 min duration in a ceramic boat (crucible) inside a tubular furnace under both nitrogen and air flow (0.025 m³/h) conditions. Their study revealed that PET degrades within the range of 400–700 °C. Most of the earlier work on thermal degradation of PET covers the thermal stability and effect of flame retardant chemicals in PET composites [10,11].

To utilize the thermal processes in the disposal of PET waste a detailed kinetic study is necessary to understand the reaction mechanism under different temperature program. Buxbaum [12], established that PET follows a random scission of the ester links under thermal treatment which involves a six centred cyclic transition state to produce vinyl ester and carboxylic acid. These primary products of pyrolysis then undergo secondary reaction to give various products like CO, CO_2, acetaldehyde, aromatic acid and their vinyl esters. Saha et al. [13] carried out TGA based kinetic study with multiple heating mass loss data of waste PET obtained from different soft drink bottles. Both nth order kinetics and ASTM E698 models were used and the activation

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energy in the range of 320–338.98 kJ/mol was reported. The same research group [14] also carried out TGA based kinetic analysis utilizing model free approach to find out the variable activation energy of PET degradation reaction and suggested that the variable kinetic parameters are more certain to predict the degradation mechanism of plastics like PET under simulated heating condition. Martin-Gullon [9] predicted the degradation reaction model based on two separate portion of the mass loss curve; first one where original PET sample thermally degraded (around 80%) quickly into char and volatiles at around 377–527 °C. In the second part, further increase in temperature slowly decomposed (6–7%) the char. The char (residue) may be combusted to reduce the residual amount.

The kinetic analysis of PET (waste) has been reported in the literature, however very few studies estimated all three kinetic parameters, viz. activation energy (E_α), pre-exponential factor (A_α) and reaction model ($f(\alpha)$) and the probable variations in the parameters with the progress of the reaction. Most of the previous work is limited to the prediction of single value kinetic parameters like activation energy for the degradation reaction of PET/Post consumer PET. However, a single activation energy unable to capture the complexity involve in the solid state reactions like PET degradation [15,16]. In the condensed phase reactions like plastic degradation, the overall rate is a function of several simultaneously occurring single step reactions with their own energy barriers. As a result, the effective activation energy value varies with the progress of the reaction or the temperature. In solid-state degradation reaction like thermal degradation of PET, the prediction of kinetics is difficult, as the reaction dynamic is dominated by product diffusion rate through the solid matrix. One approach to solve this problem involves the use of isoconversional kinetic analysis methods like advance isoconversional method (AIC) proposed by Vyazovkin and his team [7]. Isoconversional methods recommended by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) are able to capture the complexity involved in the thermal degradation of solid [17–20]. AIC method utilizes advance numerical integration of the TGA data and successfully predict the activation energy at various level of the conversion. In the present study, AIC method was applied to predict the variable activation energy in the degradation reaction of polyethylene terephthalate from waste soft drink bottles (PET-SDB) under inert (N_2) environment and oxygenated (Air: 20% O_2, 80% N_2) environment. To give a holistic approach to the degradation kinetics of the PET-SDB, the current study also includes the determination of kinetic parameters for the degradation data obtained for isothermal TGA at multiple degradation temperatures. Utilizing thermal degradation process as an alternative approach in the disposal of post-consumer PET demands efficient process design and optimization of reaction conditions. In this context, the current study present an elaborate analysis of the kinetic parameters of the thermal degradation post-consumer PET, which will help in developing efficient process design and lead to widespread implementation of the thermal processes.

2. Materials and methods

Samples were obtained from empty soft drink/water bottles. The collected bottles, identified with their resin identification code (PET = 1) were cleaned after removing all the foreign materials (labels, sticker, caps etc.). Clean and dry samples were chipped into small pieces of 2–3 mm and were mixed uniformly. The proximate analysis of the sample was carried out considering the standard ASTM methods (D317, D3173, D3175) and the obtained data are summarized in Table 1. The thermal degradation study of the sample was performed using TGA (NETZSCH 209 F1 TG) equipment in both inert (N_2 gas) and reactive (Synthetic air: 20% O_2 and 80% N_2) environments. Non-isothermal experiments were conducted at heating rates of 5, 10, 20, 40 and 50 °C/min to scan the samples in the temperature range of 30 °C to 700 °C. Isothermal analysis was carried out at four temperatures (325, 350, 375 and 400 °C) with holding time of 8 h (480 min). The maximum

Table 1
Proximate analysis of PET-SDB sample (%w/w).

Moisture content (MC)	Volatile matter (VM)	Ash content (AC)	Fixed carbon (FC)
0	97.31	0.209	2.47

possible heating rate (100 °C/min) was chosen to reach the desired temperature with less induction period. The gas flow rate for all TGA experiments was maintained at 60 ml/min (40 ml/min as purge and 20 ml/min as protective gas) and the mass vs time/temperature data were recorded.

3. Theories on kinetic analysis

3.1. Advanced isoconversional method (for non-isothermal TGA)

The kinetic analysis was carried out based on Arrhenius law of reaction kinetic, which was manipulated mathematically to fit the TGA data. The Arrhenius rate equation for non-isothermal process is given as

$$\beta \frac{d\alpha}{dT} = A \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \tag{1}$$

Where α is the conversion value, $\alpha = (W_0 - W)/(W_0 - W_\infty)$. Where, W_0, W, W_∞ are the initial weight, instantaneous weight and residual weight of the sample respectively and β is the heating rate.

Advance isoconversional method (AIC) [7] utilizes the numerical integration of experimental data denoted by $I(E_\alpha, T_\alpha) = p(x)$, where $p(x) = \int_0^\infty e^{-x}/x^2 dx$ and $x = E_\alpha/RT$.

The detailed aspects of AIC method has been explained in various studies by Vyazovkin et al. [20–24]. The values of activation energy (E_α) at various conversion can be determined by minimizing the function $\Phi(E_\alpha)$,

$$\Phi(E_\alpha) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{I[E_\beta, T_i(t_\alpha)]}{I[E_\alpha, T_j(t_\alpha)]} = \min \tag{2}$$

Where the temperature integral:

$$I[E_\alpha, T_i(t_\alpha)] = \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t_i)}\right] dt \tag{3}$$

i and *j* represent the various temperature program (ranging from 1 to n, n being the total number of temperature program) and $i \neq j$.

Eq. (2) was solved numerically and minimization was repeated for every conversion to obtain a relative dependency between E_α and α.

The possible reaction model was estimated using Criados' masterplots technique [25]. The details of the method has been reported in our previous study [26]. The mathematical form of Criados' masterplots is

$$\frac{z(\alpha)}{z(0.5)} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} = \left(\frac{T_\alpha}{T_{0.5}}\right)^2 \frac{(d\alpha/dt)_\alpha}{(d\alpha/dt)_{0.5}} \tag{4}$$

The left hand side of Eq. 4 is the theoretical masterplots which signifies characteristic of each reaction mechanism mentioned in Table 1S. The right hand side of Eq. (4), which is also known as reduced rate, was calculated from the experimental results. Comparison of the theoretical masterplots with the experimental reduced rate plot suggests the most suitable reaction model f(α). For multi-heating rate data, the master plots were obtained for all the heating rates and the most suitable model has been selected by comparing the linearity coefficient (R^2) between theoretical master plots and experimental reduced plots.

Finally, the values of pre-exponential factor (A) can be determined by the use of Constable plot [26–28]. The logarithm form of rate expression can be derived from Eq. (1):

$$\ln\left(Af\left(\alpha\right)\right)_\alpha = \frac{E_\alpha}{RT_\alpha} + \ln\left(\left(\frac{d\alpha}{dt}\right)_\alpha\right) \tag{5}$$

In a more generalised approach Eq. (4) can be written as $b = \ln(Af(\alpha))_\alpha - aE_\alpha$, where, $a = 1/RT_\alpha$ and $b = \ln((d\alpha/dt)_\alpha)$. The activation energy (E_α) and $(Af(\alpha))$ at various stages of conversion follows a logarithmic linear relationship. The values of $\ln(A_\alpha f(\alpha))$ can be determined from the intercept of a linear plot of b and aE_α using isoconversion principle. Substituting the known reaction model $f(\alpha)$ predicted by Criados' masterplots, the values of A_α (pre-exponential factor) were predicted.

3.2. McCallum method (for isothermal TGA)

The values of activation energy obtained from non-isothermal TGA can be compared with the values of activation energy obtained from isothermal TGA. The calculation method was proposed by McCallum [29]. Hill et al. [30] carried out the thermal degradation kinetics of polymethacrylonitrile under several isothermal temperature by utilizing the method recommended by McCallum [29]. The Arrhenius rate equation (Eq. 1) can also be expressed as,

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{6}$$

Further integrating Eq. 6 results

$$\int\left(\frac{d\alpha}{f(\alpha)}\right) = A\exp\left(\frac{-E}{RT}\right)\int dt \Rightarrow \Gamma(\alpha) = A\exp\left(\frac{-E}{RT}\right)t \tag{7}$$

Which can be written as,

$$\ln(t) = \ln\left[\Gamma(\alpha)\right] - \ln(A) + \frac{E}{RT} \tag{8}$$

Where, $\Gamma(\alpha)$ represents the integral expression. For multiple isothermal process the logarithmic time $(\ln(t))$ is the time taken to reach a particular conversion α, was plotted against $1/T$ for each temperature. The slopes of the plots $\ln(t)$ vs. $1/T$ provided the activation energy at different extent of conversion. The McCallum method was used based on the assumption that over a range of isothermal temperatures $\Gamma(\alpha)$ has the same value for a given conversion.

4. Results and discussion

4.1. Proximate analysis of PET-SDB

The results of the proximate analysis of PET-SDB samples are shown in Table 1. Dry samples have no moisture and negligible ash content. The proximate analysis revealed significant amount of volatile matter (97.31%) present in the sample. Under thermal degradation, higher yield of volatile matter can be expected due to high organic content. Presence of plasticizer, colour, additives and other inorganic substances may produce the trace amount of ash content.

4.2. TGA and DTG curves

TGA weight loss data for PET-SDB samples obtained under inert (N_2) and oxygenated (Air) atmosphere are shown in Fig. 1-I (a) and -I (b) respectively. Complete conversion of the sample was observed under oxygenated TGA because of the combustion of char at high temperatures, whereas degradation reaction ceased at a residue accumulation of 20% when thermal degradation takes place under inert environment (Fig. 1-I(a)). Further degradation seems continued with negligible rate. Shape of the TGA profiles were found consistent with the increase of the heating rate. The DTG plots are shown in Fig. 1-I(b) and -II(b) for both inert and oxygenated atmosphere respectively. The method of calculation of T_o and T_m, was discussed in our previous study [26]. The adopted temperature programs of the TGA, along with the

values of degradation temperatures (T_o and T_m) and residual weight left after each TGA experiment are given in Table 2. The onset temperature (T_o) and peak degradation temperature (T_m) increased with the increase of the heating rates. The degradation temperatures (T_o and T_m) have lower values for oxygenated pyrolysis then in comparison to the pyrolytic degradation, which implies that the thermal degradation of PET-SDB under oxygenated environment occurs at a faster rate than that of the degradation under pyrolytic inert condition.

Fig. 2 represents the isothermal degradation (under N_2) curves of PET-SDB at four temperatures 325, 350, 375 and 400 °C. The weight loss during non-isothermal induction period (100 °C·min^{-1}) before the temperature reached the final temperature, can be neglected as the heating time is very less (high heating rate) compared to the isothermal holding time. The residual weight left after holding the isothermal temperature for 480 min varied with the increase of isothermal temperature (Table 2). At low temperature (325 °C), incomplete conversion led to the accumulation of almost 63% residual weight (8.65 mg), whereas at high isothermal temperature of 400 °C the residual weight reached to 10% of the feed (1.43 mg). Although, the conversion process in the isothermal run at 375 and 400 °C was completed in the later stages but the residual accumulation were 18% and 10% respectively. More residue yield at lower temperature was probably due to the formation of stable ring structure with less weight loss [30].

4.3. Kinetic analysis

The kinetic triplets (E_α, A_α, and f(a)) for non-isothermal degradation were calculated with the help of isoconversional principle. The variable activation energy (E_α) values were calculated using advance isoconversional method (AIC). The variation of activation energy (E_α) with respect to conversion are shown in Fig. 3 for the degradation reaction of PET-SDB under inert (N_2) and oxygenated (air) environment. The variation of activation energy was shown over the conversion range of 0.05 – 0.8 and 0.05 – 0.95 for N_2 and air environments respectively. The estimated values of activation energies were found higher in case of pyrolytic degradation than the oxidative degradation. The calculated values of activation energies were in the range of 203–355 kJ/mol and 145–218 kJ/mol under inert and oxygenated environment respectively. In both the TGA environment (N_2 and Air) the trend of activation energy started at lower values and increased over the period of degradation while maintaining nearly constant profile in the intermediate stages. However, a rapid growth of activation energy was observed between the conversion values of 0.7 – 0.8 as the material left in the crucible converted into stable char residue. A sudden fall of activation energy from 218 kJ/mol at $\alpha = 0.8$ to 145 kJ/mol at $\alpha = 0.91$ was observed in case of oxygenated degradation (Air), which implies the rapid combustion of char (residue) at higher temperature.

The values of pre-exponential factor or frequency factor always compensate the values of activation energy in the balance kinetic equation (Eq. 5) [7]. The logarithmic values of pre-exponential factor (A_α) should be linear with the activation energy across the entire conversion range [27]. By replacing the values of $(d\alpha/dt)_\alpha$ from the experimental data and activation energy (E_α) obtained by AIC method in Eq. (5), the values of $Af(\alpha)$ was determined over the range of conversion considered. The Criados' masterplot technique was utilized to calculate the reaction model $f(\alpha)$. The Criados' masterplots for the degradation data of PET-SDB obtained under the inert atmosphere are shown in Fig. 4(a). The reaction models were determined based on the best linear fit between experimental and theoretical masterplots. The linearity coefficients were estimated for each heating rate and the linearity coefficient values were plotted (Fig. 4(b)) with respect to each heating rate. Close examination of Fig. 4(b) revealed that the PET-SDB degradation under inert condition follows more than one reaction models $(f(\alpha))$ those are listed in Table 1S. The models corresponded to equal linearity coefficient (R^2) for A2, A3, A4 and F1 for the data obtained for all the heating rates considered. To identify the most suited
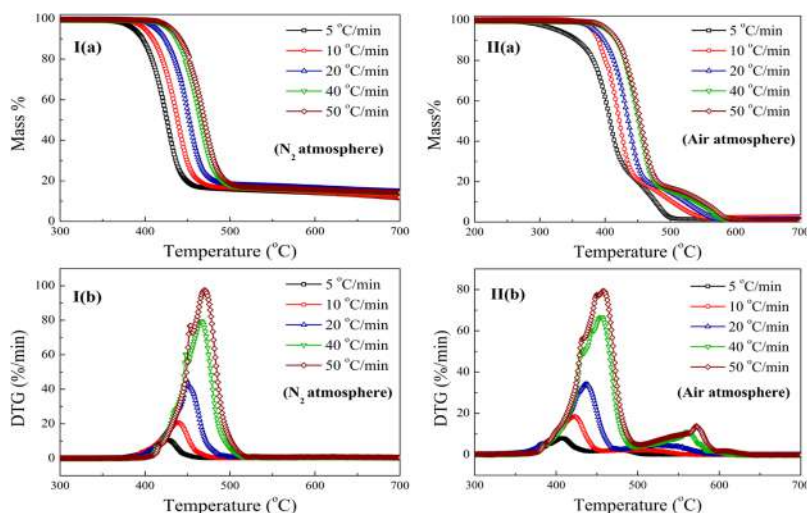
Fig. 1. (a) TGA and (b) DTG profiles of PET-SDB in presence I. N_2 and II. Synthetic air.

Table 2
Conditions of TGA and values of onset (T_o), peak degradation temperature (T_o) and residual weight of all the experiments.

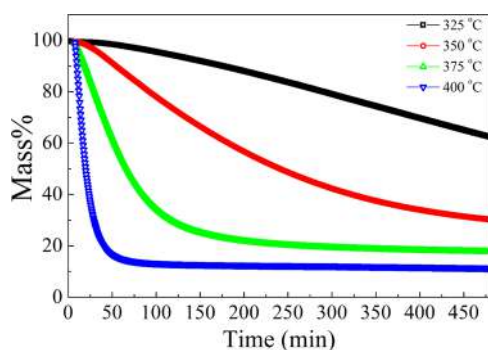| Heating condition	β °C·min⁻¹	Ffinal temperature (T_∞)°C	Isothermal holding time (t_h) min	Initial weight (W_o) mg	Onset temperature (T_o) °C	Peak degradation temperature (T_m) °C	Residual weight %
Non-isothermal (N_2)	5	700	0	8.94	385	427	11.52
	10			6.56	398	438	11.89
	20			8.68	408	448	14.75
	40			7.84	417	465	14.03
	50			6.69	427	470	14.2
Non-isothermal (Air)	5			8.98	362	406	1.066
	10			7.77	374	423	2.7
	20			7.35	389	437	1.11
	40			8.82	398	455	0.47
	50			7.54	405	458	0.53
Isothermal (N_2)	100	325	480	13.88	–	–	62.32
		350		11.42	–	–	30.21
		375		11.52	–	–	17.62
		400		12.65	–	–	11.305

Fig. 2. Isothermal weight loss of PET-SDB at various temperatures (under N_2 environment).
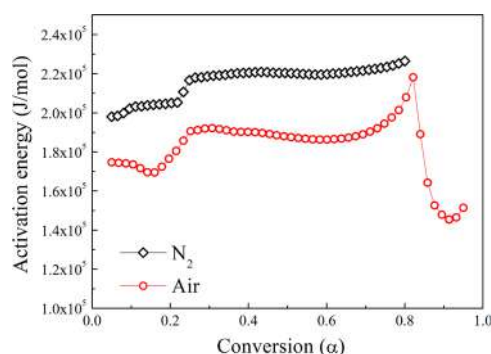

Fig. 3. Distributed activation energy (E_α) obtained by AIC method for PET-SDB under inert (N_2) and oxygenated atmosphere (Air).

reaction model among the four, the values of the pre-exponential factors were calculated by substituting the E_α and $f(\alpha)$ values in Eq. (6) for each value of α. The variation of pre-exponential factor (A_α) values in the conversion range considered are shown in Fig. 5, corresponding to all the four models. The pre-exponential values obtained were found marginally different for different reaction models. To estimate the correct set of the kinetic triplets, the $f(\alpha)$ function was confirmed by constable plots of each set of values of A_α in its logarithmic form and calculated values of E_α. The linearity of the constable plots were estimated by measuring the root mean square error (RMSE) (Table 3). The model F1 (first order given the lowest RMSE values among the four

models. However, oxygenated non-isothermal TGA profiles fallen in two-step degradation, which was clearly observed in the DTG plots (Fig. 2(b)). The division of the stages in the oxygenated DTG plot is shown in Fig. 6 for the heating rate 10 °C/min. The Criados' masterplots were evaluated for subsequent stages over a normalized conversion values for all the heating rates. In the TGA profiles under N_2 atmosphere, masterplots (Fig. 7) confirmed four possible reaction models (A2, A3, A4 and F1) (Fig. 8). All four models produced four different sets of pre-exponential factors as shown in Fig. 9. The RMSE values (Table 3) confirmed the lowest RMSE value for F1 model for PET-SDB
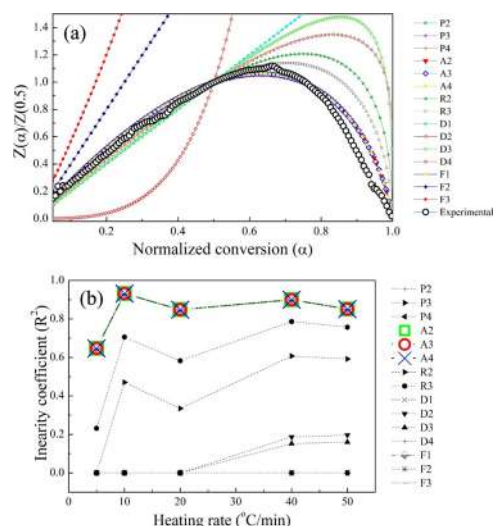
Fig. 4. (a) Criados' masterplots for non-isothermal (N_2) TGA of PET-SDB (b) Linearity coefficient (R^2) between theoretical and experimental masterplots at different heating rates.
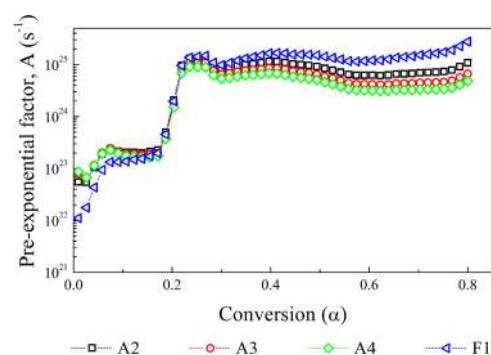

Fig. 5. Variation of pre-exponential factor (A) with conversion considering four reaction models for waste PET-SDB degradation under N_2 atmosphere.

Table 3
Root mean square error (RMSE) values between linear constable plot and calculated E_α vs. $\ln(A_\alpha)$ obtained for the four reaction models.

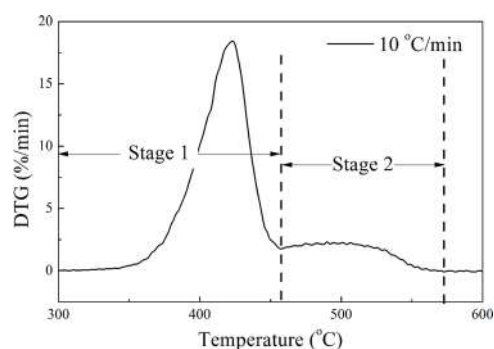| Reaction model	RMSE	
	TGA (inert)	TGA (synthetic air)
A2	0.458	1.18
A3	0.5	1.221
A4	0.523	1.243
F1	0.385	1.103

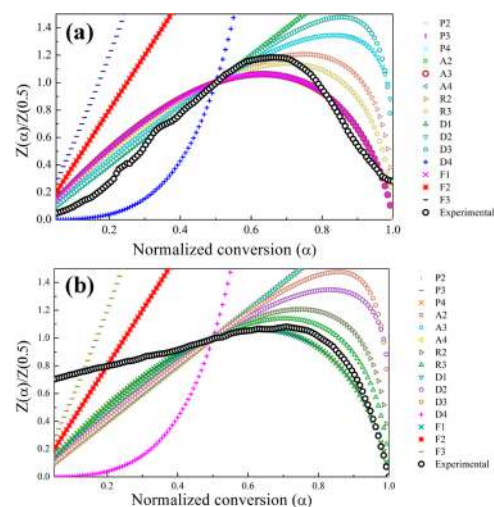**Fig. 6.** DTG (from TGA) profile of PET-SDB under air atmosphere at 10 °C/min.

Fig. 7. Criados' masterplots obtained from degradation data (in air atmosphere) of PET-SDB at (a) stage 1 and (b) stage 2.
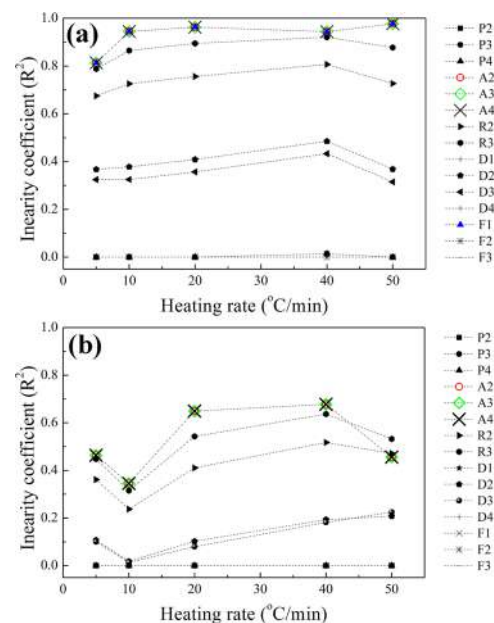

Fig. 8. Comparison of theoretical masterplots with experimental masterplots by linearity coefficient comparison at different heating rate for (a) stage 1 and (b) stage 2.
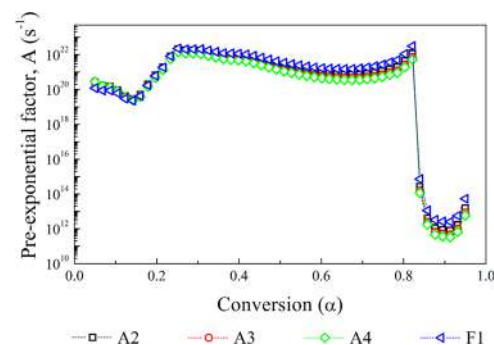

Fig. 9. Variation of pre-exponential factor (A_α) with conversion considering four reaction models for non-isothermal degradation of PET-SDB under air atmosphere.
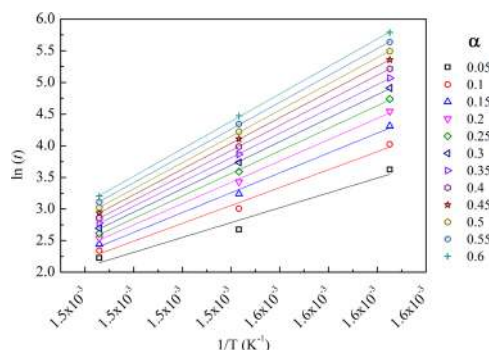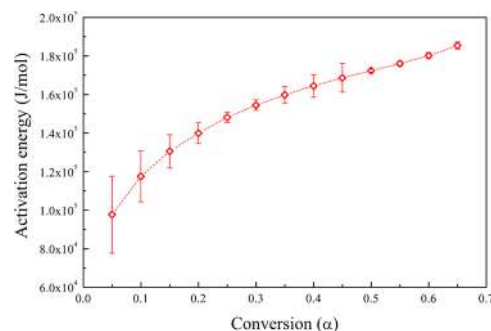
Table 4

Kinetic data comparison with the between the earlier studies and the present work.

Reference	TGA Condition	Method	E_α (kJ/mol)	Log (A_α) (s^{-1})	$f(\alpha)$
Cooney, Day and Wiles [31]	β = 0.1 – 100 °C/min; Air	Kissinger's Method	Stage 1 = 162.9 ± 72.4 Stage 2 = 202.1 ± 6.7 Stage 3 = 147.3 ± 3.5	–	F1 (first order)
		Freeman-Carroll Method	160.2 – 411.5 (stage 2 only)	–	
		Chatterjee-Conrad Method	Stage 1 = 53.5 – 169.3 Stage 2 = 147.0 – 301.4 Stage 3 = 200.6 – 292.2	–	
		Friedman Method	69.6 – 210.8		
		Ozawa Method	88.3 – 187.7	8.1 – 16.2	
Jenekhe, Lin and Sun [33]	β = 0.31 – 10 °C/min; N_2	Arrhenius plot	198.61 – 232.46	12.49 – 14.89	$(1 - \alpha)$, first order kinetics
		Isoconversional method	173.63 – 205.85	–	
Martín-Gullón, Esperanza and Font [9]	T = 27 – 800 °C, β = 5, 10, 20 °C /min, under He and O_2 (1:0, 3:1, 4:1 and 9:1)	Simplex method of Nedler and Mead	Part 1 (80% weight loss) = 256.4 (100% He) 186.0 (33% O_2 and 67% He) 194.0 (20% O_2 and 80% He) 203.5 (10% O_2 and 90% He)	Part 1 (80% weight loss) = 16.8 (100% He) 11.6 (33% O2 and 67% He) 12.2 (20% O2 and 80% He) 12.9 (10% O2 and 90% He)	For nth order, [f(α) = (1 – α)^n] n = 1.05 for part 1 (80% weight loss and 100% He) n = 1.02 (33% O2 and 67% He) n = 1.00 (20% O2 and 80% He) n = 1.00 (10% O2 and 90% He)
Saha, Maiti and Ghoshal [14]	T = 30 – 600 °C; β = 10, 15 and 25 °C /min	ASTM E698 nth Order model	162.15 – 210.64 322.3 – 338.98	26.37 – 34.81 54.76 – 57.73	n = 1; n = 1.72 – 1.82;
Current study	T = 30 – 600 °C; β = 5, 10, 20, 40 and 50 °C /min under N_2 and Air	Advance isoconversional (AIC)	203 – 355 (N_2) 145 – 218 (Air)	33.3 – 59.3 (N_2) 28.5 – 51.8 (Air)	F1 (N_2) F1 (Air)

degradation under air. Therefore, it was observed that the thermal degradation of PET-SDB under N_2 and Air followed the same F1 (first order) reaction model. A comparison of kinetic data of the present work and past studies dealing with the degradation kinetics of PET at pure form [31,32] or from the waste PET bottles [13] is summarized in Table 4. It was observed that the choice of kinetic model can affect the obtained kinetic results. Some of the values of the kinetic parameters of PET degradation reaction obtained in the past were close to the values obtained by AIC method in the current study.

A variation of activation energy was also determined from the isothermal degradation data of PET-SDB in TGA under N_2 atmosphere. The weight loss curves with respect to time are shown in Fig. 2. Applying the degradation data to Eq. (8), the ln(t) vs 1/T was plotted and shown in Fig. 10. The slope of the regression provided the global activation energy at each degree of conversion. The variable activation energy with conversion was shown in Fig. 11. The activation energy was found in the range of 98–183 kJ/mol between conversions of 0.05 to 0.6. The range of activation energy for the degradation of PET-SDB under non-isothermal TGA in N_2 atmosphere was found in the range of 196–217 kJ/mol between the conversion range of 0.05 – 0.6.

Fig. 11. Distribution of activation energy with the degree of conversion obtained from isothermal degradation profiles of PET-SDB (under N_2 atmosphere).

5. Conclusion

Polyethylene terephthalate can be found abundantly in any waste stream as empty soft drink bottles, containers, waste films and fibers etc. The degradation processes of these type of plastics by thermal means are complex and get affected by the presence of oxygen in the environment. Kinetic parameters obtained in the inert and oxygenated environment have shown different values. The activation energy values obtained by advance isoconversional methods (AIC) were in the range of 203–355 kJ/mol and 145–218 kJ/mol for N_2 and air environment respectively. The thermal degradation reaction of PET-SDB followed F1 (first order) model for both inert and oxygenated environment. Activation energy values calculated using multiple isothermal TGA were estimated in the range of 196–217 kJ/mol in the conversion range of 0.05 – 0.6. The establishment of kinetic triplets of PET-SDB degradation considering AIC method is a significant for the implementation of thermal processes like pyrolysis and combustion.

Acknowledgement

Fig. 10. Plot of ln (t) versus 1/T for isothermal TGA of PET-SDB.

(DST), Government of India.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.tca.2019.178340.

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