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KINETICS OF THERMAL DEGRADATION OF POLYMERS
Complementary use of isoconversional and model-fitting methods

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The thermal degradation of polymers has been studied quite extensively using thermogravimetric measurements. For the kinetic description, most of the times single rate heating data and model-fitting methods have been used. Since the thermal degradation of the polymers is a very complex reaction, the choice of a reliable model or a combination of kinetic models is very important. The advantages or the disadvantages of using a single heating rate or multiple heating rates data for the determination of the kinetic triplet have been investigated. Also, the activation energy has been calculated with the isoconversional and model-fitting methods. The reaction model was determined with the model-fitting method. The limits of all these procedures were investigated with experimental data of the thermal degradation of the poly(ethylene adipate) (PEAd).

Keywords: *isoconversional methods, model-fitting methods, polymer, TG, thermal degradation*

Introduction

Processes in condensed phase are extensively studied by thermoanalytical methods [1–6]. The mechanisms of these processes are very often unknown or too complicated to be characterised by a simple kinetic model [7–9]. They tend to occur in multiple steps that have different rates. To describe their kinetics, methods based on a single-step approximation are often used, either the model-free or the model-fitting ones.

The transformation rate for a solid-state reaction is generally assumed as the product of two functions, one depending only on the temperature T and the other depending only on the fraction transformed α [10]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{1}$$

where α is the degree of conversion, T the temperature and $f(\alpha)$ the conversion function (reaction model). $k(T)$ is a temperature dependent function given by the Arrhenius equation so that Eq. (1) takes the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

with A being the pre-exponential factor, E the activation energy and R the gas constant. The reaction model may take various forms, some of which are shown in Table 1. For non-isothermal experiments, the reaction rate at all times depends on both $f(\alpha)$ and $k(T)$, and the Arrhenius parameters (A and E), together with the reaction model $f(\alpha)$, are sometimes called the kinetic triplet [11].

In order to determine this triplet, various methods have been worked out. These methods can, in general, be categorized as: (*i*) isoconversional and (*ii*) model fitting methods. The isoconversional method is in fact, a ‘model-free’ method [12] which assumes that the conversion function $f(\alpha)$ does not change with the variation of the heating rate for all values of α. It involves the measuring of the temperatures corresponding to fixed values of α by experiments at different heating rates β [13]. The isoconversional methods are considered to give accurate values of the activation energy [14]. The pre-exponential factor usually can not be determined without the assumption of the reaction model ($f(\alpha)$). Few of these methods were proposed by Ozawa–Flynn–Wall (OFW) [15–17], Friedman [18, 19], Augis and Bennett [20], Kissinger–Akahira– Sunose (KAS) [21, 22], Li and Tang [23], Gao and Wang [24] and Vyazovkin [25, 26]. Model fitting methods of kinetic analysis depend on the reaction model and also assume the Arrhenius temperature dependence of the rate constant $k(T)$. They do not achieve a clean separation between the temperature dependent $k(T)$ and the reaction model $f(\alpha)$. Moreover, the temperature sensitivity of the reaction rate depends on the extent of conversion. As a result, these methods are considered to be approximate. There are several non-isothermal model-fitting methods, such as the Coats and Redfern method [27], the invariant kinetic parameter (IKP) method [28] and the multivariate non-linear regression method [29–33].

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Table 1 Sixteen different kinetic models and their conversion functions $f(\alpha)$

Kinetic model	Symbol	$f(\alpha)$
n-order reactions		
First order	F_1	$1-\alpha$
Second order	F_2	$(1-\alpha)^2$
n^{th} order	F_n	$(1-\alpha)^n$
Diffusion		
1-D diffusion	D_1	$1/2\alpha$
2-D diffusion	D_2	$[-\ln(1-\alpha)]^{-1}$
3-D diffusion–Jander	D_3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]$
3-D diffusion–Ginstling–Brounshtein	D_4	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$
Phase-boundary reactions		
Contracting area	R_2	$2(1-\alpha)^{1/2}$
Contracting volume	R_3	$3(1-\alpha)^{2/3}$
Prout–Tompkins	B_1	$\alpha(1-\alpha)$
expanded Prout–Tompkins	B_n	$(1-\alpha)^n\alpha^m$
First order with autocatalysis	C_1	$(1-\alpha)^{(1+\mathrm{Kcat}\,X)}$
n^{th} order with autocatalysis	C_n	$(1-\alpha)^{n(1+\mathrm{Kcat}\,X)}$
Nucleation and nuclei growth		
Avrami–Erofeev	A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
Avrami–Erofeev	A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
Avrami–Erofeev	A_n	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$

Most commonly, the kinetic triplet is determined by fitting a kinetic curve (α or $d\alpha/dt$ *vs.* T) obtained at a single heating rate to the rate equation in its differential Eq. (1) or integral form. The single heating rate model fitting methods can reproduce the experimental data satisfactorily. The quality of the fitting must be based also on variations of E and A from their true values. The higher the difference in E values for the selected reaction model from E values obtained by an isoconversional method, the lower is the capability that the selected model is the true one. The single and multiple heating rate methods are usually treated equally in the literature.

For the determination of the kinetic triplet, according to the literature, have been used mainly simulated data or a combination of simulated and experimental data of a single heating rate or multiple heating rates. Most of the times the experimental data that have been chosen, obey to single step kinetics. The study of more complicated systems seems to offer more information about the limits and the advantages and disadvantages of model-free and model-fitting methods. The reaction mechanism of polymer decomposition is a very complex radical chain mechanism, including initiation, propagation and termination reactions. As it is well known, two main types of reaction models are generally applied on the thermal degradation of polymers: the n^{th}-order model with only one parameter, the reaction order, and the first-order model. Other models have also been used occasionally, but they are complex models containing several fitting parameters [34–38]. Moreover, the calculation of the activation energy is accomplished using only one heating rate or different heating rates, each separately. These different choices of methods have resulted in a very wide range of reported activation energy values. With the use of a suitable correlation program we examined these cases, with the direct, however, correlation between the experimental and theoretical values using some of the above mentioned methods. For this study, experimental data of the thermal degradation of the aliphatic polyester poly(ethylene adipate) (PEAd) [39] have been chosen which exhibits only one step of mass loss. In this special case, it is interesting to explore what happens in the studied reaction, when more than one different mechanisms or the same mechanism with different activation energies coexist.

Kinetic methods

Isoconversional analysis

Ozawa–Flynn–Wall (OFW) method

This method involves the measurement of the temperature T, corresponding to a fixed value of the degree of conversion α, from the experiments at different heating rates β. The OFW method is based on the following equation:

$$\ln\beta=-1.0516\frac{E}{RT}+\text{const.} \qquad (3)$$

The plot of $\ln\beta$ *vs.* $1/T$ gives the slope $-1.0516E/R$ by which the activation energy has been evaluated. If the determined activation energy is the same for the various values of α, the existence of a single-step reaction can be concluded with certainty. On the contrary, a change of E with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis [40]. These complications are significant, especially in the case that the total reaction involves competitive mechanisms.

Friedman method

The differential isoconversional method suggested by Friedman is based on Eq. (2) that leads to:

$$\ln\left(\beta\frac{d\alpha}{dT}\right)=\ln A+\ln f(\alpha)-\frac{E}{RT} \quad (4)$$

For a constant α, the plot of $\ln[\beta(d\alpha/dT)]$ *vs.* $1/T$ obtained from curves recorded at several heating rates, should be a straight line whose slope gives us the value of E. It is obvious from Eq. (4) that if the function $f(\alpha)$ is constant for a particular value of α, then the sum $\ln f(\alpha)+\ln A/\beta$ is also constant.

Kissinger–Akahira–Sunose (KAS) method

This method is based on the expression

$$\ln\left(\frac{\beta}{T^2}\right)=\ln\left(\frac{AR}{E}\right)-\frac{E}{RT} \quad (5)$$

This is classified as an isoconversional method as we plot $\ln(\beta/T^2)$ *vs.* $1/T$ for constant conversion, α. Using this expression one gets the activation energy E at a particular α value.

Kissinger method

This well-known method assumes that the reaction rate reaches its maximum at the temperature (T_p) at the DTG peak. This assumption also implies a constant degree of conversion (α) at T_p. In many cases, the degree of conversion (α) at T_p varies with the heating rate and hence raises doubt about grouping this method into isoconversional category. The Kissinger equation [21] is

$$\ln\left(\frac{\beta}{T_p^2}\right)=-\frac{E}{RT_p}+\ln\left(\frac{AR}{E}\right) \quad (6)$$

The activation energy E can be obtained from the slope of the straight line $\ln(\beta/T_p^2)$ *vs.* $1/T_p$. This method provides the value of A apart from the value of activation energy E. Here one gets a single value of E using Eq. (6).

Augis and Bennett's method

According to the method suggested by Augis and Bennett [20],

$$\ln\left(\frac{\beta}{T_p-T_0}\right)=-\frac{E}{RT_p}+\ln A \quad (7)$$

where T_p and T_0 are the peak temperature and the onset temperature of the DTG peak respectively. The activation energy E can be obtained from the slope of the straight line $\ln[\beta/(T_p-T_0)]$ *vs.* $1/T_p$.

Model fitting methods

Model-fitting methods involve fitting different models to α-temperature curves and simultaneously determining the activation energy E and the pre-exponential factor A.

Multivariate non-linear regression method

Because all kinetic parameters affect the regress values through differential equations, they are, in the algebraic sense, nonlinear. With one-step reactions, however, the determination of the kinetic parameters can be turned into a multiple linear regression problem through suitable transformations and simultaneous conversion of Eq. (1). Nonlinear regression allows a direct fit of the model to the experimental data without a transformation, which would distort the error structure. An additional advantage lies in the fact that there are no limitations with respect to the complexity of the model. However, only iterative procedures can be employed for estimation of the kinetic parameters. The multivariate non-linear regression method applies a 6th-degree RUNGE-KUTTA process in a modified MARQUARDT [41, 42] procedure to solve a system of differential equations, which is essentially based on the differential equations relevant to the reaction types of Table 1 and their combinations. Fundamentally, multi-step processes can only be analyzed with nonlinear regression. But nonlinear regression proves to be advantageous for one-step processes as well, because it provides a considerably better quality of fit as compared to multiple nonlinear regressions.

It has been demonstrated recently that the complementary use of the model-free method with the isoconversional methods for one step reactions is very useful in order to understand the solid-state reaction kinetics [43].

Experimental

Synthesis of polyester

Synthesis of the aliphatic polyester poly(ethylene adipate) (PEAd) was performed following the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [44]. In brief, the proper amount of adipic acid (AdA) (0.55 mol) and ethylene glycol in a molar ratio 1/1.2 and the catalyst tetrabutyl titanate (TBT) ($3\cdot10^{-4}$ mol TBT/mol AdA) were charged into the reaction tube (250 mL) of the polycondensation apparatus. The reaction mixture was heated at 190°C in an argon atmosphere until the collection of almost all the theoretical amount of H_2O. In the second step of polycondensation, polyphosphoric acid (PPA) was added ($5\cdot10^{-4}$ mol PPA/mol AdA) and a vacuum (5.0 Pa) was applied slowly over about 30 min. The polycondensation temperature was kept stable at 230°C while the stirring speed was slowly increased to 720 rpm. The polycondensation reaction was finished after 1 h of heating.

Measurements

Thermogravimetric analysis was carried out with a Setaram SETSYS TG-DTA 1750°C. Samples (11±0.5 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 500°C in a 50 mL min^{-1} flow of N_2. Heating rates of 5, 10, 15 and 20°C min^{-1} were used and continuous records of sample temperature, sample mass, its first derivative and heat flow were taken.

Results and discussion

Experimental data of the thermal degradation of PEAd are used for the determination of the kinetic triplet, using a single heating rate or multiple heating rates. In Fig. 1 are presented the mass loss (%) and the derivative mass loss (DTG) curves at heating rate 5°C min^{-1}, at which one stage of mass loss can be followed. The relationship between kinetic parameters and conversion (α) can be found by using the mass loss curves recorded in TG dynamic curves. The determination of the reaction model for a single heating rate and for the multiple heating rates is based at the 'model fitting method'. Also, the determination of the activation energy, by using multiple heating rates, is based at the isoconversional methods. These methods were applied on the experimental data taken at the heating rates β=5, 10, 15 and 20°C min^{-1}, firstly at each heating rate separately. Sixteen different kinetic models were used for the fitting (Table 1) and the conversion range was $0<\alpha<1$.

The results of the fitting for the determination of the kinetic triplet for every reaction model (Table 1), using the multivariate non-linear regression method, are presented at Table 2 for each heating rate separately, according to the parameter Fexp. Here the Fexp is used in two different ways of making a decision, first to decide whether one or several models differ statistically from the best model with regard to fit quality and second to decide whether an additional step is statistically significant. As it can be seen, the classification of the kinetic models is not the same for all the heating rates and there are enough models, which have almost the same Fexp parameter. As it can be seen in Fig. 2, the fitting for the experimental mass loss with heating rate 20°C min^{-1} using the best reaction model C_n is very good. Only a small divergence is observed at the end of the degradation and it only refers to the 3% of the mass loss. This kind of divergences is expected for non-simulated data, especially for experimental data of the polymers' degradation due to the complexity of the reaction. For the kinetic description of the polymer degradation, two kinds of reaction models are mainly used at the literature [45–47], the first order (F_1) and the n^{th} reaction model (F_n), due to their simplicity. The results of the fitting with the three reaction models, the best and the other two usually used, are presented in Fig. 3. The fitting curves with the models C_n and F_n are very difficult to be distinguished. The same results can be obtained for at least the first five reaction models for each heating rate. Small divergences are shown only for the kinetic model F_1 (Fig. 3). The values of the activation energy E, the pre-exponential factor A and the reaction order n for the three reaction models (C_n, F_n, F_1) and the re-

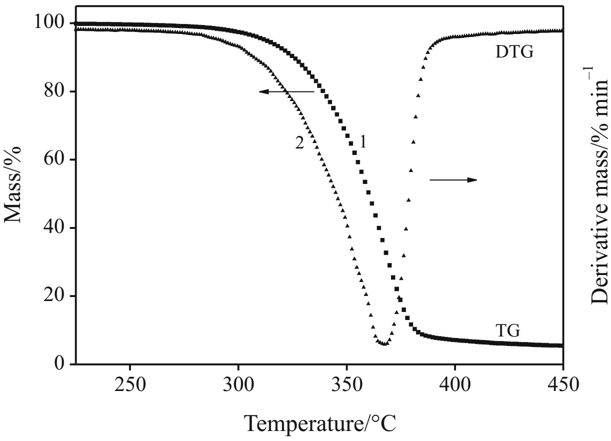

Fig. 1 TG and DTG curves of PEAd for heating rate β=5°C min^{-1}. 1 – mass loss%, 2 – DTG

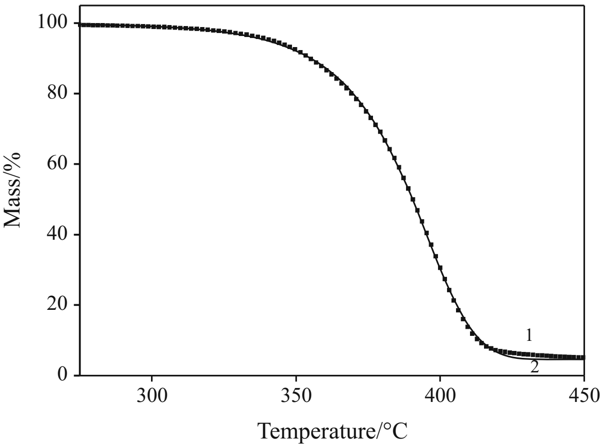

Fig. 2 Mass (%) and fitting curve with the C_n mechanism *vs.* temperature for heating rate β=20°C min^{-1}. 1 – mass (%), 2 – fitting curve

Table 2 Kinetic models for all heating rates

	Rate 5		Rate 10		Rate 15		Rate 20	
	Kinetic model	F_{exp}	Kinetic model	F_{exp}	Kinetic model	F_{exp}	Kinetic model	F_{exp}
1	C_n	1.00	C_n	1.00	C_n	1.00	C_n	1.00
2	C_1	1.00	C_1	1.00	C_1	1.13	C_1	1.01
3	D_3	1.32	R_3	1.84	A_n	1.93	F_n	1.63
4	R_3	1.33	F_n	1.85	F_n	1.98	R_3	1.76
5	F_n	1.33	D_3	1.87	B_{na}	1.99	D_3	1.84
6	R_2	1.55	R_2	2.13	F_1	2.29	A_n	2.21
7	A_n	1.81	A_n	2.44	R_3	2.52	A_3	2.27
8	D_4	1.81	D_4	2.47	D_3	2.60	A_2	2.49
9	F_1	1.87	A_3	2.51	A_2	2.64	F_1	2.93
10	A_2	1.95	A_2	2.56	A_3	2.82	R_2	2.95
11	A_3	2.03	F_1	2.62	R_2	3.99	D_4	3.83
12	D_2	2.43	D_2	3.25	D_4	5.37	D_2	6.06
13	D_1	4.50	D_1	5.82	D_2	7.78	D_1	13.25
14	B_1	7.25	B_1	8.23	D_1	14.89	F_2	25.58
15	F_2	9.08	F_2	12.38	F_2	17.32	B_1	172.7
16	B_{na}	217.5	B_{na}	353.3	B_1	193.0	B_{na}	989.4

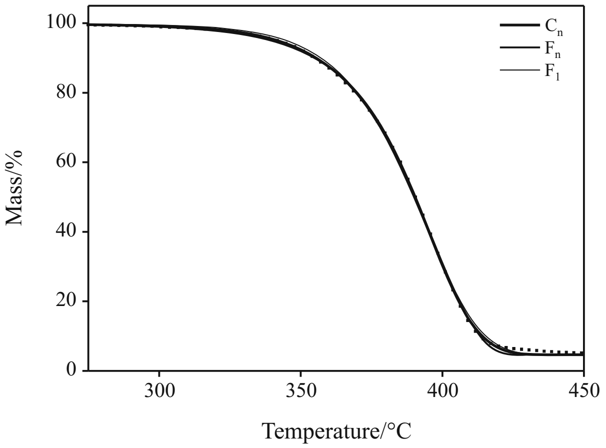

Fig. 3 Mass (%) and fitting curves with C_n, F_n and F_1 mechanisms *vs.* temperature for heating rate β=20°C min^{-1}

gression coefficients for every fitting curve are presented in Table 3. Comparing the values of *E* and *A* for the three models, we can conclude that there are large differences among them. For the same reaction model, the differences between the values of *E* and *A*, for all the heating rates, are not large. This conclusion is testified by using the calculated parameters of the heating rates 10 and 20°C min^{-1} of the C_n reaction model, on the experimental data of heating rate 10°C min^{-1}. Although the differences of the values of *E* and *A* are not great, the divergences of the fitting curves are quite clear (Fig. 4).

Experimental data of four different heating rates, 5, 10, 15, 20°C min^{-1} (Fig. 5), are used for the kinetic analysis with multiple heating rates. Another way to show the disadvantages of using only one heating rate data is to use one set of the calculated values of the kinetic triplet, for fitting the data of all the heating rates together. The results of this fitting using the kinetic model C_n and the parameters of the heating rate 15°C min^{-1} for *E* and *A* are presented in Fig. 6. It is obvious that the fitting is unacceptable, since only the fitting for heating rate 15°C min^{-1} is satisfactory.

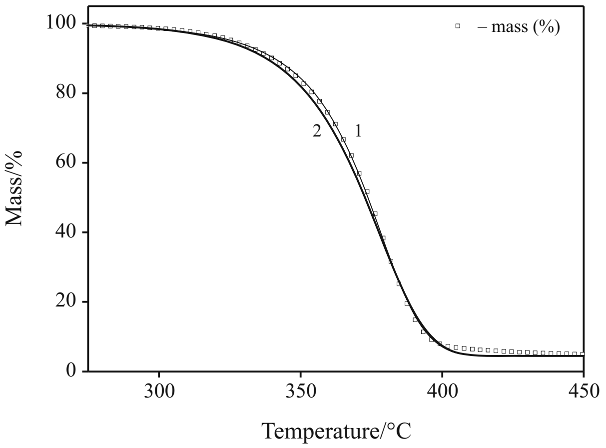

Fig. 4 Mass (%) with heating rate β=10°C min^{-1} and fitting curves with C_n mechanism with different parameters *vs.* temperature. 1 – β=10 and 2 – β=20°C min^{-1}

From the above analyses, using only experimental data of one heating rate for the fitting, it is obvious that there are more than three different reaction models that can fit the experimental data very well. These

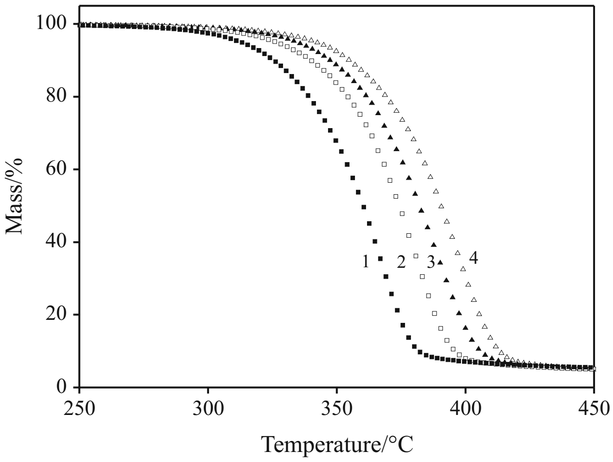

Fig. 5 Mass (%) for different heating rates *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

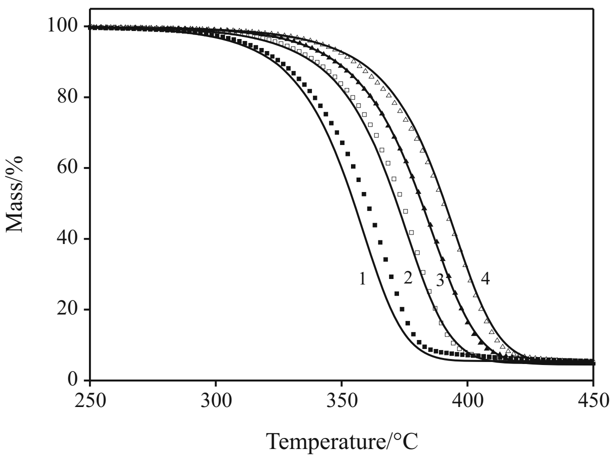

Fig. 6 Mass (%) for different heating rates and fitting curves with C_n mechanism with parameters of heating rate β=15°C min^{-1} *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

models are not the same at all the heating rates. Also, the different accepted models give different values for *E* and *A* and the same model gives different values for *E* and *A* for the different heating rates. These problems lead to the conclusion that it is difficult to choose the appropriate kinetic model and the use of only one heating rate for the determination of the kinetic triplet fails to serve any practical purpose. Probably, the only reason for which single heating rate model fitting methods can be used, is to get information about the possible complexity of the reaction model of the studied samples in a very short time. From the above analytical procedure it can be concluded, that for reliable kinetic evaluations, one should use the methods that employ kinetic curves obtained at multiple heating rates, or, more generally, at multiple heating programs (e.g., several heating rates or/and temperatures) [48–50].

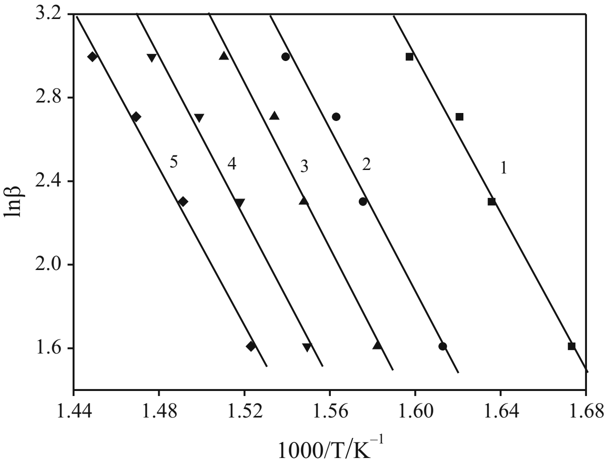

Fig. 7 OFW plots for different degrees of conversion α. 1 – α=0.1, 2 – α=0.3, 3 – α=0.5, 4 – α=0.8, 5 – α=0.95

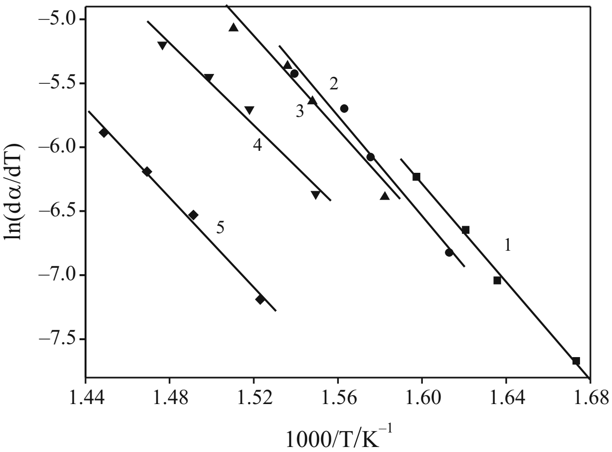

Fig. 8 Friedman plots for different degrees of conversion α. 1 – α=0.1, 2 – α=0.3, 3 – α=0.5, 4 – α=0.8, 5 – α=0.95

For the determination of the activation energy by using multiple heating rates the above analyzed isoconversional methods are used at first. Since every isoconversional method has different error, the use of more than one method can give a range of values for the activation energy at every particular value of α. The plots of lnβ *vs.* 1/*T* of the Ozawa, Flynn and Wall (OFW) method for PEAd are shown in Fig. 7. The straight lines fitting the data are nearly parallel, which is an indication that the activation energies at different degrees of conversion are almost similar. Friedman method was used by plotting ln(dα/d*T*) *vs.* 1/*T* for a constant α value and the activation energy was calculated (Fig. 8). The activation energy for different values of α is also calculated with the KAS method. The calculated values of activation energy from Augis and Bennett's and Kissinger's methods, which correspond to the peak temperature of the DTG curve, are 148.9 and 161.9 kJ mol^{-1}, respectively. These val-

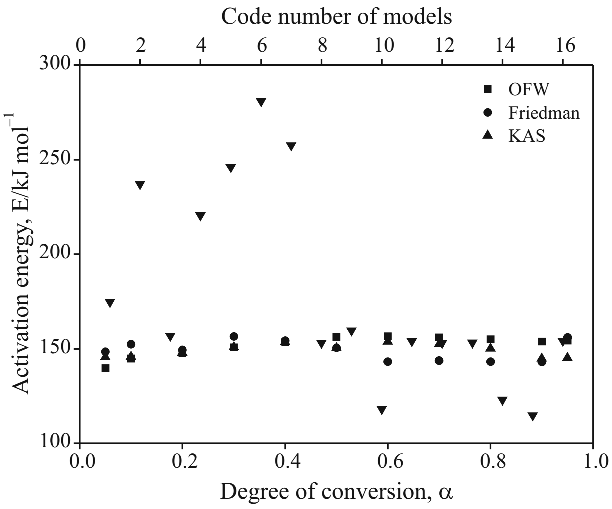

Fig. 9 Activation energy E, calculated with OFW, Friedman and KAS methods, *vs.* degree of conversion α and the calculated values of activation energy for different kinetic models

Table 3 Calculated values of E, A, n and the regression coefficient R of three kinetic models (C_n, F_n, F_1) for the conversion range $0<\alpha<1$

n^{th} order with autocatalysis (C_n)

Rate	log$A$/ s^{-1}	E/ kJ mol^{-1}	React. order, n	logK_{cat}	Regr. coef. R
5	7.58	126.4	0.97	0.48	0.999816
10	6.93	119.3	0.98	0.75	0.999865
15	7.79	128.2	1.08	0.61	0.999916
20	8.64	137.3	0.97	0.30	0.999926

n^{th} order (F_n)

Rate	log$A$/ s^{-1}	E/ kJ mol^{-1}	React. order, n	Regr. coef. R
5	10.75	161.1	0.69	0.999754
10	11.79	173.6	0.69	0.999750
15	12.06	176.9	0.85	0.999834
20	11.04	164.9	0.75	0.999879

1st order (F_1)

Rate	log$A$/s^{-1}	E/kJ mol^{-1}	Regr. coef. R
5	12.61	182.3	0.999654
10	13.81	197.2	0.999644
15	13.02	188.2	0.999804
20	12.66	184.3	0.999781

ues are in the same area as the values calculated with the other isoconversional methods.

In Fig. 9, the dependence of the activation energy on the different conversion values is presented and it is obvious that E can be considered as having almost a constant average value. The differences in the values of E calculated by the OFW and Friedman methods can be explained by a systematic error due to improper integration. The method of Friedman employs instantaneous rate values being, therefore, very sensitive to experimental noise. With OFW method, the equation used is derived assuming constant activation energy and by introducing systematic error in the estimation of E in the case that E varies with α, an error that can be estimated by comparison with the Friedman results [51].

The calculation of the activation energy using more than one isoconversional method can give an area of values for every particular value of α, where the true values of E can be found.

The multivariate non-linear regression method is used for the determination of the kinetic triplet. For this calculation the kinetic models of Table 1 are used. The calculated values of E and A for every kinetic model after the fitting are presented at Table 4. The quality of the mathematical fitting depends on the regression coefficient R (Table 4). The value of E can be determined from the model corresponding to maximum R. In some cases, the so-obtained value of E is significantly different from those obtained by the isoconversional methods. Thus, using this statistical criterion it is difficult to say which model is the real one. For such cases an R-value lower than R_{max} could correspond to the true kinetic model [52]. In our case, the best kinetic model is the C_n, which is the same as the model that it has been determined with the fitting using data of a single heating rate. From Table 4 it is obvious that there are seven kinetic models with high and comparable regression coefficients (0.99966–0.99983). The values of the activation energy for all these models are in the same area of values that have been calculated with the isoconversional methods. In Figs 10–12 are presented the plots of the fitting with the best model C_n and the models F_n and F_1, which are usually used for the kinetic description of the polymers' degradation. The quality of the fitting with the C_n and F_n models is very good. For both models only small divergences appear at the end of the degradation, an area which corresponds to the 3–4% of the mass loss. The divergence in this area is a little higher for the F_n model. Also, the values for E and A are almost the same. The other four kinetic models with the highest regression coefficients lead to plots analogous to those derived with the F_n model. The fitting with the F_1 model (Fig. 12) leads to higher divergences and it can be concluded that this model is unacceptable. Although the two methods, isoconversional and model fitting, are used complementary, seven different kinetic models give almost the same values for E and A, which are in the same area as the values calculated with the isoconversional meth-

Table 4 Calculated values of E, A of all kinetic models and its regression coefficient R. Conversion range $0<\alpha<1$

Model	log$A$/ s^{-1}	E/ kJ mol^{-1}	React. order n	R
F_1	11.93	174.7		0.99913
F_2	17.30	237.1		0.99421
F_n	10.36	156.8	0.596	0.99974
D_1	15.23	220.6		0.99552
D_2	17.14	246.1		0.99468
D_3	19.46	280.9		0.99342
D_4	17.46	257.5		0.99431
R_2	9.74	153.1		0.99970
R_3	10.13	159.6		0.99972
B_1	8.35	118.1		0.96031
B_{na}	10.20	154.0	0.695	0.99977
C_{1-x}	9.99	153.1		0.99982
C_{n-x}	10.01	153.2	0.932	0.99983
A_2	7.68	123.0		0.99513
A_3	7.00	114.7		0.98624
A_n	10.24	154.1	1.206	0.99966

ods and the fitting with these models is very good. Few of the accepted models can be ignored since the proposed mechanisms can not be connected to the degradation mechanisms of the polymers. Still after this, it is very difficult for everyone to choose the real kinetic model from the rest accepted models. This difficulty seems to be greater if we take into account that the reaction mechanisms of the polymers are very complex. For this reason, the choice of the appropriate kinetic model, considering one-step reaction, only denotes a possible mathematical form for the conversion function [53].

The quality of this fitting is at an acceptable level and the fitting can be stopped here [39]. Knowing that the thermal degradation of the polymers is a very complex reaction, in order to enhance further the quality of the fitting, we must consider more than one reaction mechanisms. This step of calculations is used in order to be able to discus the advantages and the disadvantages of the fitting using more than one reaction mechanisms, especially, when the mass does not show two steps of mass loss in which case the use of two reaction mechanisms is necessary.

These reactions can be consecutive, competitive and parallel. As it is easy to understand, the calculation of the kinetic triplet using different combination of the reactions is much more complicated now. From these combinations firstly we can ignore the competitive reactions, since the total mass loss for all the heating rates is the same (Fig. 5). In order to deter-

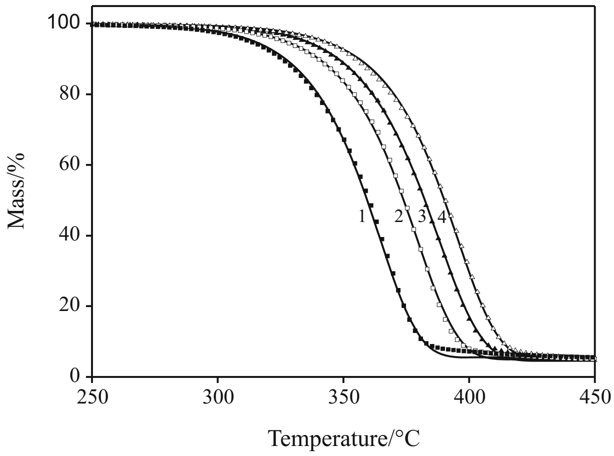

Fig. 10 Mass (%) for different heating rates and fitting curves with C_n mechanism *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

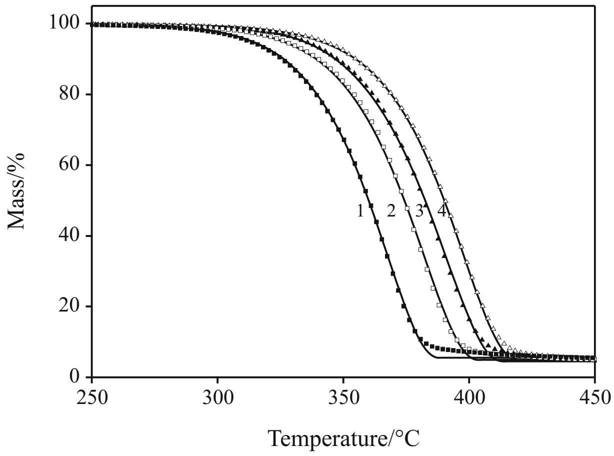

Fig. 11 Mass (%) for different heating rates and fitting curves with F_n mechanism *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

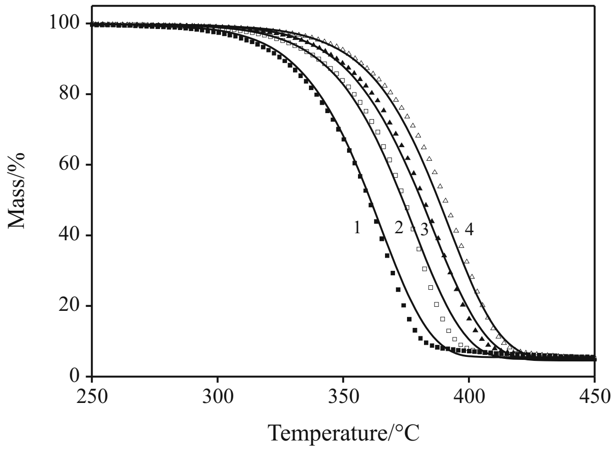

Fig. 12 Mass (%) for different heating rates and fitting curves with F_1 mechanism *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

Table 5 Calculated values of activation energy, pre-exponential factor and reaction order *n*

First mechanism	Kinetic model	E/kJ mol^{-1}	log$A$/s^{-1}	n	R
Consecutive reaction	F_n	155.0	10.38	0.29	0.999919
Parallel reaction	C_n	151.0	9.68	0.78	0.999926
Second mechanism	**Kinetic model**	**E/kJ mol^{-1}**	**log$A$/s^{-1}**	**n**	**R**
Consecutive reaction	C_n	150.7	8.82	1.80	0.999919
Parallel reaction	C_n	163.0	11.19	1.75	0.999926

mine the nature of the mechanisms through the comparison of the experimental and theoretical data, it is considered initially that the degradation of the polyester can be described only by a single mechanism. Then, knowing this mechanism, the best kinetic model, the data of the other mechanisms are determined, in order the better possible agreement between experimental and theoretical data to be achieved.

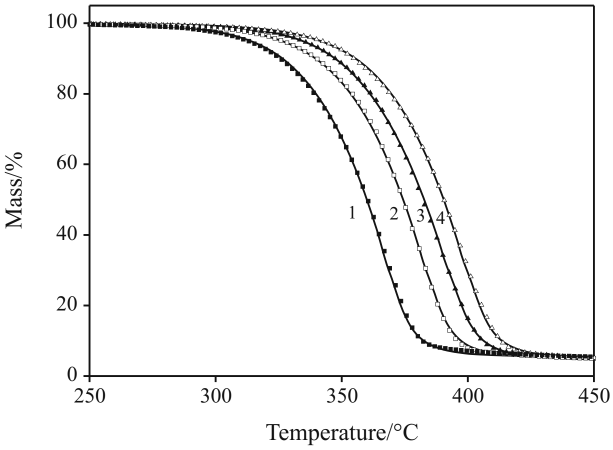

Fig. 13 Mass (%) for different heating rates and fitting curves with two consecutive mechanisms (F_n–C_n) *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

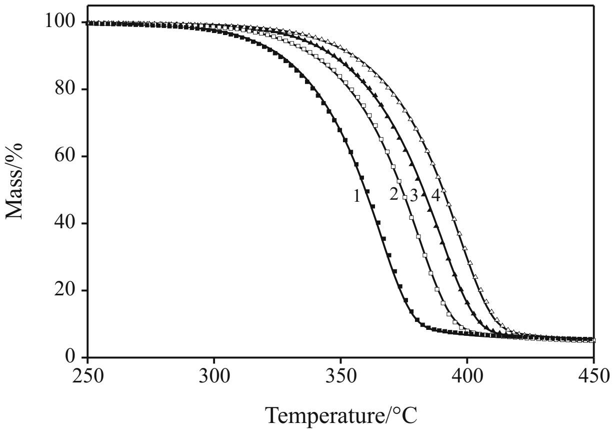

Fig. 14 Mass (%) for different heating rates and fitting curves with two parallel mechanisms (C_n–C_n) *vs.* temperature. 1 – β=5, 2 – β=10, 3 – β=15, 4 – β=20°C min^{-1}

Firstly, two consecutive mechanisms were used for the fitting. For the determination of the kinetic model of the second mechanism only three models were examined: The model C_n, which is the best kinetic model at the fitting using single and multiple heating rates data, and the models F_n and F_1, the most used models at the literature for the description of the polymers' degradation. At this stage of identification for the best possible results, we left the parameters (*E*, *A* and *n*) of the examined mechanisms to be recalculated and the results are presented in Table 5. The best fitting results for the second mechanism were taken with both the C_n and F_n kinetic models. Since the calculated value of the log(K_{cat}) has a very large negative value, and therefore the parameter K_{cat} is almost zero, the C_n kinetic model coincides with the F_n model. The results of the fitting are presented in Fig. 13 and the fitting to the experimental data is very good for the whole area of mass loss.

Secondly, the same above procedure was followed for the parallel reactions. For this combination of kinetic models, the best fitting for the second mechanism is calculated for the C_n model. Also, the fitting to the experimental data is very good for the whole area of mass loss and the calculated values are also presented in Table 5. Comparing the regression coefficients of the two kinds of combination of the models, it seems that the best fitting is for the parallel reaction, but this is only a mathematical procedure for the determination of the kinetic models. At the model-fitting method, for the two reaction mechanisms, at least 6 different parameters, two sets of kinetic triplets, are involved for the determination of the best kinetic model's combination. As it is obvious, the mathematical description of this can lead to different solutions with very high regression coefficients and very good fitting. So, the final choice for the appropriate combination is not necessary the best mathematical solution, but the solution which can describe theoretically the degradation reaction of the polymer. For this reason it is necessary to combine the results of the fitting with the conclusions of other experiments, in order the appropriate models' combination to describe better the degradation reactions [54].

Conclusions

Present study suggests that there are more than three different kinetic models that can fit the experimental data very well by using only experimental data of one heating rate for the determination of the kinetic triplet. Also, the different accepted models give different values for *E* and *A* and the same model gives different values for *E* and *A* for the different heating rates. This analytical study shows that for reliable kinetic evaluations one should use the methods that employ kinetic curves obtained at multiple heating rates.

The different isoconversional methods that have been used give values for the activation energy, which are in a very small area of values, for the particular degree of the conversion α. The model-fitting methods give very good fittings with more than one kinetic model. These have almost the same values for *E* and *A*, which are in the same area as the values calculated with the isoconversional methods. Since the reaction mechanism of the polymers is very complex, the choice of the appropriate kinetic model, considering a one-step reaction and the complementary use of the isoconversional and the model fitting methods, only denotes a possible mathematical form for the total reaction. Using two reaction mechanisms, the model-fitting method gives very high correlation coefficients and very good fittings with more than one combination of reaction models. So, it is necessary to combine the results of the fitting with the conclusions of other experiments in order the appropriate models' combination to describe better the degradation reactions.

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