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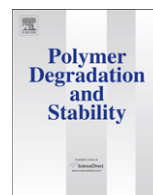SEE PROFILE

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A new model for the kinetic analysis of thermal degradation of polymers driven by random scission

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ABSTRACT

In this paper, a series of $f(\alpha)$ kinetic equations able to describe the random scission degradation of polymers is formulated in such a way that the reaction rate of the thermal degradation of polymers that go through a random scission mechanism can be directly related to the reacted fraction. The proposed equations are validated by a study of the thermal degradation of poly(butylene terephthalate) (PBT). The combined kinetic analysis of thermal degradation curves of this polymer obtained under different thermal pathways have shown that the proposed equation fits all these curves while other conventional models used in literature do not.

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1. Introduction

The ever increasing commercial importance of polymeric materials has entailed a continuous interest in their thermal stability. As a consequence, a huge number of papers dealing with this topic have been published in the last years [1–8]. The kinetic modelling of the decomposition plays a central role in many of those studies, being crucial for an accurate prediction of the materials behaviour under different working conditions [9–18]. A precise prediction requires the knowledge of the so called kinetic triplet, namely, the activation energy, the pre-exponential factor and the kinetic model, $f(\alpha)$. This latter parameter, also known as conversion function, is an algebraic expression that is associated with the physical model that describes the kinetics of a solid state reaction [19,20]. Therefore, the kinetic analysis also provides some understanding of the mechanism of the reaction under study [19–21]. Knowledge of the mechanism of thermal degradation of available macromolecules is very helpful in the field of the thermal stability of polymers [5].

Heating of polymers may produce either a breakage of the main chain, in the side chain or of the substituent atoms [5]. Random scission is a degradation mechanism often attributed to the pyrolysis of a wide number of polymers. It assumes a random

cleavage of bonds along the polymer chains, producing fragments of progressively shorter length that will eventually evaporate when the size is small enough [22–35]. However, the kinetics models describing the random scission mechanisms cannot be directly expressed as a function of the reacted fraction what makes difficult to apply to the kinetic analysis of thermal decomposition data obtained by TG or DSC. This fact would explain that most of the works focused on the study of the kinetics of polymer degradation assume "n-order" kinetic models, without any guarantee that these empirical conversion functions can actually describe correctly the polymer degradation mechanism. In the present work, the original Simha–Wall equation for depolymerisation is reformulated in such a way that the reaction rate can be directly expressed as a function of $f(\alpha)$ and the time or the temperature. The proposed equations will be validated by the study of the thermal degradation of poly(butylene terephthalate) (PBT), a commonly used commercial polymer which is widely recognized to decompose by means of a random scission mechanism [5], but it is yet to be studied using a random scission model. The analysis will be performed by means of the combined kinetic analysis method, which allows for the simultaneous analysis of a set of experimental curves recorded under any thermal schedule and without any assumption about the kinetic model followed by the reaction [36–40]. The kinetic parameters thus obtained are used to reconstruct the original curves in order to demonstrate that these new $f(\alpha)$ functions can be used successfully to describe random scission driven reactions, something that cannot be achieved by the widely used first or "n-order" kinetic models.

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2. Theoretical background

The reaction rate, $d\alpha/dt$, of a solid state reaction can be described by the following equation:

$$\frac{d\alpha}{dt} = A \exp(-E/RT)f(\alpha) \tag{1}$$

where A is the Arrhenius pre-exponential factor, R is the gas constant, E the activation energy, α the reacted fraction, T is the process temperature and $f(\alpha)$ accounts for the reaction rate dependence on α. The kinetic model, $f(\alpha)$ is an algebraic expression which is usually associated with a physical model that describes the kinetics of the solid state reaction [19]. Table 1 shows the functions corresponding to the most commonly used mechanisms found in the literature.

Eq. (1) is a general expression that describes the relationship among the reaction rate, reacted fraction and temperature independently of the thermal pathway used for recording the experimental data. In the case that the experimental data were recorded at a constant heating rate $\beta = dT/dt$, Eq. (1) can be written as follows [41]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp(-E/RT)f(\alpha) \tag{2}$$

For experiments performed under isothermal conditions, the sample temperature is rapidly increased up to a certain temperature and maintained at this temperature, while the reaction evolution is recorded as a function of the time. Under these experimental conditions, the term $A \exp(-E/RT)$ remains constant at a value k, and therefore Eq. (1) can be written as follows:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{3}$$

Sample controlled thermal analysis (SCTA) is another alternative approach which is attracting a rising interest for decomposition reactions [41–43]. In SCTA experiments, the evolution of the reaction rate with the time is predefined by the user and, most usually, it is maintained at a constant value along the entire process. In this case, the technique is named constant rate controlled analysis (CRTA). This way, by selecting a decomposition rate that is slow enough, the mass and heat transfer phenomena occurring during the reaction are minimized, which is an useful asset when dealing with reactions as complex as polymer pyrolysis. Thus, the results obtained by CRTA are more representative of the forward reaction than those resulting from more conventional methods [42,44–46]. Under constant rate

Table 1
$f(\alpha)$ kinetic functions for the most widely used kinetic models, and including the random scission models.

Mechanism	Symbol	$f(\alpha)$
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$
Random nucleation followed by an instantaneous growth of nuclei. (Avrami–Erofeev equation $n=1$)	F1	$(1-\alpha)$
Random nucleation and growth of nuclei through different nucleation and nucleus growth models. (Avrami–Erofeev equation)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Two-dimensional diffusion	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (Jander equation)	D3	$\dfrac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$
Three-dimensional diffusion (Ginstling–Brounshtein equation)	D4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
Random scission $L=2$	L2	$2(\alpha^{1/2}-\alpha)$
Random scission $L=3-8$	L3–L8	No symbolic solution

thermal analysis (CRTA) conditions, the reaction rate is maintained at a constant value $C = d\alpha/dt$ selected by the user and Eq. (1) becomes:

$$C = A \exp(-E/RT)f(\alpha) \tag{4}$$

2.1. Isoconversional analysis

Isoconversional methods (model-free methods) are used for determining the activation energy as a function of the reacted fraction without any previous assumption on the kinetic model fitted by the reaction. The Friedman isoconversional method [47] is a widely used differential method that, unlike conventional integral model-free methods, provides accurate values of activation energies even if the activation were a function of the reacted fraction [48]. Eq. (1) can be written in logarithmic form:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Af(\alpha)) - \frac{E}{RT} \tag{5}$$

Moreover, at a constant value of α, $f(\alpha)$ would be also constant and Eq. (5) would be written in the form:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \text{Const} - \frac{E}{RT_\alpha} \tag{6}$$

The activation energy $E\alpha$ can be determined from the slope of the plot of the left hand side of Eq. (6) against the inverse of the temperature T_α at constant values of α.

2.2. Combined kinetic analysis

The logarithmic form of the general kinetic Eq. (1) can be written as follows:

$$\ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = \ln A - E/RT \tag{7}$$

The plot of the left hand side of the equation versus the inverse of the temperature will yield a straight line if the proper $f(\alpha)$ is considered for the analysis. The activation energy can be calculated from the slope of such plot, while the intercept leads to the pre-exponential factor. As no assumption regarding the thermal pathway is made in Eq. (7), the kinetic parameters obtained should be independent of the thermal pathway. Thus, this method would allow for the simultaneous analysis of any sets of experimental data obtained under different thermal schedules [37,38]. To overcome the limitation related to the fact that the $f(\alpha)$ functions were proposed assuming idealized physical models which may not be necessarily fulfilled in real systems, a new procedure has been introduced in a recent work, where the following $f(\alpha)$ general expression was proposed [38]:

$$f(\alpha) = c(1-\alpha)^n \alpha^m \tag{8}$$

This equation is a modified form of the Sestak–Berggren empirical equation [49]. It has been shown that it can fit every function listed in Table 1 by merely adjusting the parameters c, n and m by means of the maximize function incorporated in Mathcad software [37,38]. Therefore, Eq. (7) works as an umbrella that covers the most common physical models and its possible deviations from ideal conditions. From Eqs. (7) and (8) we reach:

$$\ln\left(\frac{d\alpha/dt}{(1-\alpha)^n \alpha^m}\right) = \ln cA - E/RT \tag{9}$$

This last equation should fit experimental data obtained under any heating schedule. The Pearson linear correlation coefficient between the left hand side of the equation and the inverse of the
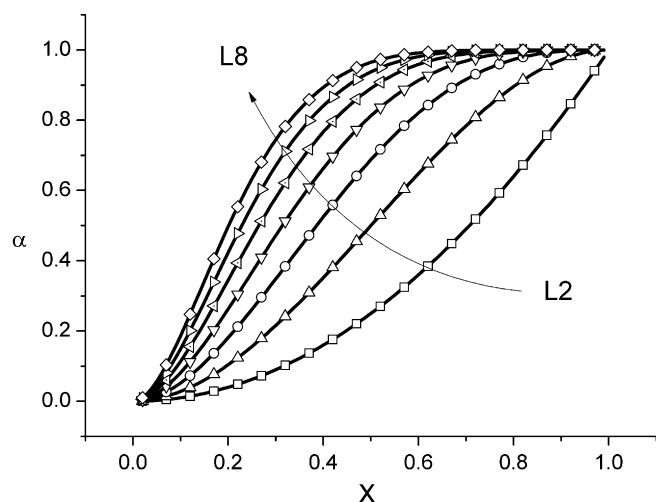
Fig. 1. Relationship between the actual fraction of bonds broken (x) and α for different random scission kinetic functions, according to Eq. (12).

temperature is set as an objective function for optimization. By means of the maximize function of the software Mathcad, parameters n and m that yield the best linear correlation are obtained, and the corresponding values of E can be calculated.

3. Proposal of random scission kinetic functions

According to Simha and Wall [50], the cleavage of bonds in random scission processes follows first order kinetics and the following expressions hold true:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(1-x) = A\,e^{-E/RT}(1-x) \tag{10}$$

$$1 - \alpha = (1-x)^{L-1}\left[1 + x\frac{(N-L)(L-1)}{N}\right] \tag{11}$$

where x, N and L are the fraction of bonds broken, the initial degree of polymerization and the minimum length of the polymer that is not volatile, respectively. As L is usually negligible in comparison to N, Eq. (11) can be simplified to:
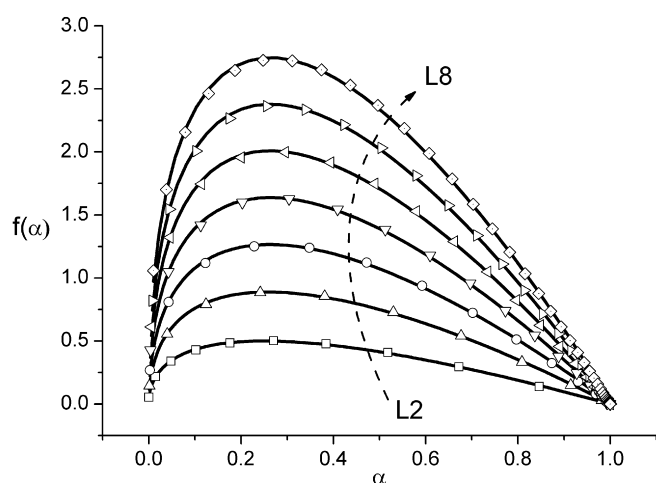

Fig. 2. Comparison of the random scission $f(\alpha)$ functions from $L = 2$ to $L = 8$ calculated numerically (solid lines) with those obtained from Eq. (8) using the c, n and m parameters included in Table 2.

Table 2
Values for the parameters n, m and c that make the Eq. (7) fit the random scission $f(\alpha)$ kinetic functions for different values of L.

L	c	n	m
2	1.204	1.119	0.4
3	2.080	1.057	0.396
4	2.929	1.039	0.394
5	3.767	1.030	0.391
6	4.597	1.024	0.389
7	5.422	1.020	0.388
8	6.242	1.017	0.386

$$\alpha = 1 - (1-x)^{L-1}[1 + x(L-1)] \tag{12}$$

As the thermal degradation processes are mainly studied by thermogravimetry, where the weight lost is directly related to the degree of degradation, it is noteworthy to point out that only the broken bonds that lead to a fragment small enough would actually evaporate and therefore be detected as mass lost. Then, a relationship between the detected weight loss and the actual reacted fraction must be established before the equations can be used. That can be achieved by means of Eq. (12), which relates the reacted fraction in terms of mass lost with the fraction of bonds broken. This relationship is shown graphically in Fig. 1. However, as x cannot be measured by conventional techniques, and L is very difficult to obtain experimentally, the application of Eq. (12) has been severely limited. Nevertheless, by differentiating Eq. (12), and incorporating Eq. (10) we get:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = L(L-1)x(1-x)^{L-2}k(1-x) \tag{13}$$

This way, taking into account Eq. (1), we can deduct the conversion function $f(\alpha)$ that describes a random scission model:

$$f(\alpha) = L(L-1)x(1-x)^{L-1} \tag{14}$$

Many kinetic analysis methods involve the fitting of experimental data to a certain kinetic model [21]. This requires the $f(\alpha)$ functions
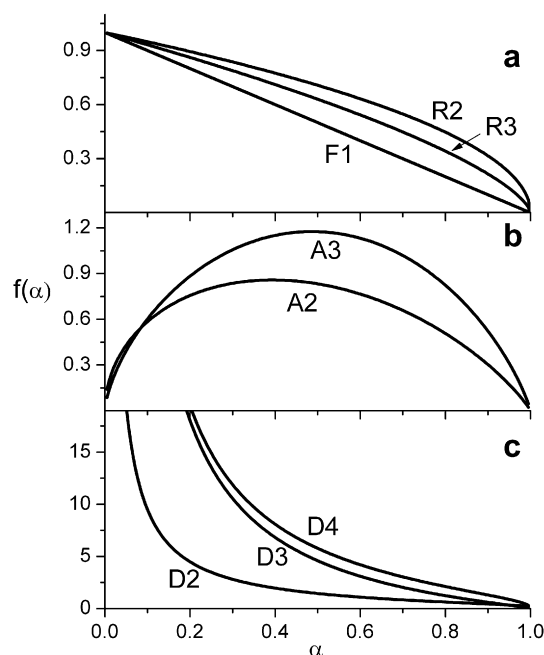

Fig. 3. The $f(\alpha)$ conversion functions for the different kinetic models most commonly used in literature for solid state reactions: "n-order" (a), nucleation and growth (b), and diffusion controlled (c) kinetic models.
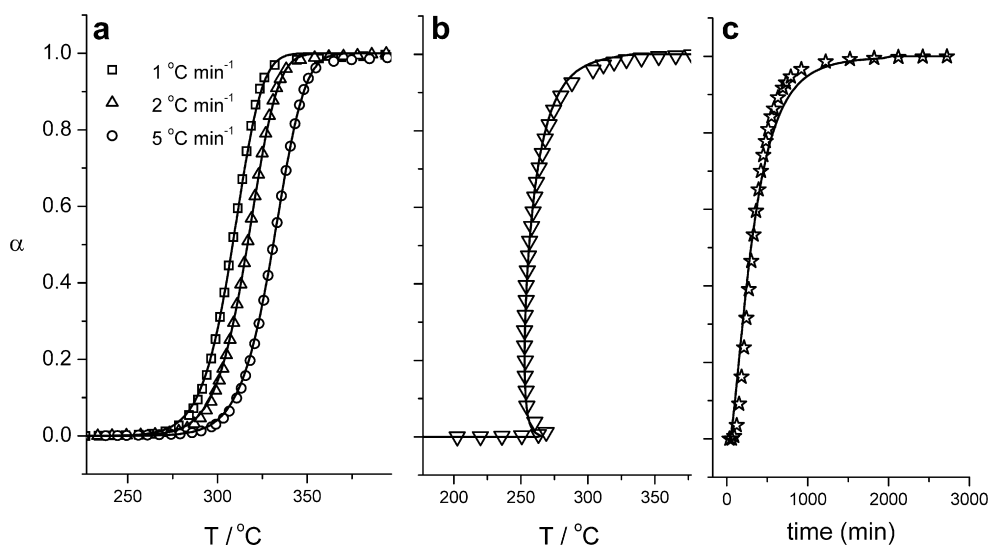
Fig. 4. Experimental curves (dotted lines) obtained for the thermal decomposition of poly(butylene terephthalate) under 70 cc N_2 flow and the following experimental conditions: (a) linear heating rate of 1, 2 and 5 °C min^{-1}; (b) sample controlled degradation rate of 8.3 10^{-4} min^{-1}; and (c) isotherm at 310 °C. Reconstructed curves (solid lines) using the following kinetic parameters: $n = 1.138$, $m = 0.294$, $E = 180$ kJ mol^{-1} and $A = 2$ 10^{-13} min^{-1}.

for the different models to be previously known. Thus, if random scission mechanisms are to be used in this way, $f(\alpha)$ must be determined. However, a symbolic solution can only be reached for $L = 2$. In this latter case, from Eqs. (12) and (13) we obtain:

$$\frac{d\alpha}{dt} = 2k(\alpha^{1/2} - \alpha) \qquad (15)$$

Therefore, $f(\alpha)$ must be:

$$f(\alpha) = 2(\alpha^{1/2} - \alpha) \qquad (16)$$

Taking into account that the relationship between x and α is established in Eq. (12), for any given L and assigning values to α, from Eqs. (12) and (14) it is possible to calculate numerically the corresponding $f(\alpha)$ conversion functions, which are plotted against α in Fig. 2.

As it was stated in Section 2.2, the general expression in Eq. (8) can be used to fit the most used kinetic models by adjusting three fitting parameters. This optimization procedure can be extended to the random scission $f(\alpha)$ functions here developed. Thus, Table 2 lists the values of c, n and m that make Eq. (8) match the functions plotted in Fig. 2. The equations resulting from introducing in Eq. (8) the proper parameters can now be used as random scission $f(\alpha)$ conversion functions in any kinetic analysis method. For the sake of comparison, Fig. 3 includes the $f(\alpha)$ conversion functions for the different kinetic models most commonly used in literature for solid state reactions: "n-order", diffusion controlled and nucleation and growth kinetic models. The shape of the functions included in Fig. 3 are quite different to those of the random scission $f(\alpha)$ conversion plots (Fig. 2). Therefore, as the results of a kinetic analysis are heavily dependent on the kinetic model considered, random scission driven reactions could never be adequately described by other models, and in particular by "n-order" models, as it is often done in literature, and doing so will only result in obtaining the wrong kinetic parameters.

4. Experimental

A commercial poly(butylene terephthalate) from Aldrich, (product number 435147) was used for performing the study. Thermogravimetry measurements were carried out with a homemade

TGA instrument that uses a CI Electronics Ltd. electrobalance connected to a gas flow system to work in inert atmosphere (70 cc min^{-1} N_2). Small samples (9 mg) were used in order to minimize heat and mass transfer phenomena. They were placed on a 1 cm diameter platinum pan inside a low thermal inertia homemade furnace. The instrument allows working either under conventional linear heating conditions or under sample controlled conditions. A description of the experimental setup can be found in references [43,51,52]. A set of thermal degradation curves, obtained under linear heating rate, constant rate and isothermal conditions, were carried out. Experimental integral curves were differentiated by means of the Origin software (OriginLab) to obtain the differential curves required for the kinetic analysis.

5. Results and discussion

Fig. 4 shows the experimental curves recorded for the thermal degradation of poly(butylene terephthalate) under linear heating
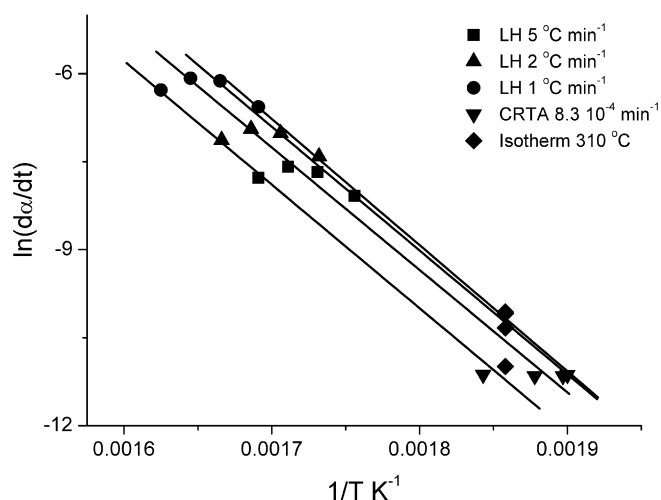

Fig. 5. Friedman plots resulting of the isoconversional analysis of the experimental curves presented in Fig. 4.

Table 3
Activation energy values for different values of conversion and their correlation coefficients, obtained by the Friedman isoconversional analysis of the curves showed in Fig. 4.

α	r	Ea (kJ)
0.1	0.999	179 ± 6
0.2	0.999	179 ± 5
0.3	0.999	179 ± 4
0.4	0.999	177 ± 5
0.5	0.998	176 ± 6
0.6	0.997	174 ± 7
0.7	0.997	175 ± 7
0.8	0.997	175 ± 8
0.9	0.995	177 ± 8

rate (a) sample controlled (b) and isothermal (c) conditions. Linear heating rate experiments were carried out at 1, 2 and 5 °C min^{-1}; sample controlled experiment at the constant reaction rate of 8.3 10^{-4} min^{-1}; and the isothermal experiment at 310 °C.

Fig. 5 shows some of the Friedman isoconversional plots obtained from the simultaneous analysis performed by means of Eq. (11) for the experimental curves included in Fig. 4. The activation energy calculated from the slope of the Friedman plots for different α values are included in Table 3 together with their corresponding linear regression coefficients. These results demonstrate that a constant activation energy $E = 176$ kJ mol^{-1} can describe the entire process and is independent of the α values.

The experimental curves presented in Fig. 4 will be analyzed first by means of the combined kinetic analysis method according to Eq. (7), assuming a "n-order" function as it is frequently done in the literature. The results will then be compared with those obtained when the fitting procedure is performed using the random scission equation as the conversion function, as is proposed here.

5.1. Fit to a "n-order" function

Fig. 6 shows the result of the combined analysis of every experimental curve in Fig. 4. The left hand side of the Eq. (7), using $(1 - \alpha)^n$ as $f(\alpha)$ function, is plotted versus $1/T$. The fit of the experimental data to the "n-order" kinetic function is not good, especially the points at both high and low α values that present an important deviation. The best fit is obtained for an order $n = 0.923$, and leads
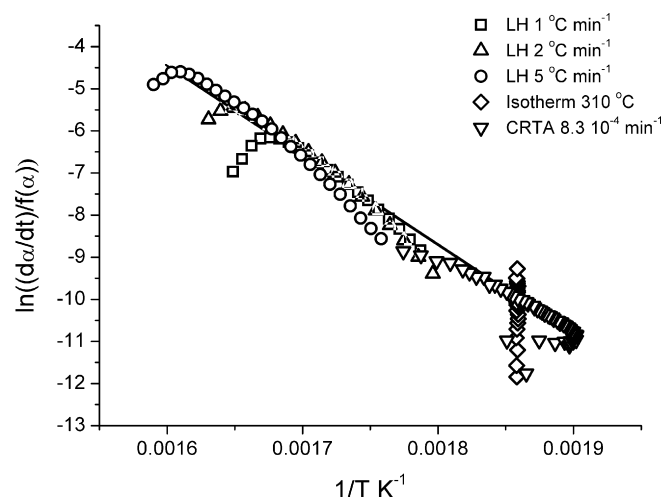

Fig. 6. Combined kinetic analysis of the experimental curves included in Fig. 3 for the results of the optimization procedure of Eq. (7), that is $n = 0.923$, $E = 176$ kJ mol^{-1} and $A = (6.6 \pm 1.5)\ 10^{12}$ min^{-1}, when $(1 - \alpha)^n$ is used as the conversion function $f(\alpha)$.

to an activation energy value of 176 ± 1 kJ mol^{-1}, and a correlation factor of 0.990. The slope of the plot leads to the activation energy and the intercept to an Arrhenius pre-exponential factor of $(6.6 \pm 1.5)\ 10^{12}$ min^{-1}. Despite of the not so good fit, the activation energy obtained is interestingly the same that was yielded by the isoconversional analysis, in which no kinetic model was assumed.

In order to check the validity of the kinetic parameters calculated by the method, a set of curves have been simulated assuming identical heating conditions as those used in the experiments, and the kinetic parameters obtained from the analysis. The simulations have been performed from Eq. (1) and the equations that define the heating conditions, i.e. linear heating or constant rate. Both the simulated and the original experimental curves are plotted in Fig. 7 for comparison. It seems clear from the simulated curves that the parameters obtained from the analysis fail to properly reconstruct the experimental data, mainly at low values of α. It can be deduced from the sample controlled experiment, Fig. 7b, the existence of a short induction period at the beginning of the process that the "n-order" model is unable to account for. This inability is responsible for the incorrect reconstruction of the experimental curves.
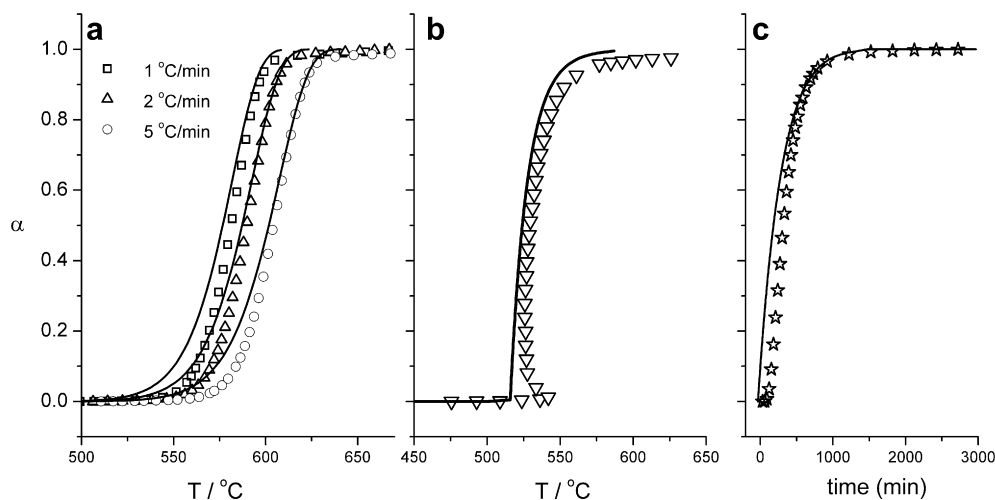

Fig. 7. Experimental curves (dotted lines) obtained for the thermal decomposition of poly(butylene terephthalate) under 70 cc N$_2$ flow and the following experimental conditions: (a) linear heating rate of 1, 2 and 5 °C min^{-1}; (b) sample controlled degradation rate of 8.3 10^{-4} min^{-1}; and (c) isotherm at 310 °C. Reconstructed curves (solid lines) with the kinetic parameters obtained when $(1 - \alpha)^n$ is used as the conversion function $f(\alpha)$, that is $n = 0.923$, $E = 176$ kJ mol^{-1} and $A = (6.6 \pm 1.5)\ 10^{12}$ min^{-1}.
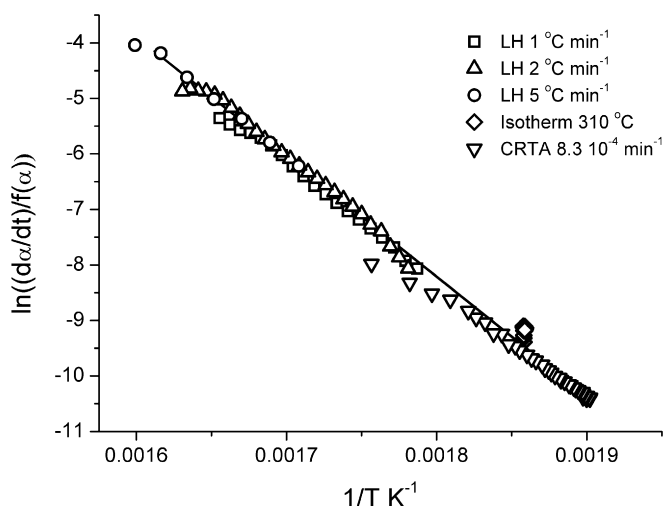
Fig. 8. Combined kinetic analysis of curves included in Fig. 4 by means of Eq. (9) for the resulting of the optimization procedure, i.e. $n = 1.138$ and $m = 0.294$.

Fig. 9. Comparison of the $f(\alpha)$ functions (lines) normalized at $\alpha = 0.5$ corresponding to some of the ideal kinetic models included in Table 1 with the reduced Sestak–Berggren equation (squares) including the parameters n and m calculated by means of the Eq. (9) for the thermal degradation of poly(butylene terephthalate).

5.2. Fit by means of the random scission equation

The combined kinetic analysis of the whole set of experimental data shown in Fig. 4 was performed by means of the Eq. (9). Fig. 8 shows the plot of the values obtained for the left hand side of Eq. (9) versus $1/T$. It is clear that all experimental data can be properly fitted by a single straight line with $n = 1.138$ and $m = 0.294$, giving a correlation factor of 0.997. The slope of the plot leads to an activation energy value of 180 ± 1 kJ mol^{-1} and the intercept to an Arrhenius pre-exponential factor of (2.0 ± 0.3) 10^{13} min^{-1}. The calculated activation energy is very close to that obtained by means of Friedman isoconversional analysis, in which no kinetic model had been previously assumed, thus validating the kinetic parameters obtained by the combined kinetic analysis procedure.

Fig. 4 shows the set of curves that have been simulated using the kinetic parameters obtained from the combined analysis, assuming identical heating conditions as those used in the experiments. This time, as it can be observed in Fig. 4, both the reconstructed (simulated) curves and the experimental ones match almost exactly, proving that the kinetic parameters calculated by means of the Sestak Berggren equation, i.e. activation energy, pre-exponential factor and conversion function, are perfectly suitable to describe the process.

Fig. 9 shows the comparison of $f(\alpha)$ function resulting from the combined analysis, i.e. $(1 - \alpha)^{1.138} \alpha^{0.294}$, with some of the conversion functions listed in Table 1, and with the random scission $f(\alpha)$ functions corresponding to $L = 2$ and $L = 8$. All conversion functions are normalized at $f(0.5)$ for an easier differentiation in the shape between the different models. The plot shows that the conversion function associated with the thermal degradation of PBT has a very close resemblance to a random scission model, although it does not exactly match it, probably due to the deviation of the real process from the ideal conditions assumed in the model.

The results here obtained are in good agreement with the statements previously made in the literature about the fact that first order models are able to describe polymer degradation only at high degrees of conversion [53,54]. As it can be observed in figure 9, both first order and random scission functions are very similar for α values over 0.5. The differences in both models could be attributed to the fact that at the beginning, the chain cleavage would hardly yield a loss of mass, hence the induction time that appears in the CRTA curve at very low values of α. After the reaction has underwent some progress, and the polymer chains have been sufficiently shortened, successive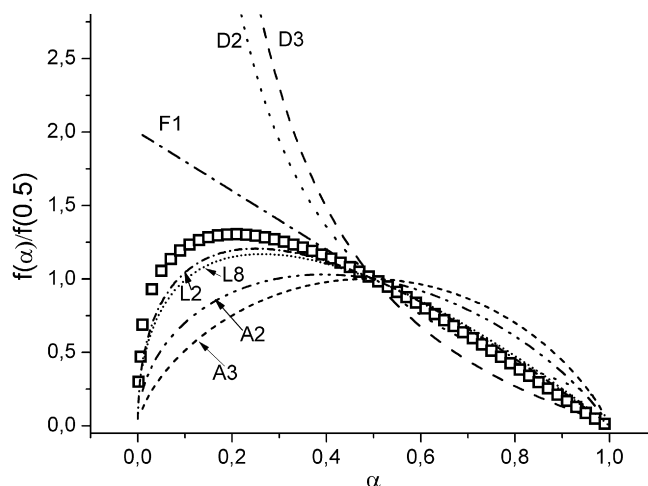 ruptures will start producing fragments small enough to evaporate so that eventually the system has to cool down in order to maintain the reaction rate that was predetermined in the experiment setup. At this point, both conversion functions become very similar, giving the wrong impression that a random scission driven process can be described by a first order model at high values of α.

6. Conclusions

In this work, Simha–Wall equations for the description of random scission mechanisms have been reformulated and new $f(\alpha)$ conversion functions for these models have been developed. These new equations have been applied together with combined kinetic analysis to study the thermal degradation of poly(butylene terephthalate). Experimental curves obtained under linear heating, isothermal and sample controlled conditions have been analyzed simultaneously, obtaining kinetic parameters which can be used to successfully reconstruct all the curves. The close match between the reconstructed curves and the original ones proves the validity of the kinetic analysis method and the results. The close similarity between the experimental conversion function obtained from the combined analysis with that corresponding to random scission proves the latter as the mechanism that drives the decomposition of PBT.

Additionally, it has been demonstrated that first order or "*n*-order" conversion functions are completely different from that of random scission mechanisms. Thus, random scission driven reactions could never be correctly described by means of "*n*-order" empirical models, as it has been done frequently in the literature for describing the thermal degradation of polymers.

Acknowledgement

References

[1] Simon P, Cibulkova Z, Thomas P. Accelerated thermooxidative ageing tests and their extrapolation to lower temperatures. Journal of Thermal Analysis and Calorimetry 2005;80(2):381–5.
[2] Capone C, Di Landro L, Inzoli F, Penco M, Sartore L. Thermal and mechanical degradation during polymer extrusion processing. Polymer Engineering and Science 2007;47(11):1813–9.

[3] Dobkowski Z. Thermal analysis techniques for characterization of polymer materials. Polymer Degradation and Stability 2006;91(3):488–93.

[4] Han MG, Kim S. Controlled degradation of poly(ethyl cyanoacrylate-co-methyl methacrylate) (PECA-co-PMMA) copolymers. Polymer 2009;50(5):1270–80.

[5] Pielichowski J, Njuguna J, editors. Thermal degradation of polimeric materials. Shawbury: Rapra Technology Ltd.; 2005.

[6] Stolov AA, Simoff DA, Li J. Thermal stability of specialty optical fibers. Journal of Lightwave Technology 2008;26(17-20):3443–51.

[7] Wolfrum J, Eibl S, Lietch L. Rapid evaluation of long-term thermal degradation of carbon fibre epoxy composites. Composites Science and Technology 2009;69(3-4):523–30.

[8] Gevorgyan SA, Jorgensen M, Krebs FC. A setup for studying stability and degradation of polymer solar cells. Solar Energy Materials and Solar Cells 2008;92(7):736–45.

[9] Madras G, McCoy BJ. Distribution kinetics for polymer mixture degradation. Industrial & Engineering Chemistry Research 1999;38(2):352–7.

[10] Mamleev V, Bourbigot S, Yvon J. Kinetic analysis of the thermal decomposition of cellulose: the main step of mass loss. Journal of Analytical and Applied Pyrolysis 2007;80(1):151–65.

[11] Paik P, Kar KK. Thermal degradation kinetics and estimation of lifetime of polyethylene particles: effects of particle size. Materials Chemistry and Physics 2009;113(2-3):953–61.

[12] Reverte C, Dirion JL, Cabassud M. Kinetic model identification and parameters estimation from TGA experiments. Journal of Analytical and Applied Pyrolysis 2007;79(1-2):297–305.

[13] Vyazovkin S, Dranca I, Fan XW, Advincula R. Kinetics of degradation and relaxation of polystyrene clay nanocomposite. Abstracts of Papers of the American Chemical Society 2004;227:U559.

[14] Budrugeac P, Segal E. Application of isoconversional and multivariate non-linear regression methods for evaluation of the degradation mechanism and kinetic parameters of an epoxy resin. Polymer Degradation and Stability 2008;93(6):1073–80.

[15] Budrugeac P. Some methodological problems concerning the kinetic analysis of non-isothermal data for thermal and thermo-oxidative degradation of polymers and polymeric materials. Polymer Degradation and Stability 2005;89(2):265–73.

[16] Perez-Maqueda LA, Sanchez-Jimenez PE, Criado JM. Evaluation of the integral methods for the kinetic study of thermally stimulated processes in polymer science. Polymer 2005;46(9):2950–4.

[17] Vyazovkin S, Sbirrazzuoli N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. Macromolecular Rapid Communications 2006;27(18):1515–32.

[18] McCoy BJ, Madras G. Discrete and continuous models for polymerization and depolymerization. Chemical Engineering Science 2001;56(8):2831–6.

[19] Khawam A, Flanagan DR. Solid-state kinetic models: basics and mathematical fundamentals. Journal of Physical Chemistry B 2006;110(35):17315–28.

[20] Koga N, Tanaka H. A physico-geometric approach to the kinetics of solid-state reactions as exemplified by the thermal dehydration and decomposition of inorganic solids. Thermochimica Acta 2002;388(1-2):41–61.

[21] Khawam A, Flanagan DR. Basics and applications of solid-state kinetics: a pharmaceutical perspective. Journal of Pharmaceutical Sciences 2006;95(3):472–98.

[22] Bruns MC, Koo JH, Ezekoye OA. Population-based models of thermoplastic degradation: using optimization to determine model parameters. Polymer Degradation and Stability 2009;94(6):1013–22.

[23] Zhou QY, Xanthos M. Nanosize and microsize clay effects on the kinetics of the thermal degradation of polylactides. Polymer Degradation and Stability 2009;94(3):327–38.

[24] Choukourov A, Grinevich A, Polonskyi O, Hanus J, Kousal J, Slavinska D, et al. Vacuum thermal degradation of poly(ethylene oxide). Journal of Physical Chemistry B 2009;113(10):2984–9.

[25] Lu L, Yu HY, Wang SF, Zhang Y. Thermal degradation behavior of styrene-butadiene-styrene tri-block copolymer/multiwalled carbon nanotubes composites. Journal of Applied Polymer Science 2009;112(1):524–31.

[26] Konaganti VK, Madras G. Photocatalytic and thermal degradation of poly(methyl methacrylate), poly(butyl acrylate), and their copolymers. Industrial & Engineering Chemistry Research 2009;48(4):1712–8.

[27] Caceres CA, Canevarolo SV. Chain scission in the thermo mechanical degradation of polystyrene under multiple extrusions. Polimeros-Ciencia E Tecnologia 2008;18(4):348–52.

[28] Kim D, Kim BK, Cho YM, Han M, Kim BS. Kinetics of polycarbonate glycolysis in ethylene glycol. Industrial & Engineering Chemistry Research 2009;48(2):685–91.

[29] Zhou XM. Thermal behavior of PES/PEES copolymers with different sequence distribution: comparative study of the kinetics of degradation. Journal of Applied Polymer Science 2009;111(2):833–8.

[30] Daraboina N, Madras G. Thermal and photocatalytic degradation of poly(methyl methacrylate), poly(butyl methacrylate), and their copolymers. Industrial & Engineering Chemistry Research 2008;47(18):6828–34.

[31] Liu Y, Wei RQ, Wei J, Liu XN. Thermal degradation of poly(L-lactide) with high molecular weight into L-lactide. Progress in Chemistry 2008;20(10):1588–94.

[32] Price D, Cunliffe LK, Bullet KJ, Hull TR, Milnes GJ, Ebdon JR, et al. Thermal behavior of covalently bonded phosphonate flame-retarded poly(methyl methacrylate) systems. Polymers for Advanced Technologies 2008;19(6):710–23.

[33] Wallis MD, Bhatia SK. Thermal degradation of high density polyethylene in a reactive extruder. Polymer Degradation and Stability 2007;92(9):1721–9.

[34] Habibi A, De Wilde J. Kinetic modeling of the thermal degradation of methacrylate copolymers by thermogravimetric methods. International Journal of Chemical Reactor Engineering 2007;5:18.

[35] Staggs JEJ. Population balance models for the thermal degradation of PMMA. Polymer 2007;48(13):3868–76.

[36] Sanchez-Jimenez PE, Perez-Maqueda LA, Perejon A, Criado JM. Combined kinetic analysis of thermal degradation of polymeric materials under any thermal pathway. Polymer Degradation and Stability 2009;94(11):2079–85.

[37] Perez-Maqueda LA, Criado JM, Gotor FJ, Malek J. Advantages of combined kinetic analysis of experimental data obtained under any heating profile. Journal of Physical Chemistry A 2002;106(12):2862–8.

[38] Perez-Maqueda LA, Criado JM, Sanchez-Jimenez PE. Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism. Journal of Physical Chemistry A 2006;110(45):12456–62.

[39] Criado JM, Perez-Maqueda LA, Gotor FJ, Malek J, Koga N. A unified theory for the kinetic analysis of solid state reactions under any thermal pathway. Journal of Thermal Analysis and Calorimetry 2003;72(3):901–6.

[40] Perez-Maqueda LA, Criado JM, Malek J. Combined kinetic analysis for crystallization kinetics of non-crystalline solids. Journal of Non-Crystalline Solids 2003;320(1-3):84–91.

[41] Criado JM, Perez-Maqueda LA. Sample controlled thermal analysis and kinetics. Journal of Thermal Analysis and Calorimetry 2005;80(1):27–33.

[42] Rouquerol J. A general introduction to SCTA and to rate-controlled SCTA. Journal of Thermal Analysis and Calorimetry 2003;72(3):1081–6.

[43] Criado JM, Perez-Maqueda LA, Dianez MJ, Sanchez-Jimenez PE. Development of a universal constant rate thermal analysis system for being used with any thermoanalytical instrument. Journal of Thermal Analysis and Calorimetry 2007;87(1):297–300.

[44] Koga N, Criado JM. The influence of mass transfer phenomena on the kinetic analysis for the thermal decomposition of calcium carbonate by constant rate thermal analysis (CRTA) under vacuum. International Journal of Chemical Kinetics 1998;30(10):737–44.

[45] Sorensen OT, Rouquerol J, editors. Sample controlled thermal analysis. Budapest: Kluwer; 2003.

[46] Perez-Maqueda LA, Ortega A, Criado JM. The use of master plots for discriminating the kinetic model of solid state reactions from a single constant-rate thermal analysis (CRTA) experiment. Thermochimica Acta 1996;277:165–73.

[47] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to Phenolic Plastic Journal of Polymer Science Part C-Polymer Symposium 1964;6(Part C):183–95.

[48] Criado JM, Sanchez-Jimenez PE, Perez-Maqueda LA. Critical study of the isoconversional methods of kinetic analysis. Journal of Thermal Analysis and Calorimetry 2008;92(1):199–203.

[49] Sestak J, Berggren G. Study of the kinetics of the mechanism of solid-state reactions at increased temperature. Thermochimica Acta 1971;3:1–12.

[50] Simha R, Wall LA. Kinetics of chain depolymerization. Journal of Physical Chemistry 1952;56(6):707–15.

[51] Alcala MD, Criado JM, Gotor FJ, Ortega A, Perez-Maqueda LA, Real C. Development of a new thermogravimetric system for performing constant rate thermal analysis (CRTA) under controlled atmosphere at pressures ranging from vacuum to 1 bar. Thermochimica Acta 1994;240(1-2):167–73.

[52] Dianez MJ, Perez-Maqueda LA, Criado JM. Direct use of the mass output of a thermobalance for controlling the reaction rate of solid-state reactions. Review of Scientific Instruments 2004;75(8):2620–4.

[53] Westerhout RWJ, Waanders J, Kuipers JAM, vanSwaaij WPM. Kinetics of the low-temperature pyrolysis of polyethene, polypropene, and polystyrene modeling, experimental determination, and comparison with literature models and data. Industrial & Engineering Chemistry Research 1997;36(6):1955–64.

[54] Gao ZM, Amasaki I, Nakada M. A thermogravimetric study on thermal degradation of polyethylene. Journal of Analytical and Applied Pyrolysis 2003;67(1):1–9.