



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:

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

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]:

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

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:

$$\frac{d\alpha}{dt} = k f(\alpha) \quad (3)$$

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

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:

$$C = A \exp(-E/RT) f(\alpha) \quad (4)$$

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:

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

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

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

The activation energy E_α 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:

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

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]:

$$f(\alpha) = c(1 - \alpha)^n \alpha^m \quad (8)$$

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:

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

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

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	$\frac{3(1 - \alpha)^{2/3}}{2[1 - (1 - \alpha)^{1/3}]}$
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

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