Resources, Conservation and Recycling 74 (2013) 75–81

Contents lists available at SciVerse ScienceDirect

Resources, Conservation and Recycling

journal homepage: www.elsevier.com/locate/resconrec

Limitations of model-fitting methods for kinetic analysis: Polystyrene thermal degradation

Pedro E. Sánchez-Jiménez*, Luis A. Pérez-Maqueda, Antonio Perejón, José M. Criado

Instituto de Ciencia de Materiales de Sevilla, C.S.I.C.-Universidad de Sevilla, C. Américo Vespucio n 49, 41092 Sevilla, Spain

ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form 15 February 2013
Accepted 20 February 2013

Keywords:
Kinetic analysis
Integral methods
Chain scission
Kinetic model
Polystyrene

ABSTRACT

In this paper, some clarifications regarding the use of model-fitting methods of kinetic analysis are provided in response to the lack of plot linearity and dispersion in the activation energy values for the thermal degradation of polystyrene found in the literature and some results proposing an *n*th order model as the most suitable one. In the present work, two model-fitting methods based on the differential and integral forms of the general kinetic equation are evaluated using both simulated and experimental data, showing that the differential method is recommended due to its higher discrimination power. Moreover, the intrinsic limitations of model-fitting methods are highlighted: the use of a limited set of kinetic models to fit experimental data and the ideal nature of such models. Finally, it is concluded that a chain scission model is more appropriate than first order.

1. Introduction

An important volume of work has been devoted to the determination of the activation energy and kinetic model describing the thermal degradation of polystyrene (Brems et al., 2011; Chen et al., 2007; Chen and Vyazovkin, 2006; Faravelli et al., 2001; Peterson et al., 2001; Sanchez-Jimenez et al., 2012; Snegirev et al., 2012; Sterling et al., 2001; Westerhout et al., 1997). However, results show a wide divergence in the activation energy values and the kinetic models proposed. Also, both complex and one-step mechanisms are suggested. A recent paper questions the application of general kinetic models such as diffusion or nucleation for the kinetic analysis of polymer pyrolysis (Brems et al., 2011). In that paper, the pyrolysis of polystyrene is studied by fitting the experimental data, recorded under dynamic heating conditions, to some of the most widely used kinetic models by means of the Coats–Redfern integral model-fitting method (Coats and Redfern, 1964). A lack of plot linearity and inconsistent activation energy values are observed and the authors conclude that simple first or second order models are good enough for determining the activation energy and, therefore, constitute "the most suitable design approach". Other works employing similar single-curve model-fitting kinetic procedures reached analogous conclusions (Ahmad et al., 2010; Ahmed and Gupta, 2009; Krishna and Pugazhenthi, 2011). However, some other works, employing isoconversional and non-linear model fitting methods, have revealed the unsuitability of *n*th order reaction models and suggest an acceleratory model instead (Chen et al., 2007; Sanchez-Jimenez et al., 2010; Snegirev et al., 2012; Vyazovkin et al., 2004). Such was confirmed by Sanchez-Jimenez et al. (2010, 2012), proposing a random chain scission model. Since several authors have found that the activation energy does not change with the reacted fraction (Peterson et al., 2001; Sanchez-Jimenez et al., 2012; Snegirev et al., 2012), it can reasonably be assumed that the process is single step and other results can be a consequence of both inappropriate kinetic procedures or non-adequately controlled experimental conditions since it has been proved that heat and mass transfer phenomena can affect greatly to the calculated kinetic parameters.

Here, we aim to provide some clarifications regarding the use of model-fitting methods that might explain such discrepancy. Model-fitting methods are frequently used for performing the kinetic modeling of the pyrolysis of polymers and plastic waste because of their simplicity. A number of methods have been proposed, but all basically consist on fitting the experimental data to a conversion function, also known as kinetic model, which relates the extent of conversion with the reaction rate (Perez-Maqueda et al., 2005b). Kinetic models are mathematical functions developed from certain physico-geometrical assumptions regarding the reactants shape and the reaction driving force. Therefore, they can be identified with a reaction mechanism (Khawam and Flanagan, 2006). However, two important limitations must be considered when such models are applied to real systems. Firstly, the kinetic models are built on strict assumptions that might not be fulfilled in a real process. Certainly, most of the models were proposed

* Corresponding author. Tel.: +34 954489548; fax: +34 954460665.
E-mail address: pedro.enrique@icmse.csic.es (P.E. Sánchez-Jiménez).

0921-3449/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.resconrec.2013.02.014

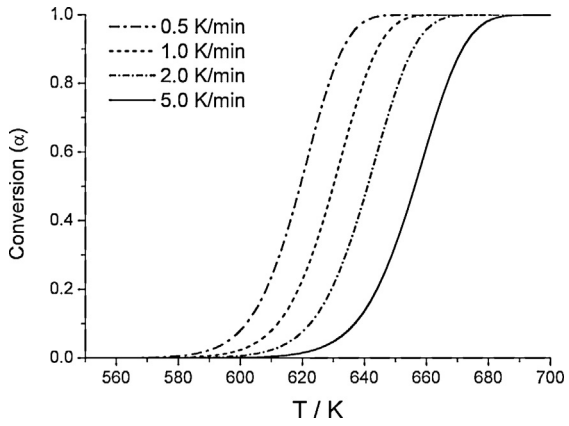

Fig. 1. Kinetic curves simulated according the following kinetic parameters: $E_a = 200$ kJ/mol, $A = 3 \times 10^{15}$ s^{-1}, and $f(\alpha) = 2(\alpha^{1/2} - \alpha)$.

for solid state reactions in general and some of them, such as the nucleation and growth or the geometrical shrinkage ones, might not seem entirely appropriate for polymer degradation processes. Other models such as those based on a power law were developed by assuming a mechanism of nucleation and growth of nuclei without overlap of the growth nuclei (Khawam and Flanagan, 2006). Thus, the power kinetic laws cannot be applied to the whole reaction range but only to the acceleratory period at which the overlapping of nuclei has not yet started. The potential laws become the well-known Avrami–Erofeev kinetic models if the overlapping of growing nuclei is taken into account. Thus, Avrami–Erofeev kinetic equations instead of power laws should be used for performing the kinetic analysis on the whole reacted fraction. Secondly, any list of models is inevitably incomplete and it is perfectly possible that the studied process is not described by any of them. For example, a kinetic model of random scission, based on the cleavage and ulterior volatilization of polymeric chains, was recently proposed (Sanchez-Jimenez et al., 2010). That model is especially suitable to polymeric degradation studies, and has a clear physical meaning. Actually, since its publication, we have found a number of polymers such as cellulose, polystyrene and polybutylen terephtalate, that decompose according to a random scission model (Sanchez-Jimenez et al., 2010, 2011, 2012). Here, we attempt to provide some insight about the use of model-fitting methods and highlight some of its limitations in order to clarify why in some cases the experimental data cannot be properly fitted by any kinetic model (Brems et al., 2011).

2. Experimental

The polystyrene studied was supplied by Goodfellow (powder, product number 261595). Thermogravimetric (TGA) measurements were carried out in a TA Instruments Q5000IR thermobalance (TA Instruments, Crawley, UK) connected to a gas flow system to work in inert atmosphere (150 mL/min). Small mass samples (~10 mg) were used in order to minimize mass and heat transfer phenomena. Experiments were recorded under linear heating rate conditions, at 0.5, 1, 2 and 5 K/min. The α–T plots obtained from these two methods were differentiated by means of the Origin software (OriginLab) to get the differential curves employed in the kinetic analysis.

3. Results and discussion

Fig. 1 includes a set of curves simulated according to the following kinetic parameters: $E_a = 200$ kJ/mol, $A = 3 \times 10^{15}$ s^{-1}, and L2 random scission kinetic model $f(\alpha) = 2(\alpha^{1/2} - \alpha)$. Such were the parameters obtained for the degradation of polystyrene in a previous study and will serve to compare experimental and simulated results (Sanchez-Jimenez et al., 2012). The simulations were performed by means of a numerical integration method (Runge–Kutta) using the Mathcad software and assuming heating rates of 0.5, 1, 2 and 5 K/min. The selected conversion function, $f(\alpha)$, corresponds to a L2 chain scission kinetic model, as described elsewhere (Sanchez-Jimenez et al., 2010). All four simulated curves have been fitted to some of the most common kinetic models using the same Coats–Redfern integral method employed in Brems' work (Brems et al., 2011). The resulting plots are shown in Fig. 2. When dealing with real experimental data it is common to restrict the fit to data within a limited range of conversion because the low and high ends of the conversion range are often distorted due to experimental errors. Such restriction was also employed in Brems' paper (Brems et al., 2011). Thus, we have carried out the fitting procedure using data within the range $0.1 \leq \alpha \leq 0.9$. Fig. 2 shows the plots obtained from fitting the simulated curves to the different kinetic models employed, along with the activation energies deduced from the slope of each plot. In principle, when the data is fitted to the correct kinetic model, a straight line is expected. However, all F1, A2 and L2 models yields a linear plot, but only when the data are fitted to L2, the activation energy yielded by the method is the correct one, i.e., 200 kJ/mol. Thus, unless the activation energy is previously known, it would be difficult to discriminate the correct kinetic model obeyed by the process using this method because more than one kinetic model can provide a good fit to the data. Additionally, it is clear that the fits of the data simulated assuming different heating rates to a certain model are parallel in every case. Consequently, since the activation energy is deducted from the slopes, the value delivered by the method must be the same whatever the heating rate.

An alternative to the previous method consists on fitting the experimental data to the different kinetic models using directly the differential form of the general kinetic equation. After reorganizing terms and taking logarithms, in presents the following form (Sanchez-Jimenez et al., 2009):

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

The plot of the left hand side of the equation above versus the inverse of the temperature yields a straight line when the right $f(\alpha)$ is selected. Moreover, when data from curves recorded under different heating rates are plotted together, all of them will lie along a straight line if the right $f(\alpha)$ is selected since the intercept now depends exclusively on the pre-exponential factor. The reduced chance of selecting an incorrect model constitutes an important advantage over model-fitting methods based on the integral form of the kinetic equation. This is clearly shown in Fig. 3, which includes the plots obtained when the curves in Fig. 1 are fitted to several models according to Eq. (1). It is evident that L2 is the only model that correctly fits all the simulated data, yielding an activation energy of 200 kJ/mol and a preexponential factor of 4.8×10^{15} s^{-1}. Thus, both the activation energy and the kinetic model can be unambiguously determined by this method. It is also worth noticing that when fitting to inappropriate models, the plots corresponding to different heating rates do not yield straight lines but lead to parallel plots. This behavior allows to conclude that the same activation energy would be obtained from the Coats–Redfern method when applied to individual α–T curves recorded at different heating rates.

Finally, a set of experimental curves corresponding to the thermal degradation of polystyrene, one of the two polymers studied in Brems' work, is used to confirm the observations made with the simulated curves. The experimental curves, shown in Fig. 4, were