

COMBINED KINETIC ANALYSIS OF THERMAL DEGRADATION OF POLYMERIC MATERIALS UNDER ANY THERMAL PATHWAY.

P.E Sánchez-Jiménez^{*}, L.A. Pérez-Maqueda, A. Perejón and J.M. Criado.

Instituto de Ciencia de Materiales de Sevilla, C.S.I.C.-Universidad de Sevilla, C. Américo

Vespucio n°49, 41092 Sevilla, Spain

Abstract

Combined kinetic analysis has been applied for the first time to the thermal degradation of polymeric materials. The combined kinetic analysis allows the determination of the kinetic parameter from the simultaneous analysis of a set of experimental curves recorded under any thermal schedule. Besides, the method does not make any assumption about the kinetic model or activation energy and allows the analysis even when the process does not follow one of the ideal kinetic models already proposed in literature. In the present paper the kinetics of the thermal degradation of both polytetrafluoroethylene (PTFE) and polyethylene (PE) have been performed. It has been concluded, without previous assumptions on the kinetic model, that the thermal degradation of PTFE obeys a first order kinetic law, while the thermal degradation of PE follows a diffusion-controlled kinetic model.

Keywords: Kinetics, Polymer degradation, SCTA

^{*} Corresponding author.

Current address: Department of Mechanical Engineering, University of Colorado at Boulder, Boulder CO 80309-0427
USA Tel +1 303 735 2651 Fax: +1 303 492 3498

Email addresses: Pedro.Sanchez@colorado.edu (P.E. Sanchez), maqueda@cica.es (L.A. Pérez-Maqueda)

1. Introduction

Thermal stability studies of polymers are a matter of great interest because of the technical and commercial importance of these materials [1-5] with the kinetic analysis of thermal degradation playing an important role in such studies [6-22]. A reliable evaluation of the kinetic parameters permits a theoretical interpretation of the experimental data and provides a mathematical description needed to extrapolate the reaction behaviour to conditions different from the experimental ones [23-25].

Thermal analysis methods, mainly differential scanning calorimetry and thermogravimetry, are extensively used in thermal degradation studies of polymers. Experimental data for the kinetic analysis can be recorded under different experimental conditions. Thus, different temperature versus time programs, both isothermal and nonisothermal, have been proposed. In the isothermal experiment, samples should be rapidly heated up to the final temperature and maintained at this temperature while the thermal degradation is recorded as a function of the time. In this latter case, the low thermal conductivity of polymers makes it difficult to reach a steady state at the selected temperature before the reaction starts [26, 27]. Additionally, the length of the experiment is not known in advance and it will be determined by the selected temperature. Thus, this temperature should be properly chosen to avoid extremely long or short experiments. An alternative to isothermal experiment is the linear heating rate program, where temperature varies in a wide range of values while the thermal degradation is recorded as a function of the temperature. This linear heating rate program is the most widely used [28]. In any case, it is not uncommon to find in the literature a serious disagreement between the kinetic parameters calculated from data obtained under isothermal and non-isothermal conditions [26, 29, 30]. Sample

Controlled Thermal Analysis (SCTA) constitutes an interesting non isothermal method which has been rarely applied to the kinetic analysis of thermal degradation of polymers [31]. 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 known as Constant Rate Thermal Analysis (CRTA). Thus, mass and heat transfer phenomena occurring during the decomposition process can be minimized by selecting a constant decomposition rate that is low enough, yielding results which are more representative of the forward reaction [31-33].

The pyrolysis of organic materials, such as polymers, is a chemically complex process, where several reactions may be occurring simultaneously [1, 34-36]. Because of this complexity, a large number of papers found in the literature assume first order or n-order kinetic models to describe the thermal degradation of polymers [8, 23, 30, 34, 37-45], what would entail a non realistic description of the real reaction leading to erroneous kinetic parameters. Combined kinetic analysis is a procedure recently proposed that allows for the simultaneous analysis of a set of experimental curves recorded under any thermal schedule [27, 46-48]. To overcome the difficulty of finding a kinetic model which is able to describe accurately the real process, the combined kinetic analysis procedure have been recently upgraded by the use of an empirical kinetic equation based on that proposed by Sestak-Berggren [49] that fits every kinetic function corresponding to the ideal models used in literature and their probable deviations from ideality [46]. Thus, the combined kinetic analysis can be used to obtain the kinetic triplet, i.e. activation energy, preexponential factor and kinetic mode, from a set of data obtained under different experimental conditions and without any previous assumption about the kinetic model or the activation energy of the process.

The aim of this work is the application for the first time of the combined kinetic analysis to the study of two widely used commercial polymers, polytetrafluoroethylene (PTFE), and polyethylene (PE), proving that data obtained under different experimental conditions may all together be described by the same kinetic parameters. Moreover, the kinetic parameters obtained will be used to reconstruct the original curves in order to demonstrate their validity, something that is rarely done in most kinetic studies found in literature.

2. Theoretical background.

The reaction rate, da/dt , of a solid state reaction can be described by the following general equation [31]:

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

where A is the Arrhenius preexponential 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 [50]. Table 1 show the functions corresponding to the most commonly used kinetic mechanisms found in 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 reaction rate $\beta=dT/dt$, Eq (1) can be written as follows [51]:

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

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:

$$C = A \exp(-E/RT) f(\alpha) \quad (3)$$

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 [52] 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 [53].

Eq (1) can be written in logarithmic form:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(Af(\alpha)) - \frac{E}{RT} \quad (4)$$

Moreover, at a constant value of α , $f(\alpha)$ would be also constant and Eq (4) would be written in the form

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

The activation energy at a constant α value can be determined from the slope of the plot of the left hand side of Eq (4) against the inverse of the temperature, at constant values of α .

2.2 Combined Kinetic Analysis

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

$$\ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = \ln A - \frac{E}{RT} \quad (6)$$

If the proper $f(\alpha)$ function is selected, the plot of the left hand side of Eq (6) versus $1/T$ would yield a straight line whose slope leads to the activation energy, while the intercepts allows to determine the preexponential factor of Arrhenius once the activation energy is known. It is noteworthy to point out that the relationships among the triplet $d\alpha/dt$ - α - T quoted by Eq (6) is independent of the thermal pathway used for reaching a particular value of the triplet, what leads to the conclusion that Eq (6) would allow the simultaneous analysis of any sets of experimental data obtained under different heating schedules [27].

There is an important limitation related with the way the proper $f(\alpha)$ function is selected. The $f(\alpha)$ kinetic equations proposed in literature have been developed assuming idealized physical conditions that would not be necessarily fulfilled by the real solid state reaction. Deviation from the ideal models described in Table 1 would be expected due to factors such as heterogeneous distribution in particle size, particle shapes, etc. To

overcome this problem, a new procedure has been introduced in a recent work, where the following $f(\alpha)$ general expression was proposed [46]:

$$f(\alpha) = c(1 - \alpha)^n \alpha^m \quad (7)$$

This equation is a modified form of the Sestak-Berggren empirical equation [49]. It has been shown that it can fit every function in Table 1 by merely adjusting the parameters c , n and m [46]. Therefore, Eq (7) works as an umbrella that covers the most common physical models and its possible deviations from ideal conditions. From Eq (6) and (7), we get

$$\ln\left(\frac{d\alpha/dt}{(1 - \alpha)^n \alpha^m}\right) = \ln cA - \frac{E}{RT} \quad (8),$$

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

3. Experimental

The following commercial polymers were studied: polytetrafluoroethylene (Aldrich, product number 182478) and polyethylene (Aldrich, product number 332119).

Thermogravimetry measurements were carried out with homemade TGA instrument that uses a CI Electronics Ltd electrobalance connected to a gas flow system to work in inert atmosphere ($70 \text{ cc min}^{-1} \text{ N}_2$). 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 set-up can be found in references [54-56]. A set of thermal degradation curves, obtained under both linear heating rate and constant rate controlled conditions, were carried out for each polymer. Experimental integral curves were differentiated by means of the Origin software (OriginLab) to obtain the differential curves required for the kinetic analysis.

4. Results and discussion

4.1 Polytetrafluoroethylene

Fig 1 shows the experimental curves recorded for the thermal degradation of PTFE under linear heating rate (1a) and sample controlled (1b) conditions. Linear heating rate experiments were carried out at 1, 2 and $5 \text{ }^\circ\text{C min}^{-1}$, while sample controlled were conducted at reaction rates of $5 \cdot 10^{-4}$ and $8.3 \cdot 10^{-4} \text{ min}^{-1}$.

In Fig 2, the $5 \cdot 10^{-4} \text{ min}^{-1}$ CRTA curve is presented as an example of the kind of experimental curves obtained under constant rate experimental conditions. Both the temperature and the reacted fraction are plotted as a function of time as directly recorded by the instrument. It can be observed that the temperature rises until reaching

the constant reaction rate previously selected with our experimental arrangement forcing α to fit a straight line as a function of the time.

Fig 3 shows several of the isoconversional Friedman plots obtained from the simultaneous analysis, according with Eq (4), of the α -T curves shown in Fig 1 that were obtained under constant heating rate and CRTA heating schedules, respectively. The values of the activation energy calculated from the slope of the Friedman plots for different α values are included in Table 2 together with their corresponding linear correlation coefficients. These results demonstrate that a constant activation energy $E = 286 \text{ kJ mol}^{-1}$ has been obtained along the entire α range.

The combined kinetic analysis of these curves was performed by means of eq (8). Fig 4 shows the simultaneous plot of the values calculated for the left hand side of eq (8) from the whole set of experimental data in Fig 1 versus $1/T$. It is clearly shown that all experimental data are fitted by a single straight line with $n = 0.901$ and $m = -0.081$, giving a correlation coefficient of 0.999. The slope of the plot leads to an activation energy value of $283 \pm 2 \text{ kJ/mol}$ and the intercept to an Arrhenius pre-exponential factor of $(4.1 \pm 1.1) 10^{16}$. It must be pointed out that the activation energy obtained closely agrees with the one calculated from the Friedman isoconversional analysis without any previous assumption of the kinetic model.

Fig 5 shows the comparison of the $f(\alpha)$ function resulting from the combined analysis with some of the conversion functions often used in the literature, which are listed in Table 1. It is clear from this figure that the conversion function associated with the thermal degradation of PTFE closely follows a F1 kinetic model.

The simulation of curves obtained with the calculated kinetic parameters is a useful method for checking the results obtained by this kinetic analysis. Thus, a set of curves have been simulated assuming identical heating conditions as those used in the

experiments and the kinetic parameters obtained from the combined kinetic analysis. The simulations have been performed from Eq (1) and the equations that define the heating conditions, i.e. linear heating or constant rate. As it is shown in Fig 1, both the reconstructed (simulated) curves and the experimental ones match almost exactly, proving the validity of the kinetic parameters obtained from the analysis. Additionally, curves obtained under different experimental conditions are expected to be affected by different heat and mass transfer phenomena. The fact that all of the curves are reconstructed with the same kinetic parameters seems to indicate that these mass and heat transfer phenomena have been successfully minimized.

4.2 Polyethylene

Fig 6 shows the experimental curves recorded for the thermal degradation of polyethylene under linear heating rate (6a) and sample controlled (6b) conditions. Linear heating rate experiments were carried out at 0.5, 1, 2 and 10 °C min⁻¹, while sample controlled experiments were conducted at constant decomposition rates of 1.6 10⁻³ and 8.3 10⁻⁴ min⁻¹, respectively.

Fig 7 shows some of the isoconversional Friedman plots obtained at different values of α from the simultaneous analysis of the α -T plots obtained under linear heating and CRTA temperature control, respectively, that are shown in Fig 6. The values of E obtained for different α values are included in Table 3 together with their corresponding correlations coefficients. These results allow to conclude that a constant activation energy $E = 253 \text{ kJ mol}^{-1}$ is obtained all over the thermal decomposition range of polyethylene.

Fig 8 shows the result of the simultaneous combined kinetic analysis, by means of Eq (8), of the whole set of curves obtained under different heating schedules for the thermal

decomposition of polyethylene that are reported in Fig 6. All experimental data are fitted by a single straight line when n is 0.641 and m is -0.646, with a correlation factor of 0.997. The slope of the plot leads to an activation energy value of $246 \pm 1 \text{ kJ mol}^{-1}$ and the intercept to an Arrhenius preexponential factor of $(3.2 \pm 0.4) 10^{16} \text{ min}^{-1}$. Fig 9 presents the comparison between the function $f(\alpha)$ obtained from the combined analysis and some of the more frequently used conversion functions used in the literature, showing that the conversion function associated to the thermal degradation of polyethylene approximately fits the master plot of diffusion controlled kinetic models. As in the case of the PTFE, the kinetic parameters resulting of the combined kinetic analysis have been used to simulate all the degradation curves shown in Fig 6 and, as it can be observed, both reconstructed and experimental curves match nicely, proving the validity of these kinetic parameters.

5. Conclusions

In this work, the method of combined kinetic analysis has been applied to study the thermal degradation of two commercial polymers, polytetrafluoroethylene and polyethylene. Experimental curves obtained under linear heating 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 here proposed.

Additionally, it has been demonstrated that the “n order” kinetic law cannot be used as a universal model for describing the thermal degradation of polymers as frequently assumed in literature. The assumptions of unrealistic kinetic models would lead to

wrong values of the kinetic parameters, making impossible the extrapolation to conditions different to those used for obtaining the experimental data.

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Figures Caption

Fig. 1. Experimental curves (solid lines) obtained for the thermal decomposition of polytetrafluoroethylene under the following experimental conditions: (a) linear heating rate of 1, 2 and 5 °C min⁻¹ and (b) sample controlled degradation rate of 5 10⁻⁴ and 8.3 10⁻⁴ min⁻¹. Reconstructed curves using the kinetic parameters obtained from the kinetic combined analysis are plotted as dots.

Fig. 2. Experimental curve corresponding to the thermal decomposition of PTFE under constant reaction rate conditions of 5 10⁻⁴ min⁻¹.

Fig. 3. Friedman plots resulting of the isoconversional analysis for some selected α values of the experimental curves presented in Fig. 1.

Fig. 4. Combined kinetic analysis of experimental curves included in Fig. 1 by means of Eq. (8) for the n and m parameters resulting of the optimization procedure, i.e. $n = 0.901$ and $m = -0.081$.

Fig. 5. Comparison of the $f(\alpha)$ functions (solid lines) normalized at $\alpha = 0.5$ corresponding to some of the ideal kinetic models included in Table 1 with the reduced Sestak-Berggren equation (dots) and the resulting values of n and m parameters, i.e. $n = 0.901$ and $m = -0.081$, for the thermal degradation of polytetrafluoroethylene.

Fig. 6. Experimental curves (solid lines) obtained for the thermal decomposition of polyethylene under the following experimental conditions: (a) linear heating rate of 0.5,

1, 2 and $10\text{ }^{\circ}\text{C min}^{-1}$ and (b) sample controlled degradation rate of $8.3\ 10^{-4}$ and $1.6\ 10^{-3}\ \text{min}^{-1}$. Reconstructed curves using the kinetic parameters obtained from the kinetic combined analysis are plotted as dots.

Fig. 7. Friedman plots resulting of the isoconversional analysis for some selected α values of the experimental curves presented in Fig. 6.

Fig. 8. Combined kinetic analysis of curves included in Fig. 6 by means of Eq. (8) for the n and m parameters resulting of the optimization procedure, i.e. $n = 0.641$ and $m = -0.646$.

Fig. 9. Comparison of the $f(\alpha)$ functions (solid lines) normalized at $\alpha = 0.5$ corresponding to some of the ideal kinetic models included in Table 1 with the reduced Sestak-Berggren equation (dotted line) and the resulting values of n and m parameters, i.e. $n = 0.641$ and $m = -0.646$, for the thermal degradation of polyethylene.

TABLE 1. $f(\alpha)$ kinetic functions for the most widely used kinetic 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 eqn. $n = 1$)	F1	$(1 - \alpha)$
Random nucleation and growth of nuclei through different nucleation and nucleus growth models. (Avrami-Erofeev eqn.)	An	$n(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n}$
Two-dimensional diffusion	D2	$1/[- \ln(1 - \alpha)]$
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	$\frac{3}{2[(1 - \alpha)^{-1/3} - 1]}$

TABLE 2. Activation energy values for different values of conversion and their correlation coefficients, obtained by the Friedman isoconversional analysis of the curves showed in Fig. 1.

α	r	E_a (kJ mol ⁻¹)
0.1	0.991	298 ± 16
0.2	0.996	288 ± 13
0.3	0.995	287 ± 14
0.4	0.995	287 ± 14
0.5	0.997	282 ± 11
0.6	0.997	282 ± 11
0.7	0.996	280 ± 13
0.8	0.996	283 ± 12
0.9	0.997	286 ± 13

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. 6.

α	r	E_a (kJ mol ⁻¹)
0.1	0.997	241 ± 10
0.2	0.996	246 ± 11
0.3	0.997	252 ± 10
0.4	0.997	255 ± 10
0.5	0.997	254 ± 9
0.6	0.998	259 ± 8
0.7	0.998	257 ± 7
0.8	0.998	254 ± 8
0.9	0.998	257 ± 8

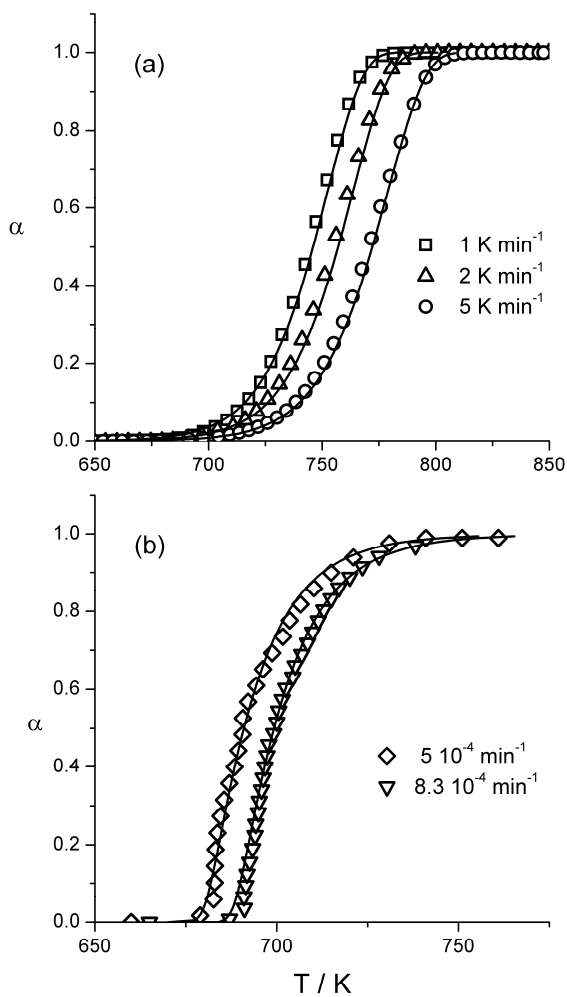


Fig. 1. Experimental curves (solid lines) obtained for the thermal decomposition of polytetrafluoroethylene under the following experimental conditions: (a) linear heating rate of 1, 2 and 5 °C min⁻¹ and (b) sample controlled degradation rate of 5×10^{-4} and 8.3×10^{-4} min⁻¹. Reconstructed curves using the kinetic parameters obtained from the kinetic combined analysis are plotted as dots.

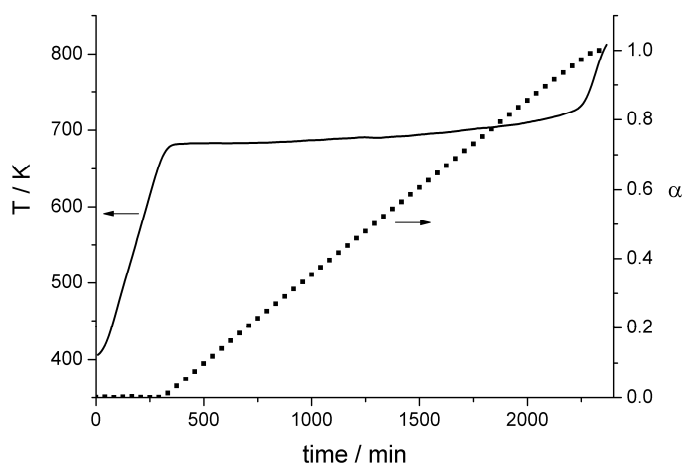


Fig. 2. Experimental curve corresponding to the thermal decomposition of PTFE under constant reaction rate conditions of $5 \cdot 10^{-4} \text{ min}^{-1}$.

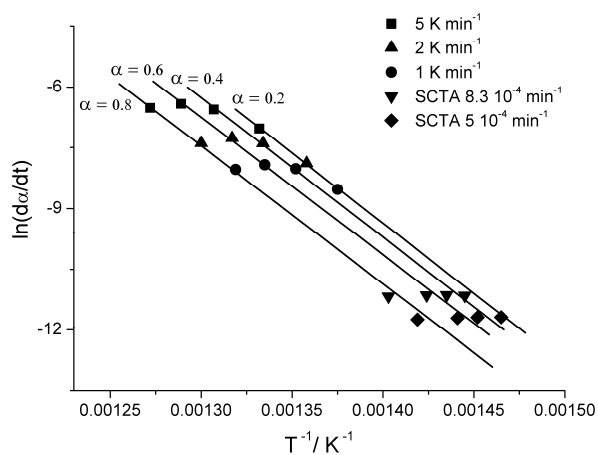


Fig. 3. Friedman plots resulting of the isoconversional analysis for some selected α values of the experimental curves presented in Fig. 1.

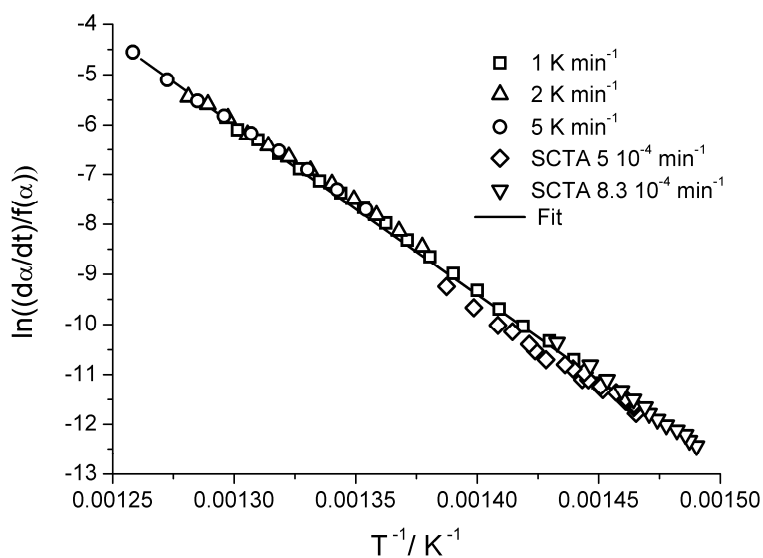


Fig. 4. Combined kinetic analysis of experimental curves included in Fig. 1 by means of Eq. (8) for the n and m parameters resulting of the optimization procedure, i.e. $n = 0.901$ and $m = -0.081$.

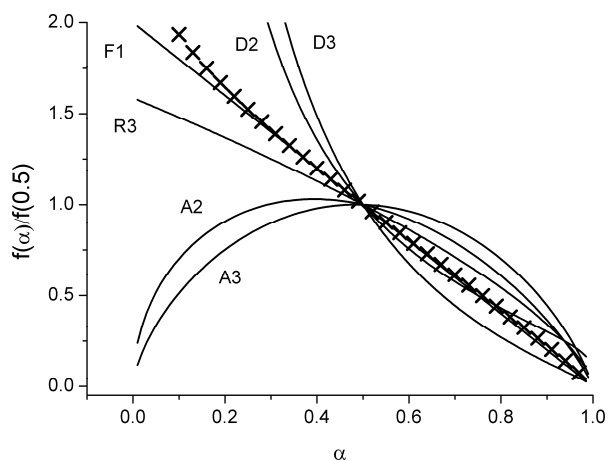


Fig. 5. Comparison of the $f(\alpha)$ functions (solid lines) normalized at $\alpha = 0.5$ corresponding to some of the ideal kinetic models included in Table 1 with the reduced Sestak-Berggren equation (dots) and the resulting values of n and m parameters, i.e. $n = 0.901$ and $m = -0.081$, for the thermal degradation of polytetrafluoroethylene.

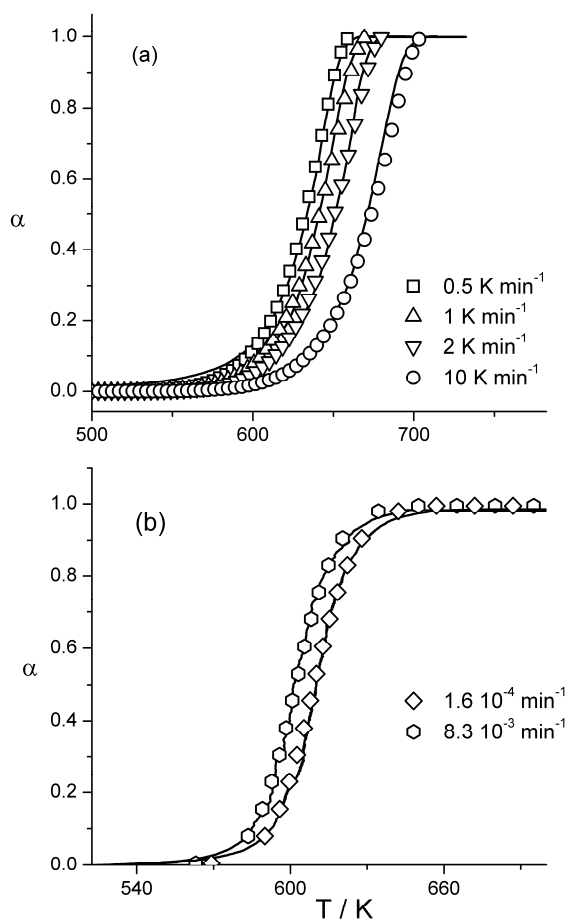


Fig. 6. Experimental curves (solid lines) obtained for the thermal decomposition of polyethylene under the following experimental conditions: (a) linear heating rate of 0.5, 1, 2 and 10 °C min⁻¹ and (b) sample controlled degradation rate of 8.3 10⁻⁴ and 1.6 10⁻³ min⁻¹. Reconstructed curves using the kinetic parameters obtained from the kinetic combined analysis are plotted as dots.

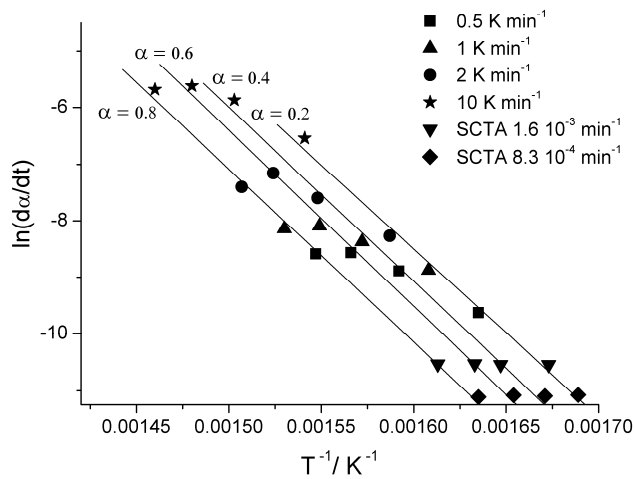


Fig. 7. Friedman plots resulting of the isoconversional analysis for some selected α values of the experimental curves presented in Fig. 6.

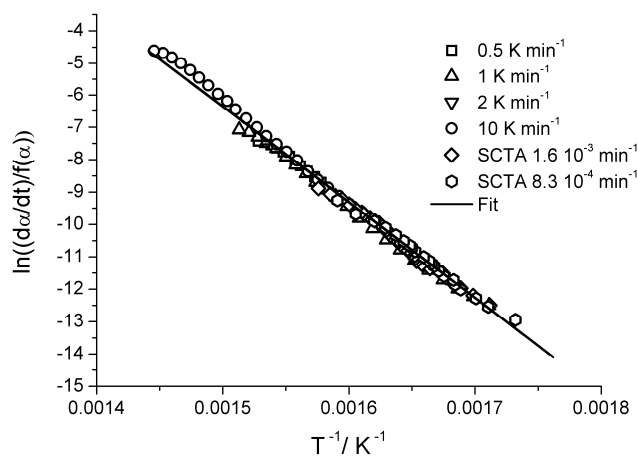


Fig. 8. Combined kinetic analysis of curves included in Fig. 6 by means of Eq. (8) for the n and m parameters resulting of the optimization procedure, i.e. $n = 0.641$ and $m = -0.646$.

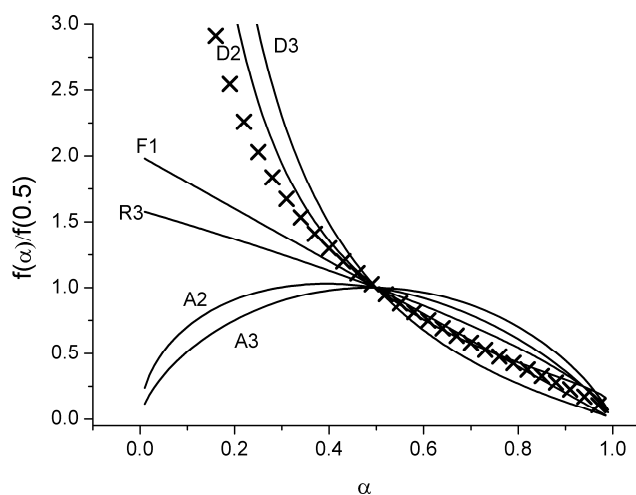


Fig. 9. Comparison of the $f(\alpha)$ functions (solid lines) normalized at $\alpha = 0.5$ corresponding to some of the ideal kinetic models included in Table 1 with the reduced Sestak-Berggren equation (dotted line) and the resulting values of n and m parameters, i.e. $n = 0.641$ and $m = -0.646$, for the thermal degradation of polyethylene.