

# ENHANCED GENERAL ANALYTICAL EQUATION FOR THE KINETICS OF THE THERMAL DEGRADATION OF POLY(LACTIC ACID) / MONTMOTILLONITE NANOCOMPOSITES DRIVEN BY RANDOM SCISSION

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## Abstract

An enhanced general analytical equation has been developed in order to evaluate the kinetic parameters of the thermal degradation of nanocomposites, composed of poly(lactic acid) (PLA) and organo-modified montmorillonite (OMMT) nanoparticles. This improvement has consisted of replacing the n-order conversion function by a modified form of the Sestak-Berggren equation  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  that led to a better adjustment of experimental data and also adequately represented the conventional mechanisms for solid-state processes. The kinetic parameters so obtained have been compared to those determined by conventional differential and isoconversional methods. Given that the thermal degradation of PLA has been argued to be caused by random chain scission reactions of ester groups, the conversion function  $f(\alpha) = L(L - 1)x(1 - x)^{L-1}$ , corresponding to a random scission mechanism, has been tested. Once optimized the kinetic model, the thermal degradation kinetics of nanocomposites (0.5 an was compared to that of the polymer

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matrix. Moreover, the thermal stability of nanocomposites was tested and compared to that of the polymer matrix.

**Keywords:** poly(lactic acid); montmorillonite; nanocomposites; thermal degradation; enhanced kinetic model; general analytical equation; random scission

## 1. Introduction

Poly(lactic acid) (PLA) is a thermoplastic, high-strength, high-modulus polymer that can be made from annually renewable resources to yield articles for use in either the industrial packaging field or the biocompatible/bioabsorbable medical device market. It is easily processed on standard plastics equipment to yield molded parts, films, or fibers [1]. Thus, it can be reasonably substituted for certain petroleum-based plastics in high volume applications. In order for PLA to increase its application window and be processed on large-scale production lines such as injection molding, blow molding, thermoconforming, and extrusion, the polymer must possess adequate thermal stability or low thermal degradation during processing and use, and maintain its molecular weight and properties.

Melt degradation of polymers can be defined as molecular deterioration as a result of overheating. At high temperatures the components of the long chain polymer backbone can begin to separate (molecular scission) and react with another molecule to change the polymer properties. It has to be noted that thermal degradation of PLA is very complex and various mechanisms have been postulated, including various non-radical and radical reactions: random chain scission reactions, depolymerization, oxidative degradation, intramolecular and intermolecular transesterifications, hydrolysis, pyrolytic elimination and radical reactions [2-14].

In order to improve the thermal, mechanical, and other properties of the organic polymeric materials, inorganic fillers are added into the polymer formulations to form organic-inorganic composites. The formation of nanocomposites has been studied because of their high interfacial areas and exceptional properties. Nanoscale spherical particles, nanotubes, and layered clay [15-22] are major fillers in preparation of nanocomposites. Considerable efforts have been made to reduce thermal degradation rate and enhance thermal stability so that PLA can have wider applications without a compromise of the product properties prior to the onset of degradation. Among the many methods that can be used to reduce PLA thermal degradation, a promising one is to prepare nanocomposites by adding organo-modified montmorillonite (OMMT) clays in the PLA matrix. Additional advantages would be: 1) the final product cost may be reduced; 2) OMMT can improve physical and mechanical properties; 3) the parameters during melt processing do not need to be changed at low filler loading.

Due to its applicability in the macroscopic scale, the modeling of the thermal decomposition processes in inert or in reactive conditions has been broadly applied by using isoconversional, integral, differential and special methods proposed by different authors with good acceptance because its versatility in different polymeric materials. The kinetic 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 depolymerization processes was 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 analysis was performed by means of the differential kinetic analysis method that 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 [23-28]. The kinetic

parameters thus obtained were 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 first or n-order kinetic models. On the other hand, a modified form of the Sestak-Berggren equation (1971) [29] was introduced, as a conversion function, into the general analytical equation (GAE) developed by Carrasco (1993) [30] in order to improve the calculation of the kinetic parameters, thus resulting in an enhanced general analytical equation.

## 2. Theoretical background

The reaction rate of a solid-state reaction can be described by the following equation:

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

where  $k$  is the kinetic constant,  $A$  is the Arrhenius pre-exponential factor,  $R$  is the gas constant,  $E$  the activation energy,  $\alpha$  the reacted fraction or conversion,  $T$  is the process temperature and  $f(\alpha)$  accounts for the reaction rate dependence on  $\alpha$ . Equation (1) is a general expression that describes the relationship among the reaction rate, conversion 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  $\beta = dT/dt$ , equation (1) can be written as follows:

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

Sample Controlled Thermal Analysis (SCTA) is another alternative approach with is attracting a rising interest for decomposition reactions [31-33]. 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 Thermal Analysis (CRTA). This way, by selecting a decomposition rate that is slow enough, the mass and heat transfer phenomena limitations are minimized. 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 equation (1) becomes:

$$C = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

### 2.1. Analysis based on parameters at the maximum reaction rate

The most known method which is based on parameters at the maximum reaction rate was proposed by Kissinger (1957) [34]. Its equation can be formulated as follows:

$$\ln \frac{\beta}{T_m^2} = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T_m} \quad (4)$$

where  $T_m$  is the temperature at the maximum reaction rate.

### 2.2. Isoconversional kinetic analysis

Isoconversional methods (*i.e.* model-free methods) are used for determining the activation energy as a function of the conversion without any previous assumption on the kinetic model fitted by the reaction. The main used methods are those proposed by Friedman (1964) [35] and Flynn-Wall-Ozawa (1966, 1970) [36-37]. These methods provide accurate values of activation energies even if

the activation energy was a function of the conversion. Friedman method is a differential procedure which calculates kinetic parameters at a given  $\alpha$ . Flynn-Wall-Ozawa method is an integral procedure which also determines parameters at a given  $\alpha$ . The two latter methods are useful for evaluating the activation energy as a function of conversion.

Friedman equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[A f(\alpha)] - \frac{E}{R} \frac{1}{T} \quad (5)$$

Flynn-Wall-Ozawa equation:

$$\ln \beta = \left( \ln \frac{AE}{R g(\alpha)} - 5.3305 \right) - \frac{1.05228}{R} \frac{1}{T} \quad (6a)$$

$$\text{where } g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \quad (6b)$$

### 2.3. Differential kinetic analysis

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

$$\ln\left(\frac{\frac{d\alpha}{dt}}{f(\alpha)}\right) = \ln A - \frac{E}{R} \frac{1}{T} \quad (7)$$

As no assumption regarding the thermal pathway is made in equation (7), the kinetic parameters obtained should be independent of the thermal pathway. 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 [25]:

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

This equation is a modified form of the Sestak-Berggren empirical equation [29]. It has been shown that it can fit every function (for the different mechanisms of solid-state reactions) by merely adjusting the parameters  $c$ ,  $n$  and  $m$  by means of the maximize function incorporated in Mathcad software.

From equations (7) and (8), we reach:

$$\ln \left[ \frac{\frac{d\alpha}{dt}}{(1 - \alpha)^n \alpha^m} \right] = \ln(c A) - \frac{E}{R} \frac{1}{T} \quad (9)$$

If  $c = 1$  and  $m = 0$ , the  $n$ -order kinetic equation can be found and then equation (9) becomes:

$$\ln \left[ \frac{\frac{d\alpha}{dt}}{(1 - \alpha)^n} \right] = \ln A - \frac{E}{R} \frac{1}{T} \quad (10)$$

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, parameter n (n-order kinetics) as well as n and m (modified Sestak-Berggren equation) that yield the best linear correlation are obtained, and the corresponding values of activation energy can be calculated.

#### 2.4. The general analytical equation

The general analytical equation (GAE) was developed by Carrasco in 1993 [30,38-39]. The primitive of the kinetic equation (2) contains an infinite number of terms. Often it is possible to truncate the series at the first two terms (when  $RT \ll E$ ) and the solutions are the following for the two models previously described (n-order kinetics and a modified form of the Sestak-Berggren equation):

$$\ln \left[ \beta \frac{1 - (1 - \alpha)^{1-n}}{(1-n) T^2 \left(1 - \frac{2RT}{E}\right)} \right] = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T} \quad (11)$$

$$\ln \left[ \beta \frac{\frac{1 - (1 - \alpha)^{1-n}}{1-n} + \frac{\alpha^{1-m}}{1-m}}{T^2 \left(1 - \frac{2RT}{E}\right)} \right] = \ln \frac{cAR}{E} - \frac{E}{R} \frac{1}{T} \quad (12)$$

This latter equation provides a new enhanced method to determine kinetic parameters because it considers the general analytical equation and the general expression  $f(\alpha) = c(1 - \alpha)^n \alpha^m$ , which represents all the reaction mechanisms (random scission, nucleation and growth, geometrical, diffusion and reaction-order).



### 2.5. Random scission kinetic analysis

According to Simha and Wall (1952) [40], the cleavage of bonds in random scission processes follows a first order kinetics and the following expressions hold true:

$$\frac{dx}{dt} = k (1 - x) = A \exp\left(-\frac{E}{RT}\right) (1 - x) \quad (13)$$

$$1 - \alpha = (1 - x)^{L-1} \left[1 + x \frac{(N - L)(L - 1)}{N}\right] \quad (14)$$

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  $N$  is usually negligible in comparison to  $L$ , equation (14) can be simplified to:

$$\alpha = 1 - (1 - x)^{L-1} [1 + x (L - 1)] \quad (15)$$

Given that  $x$  cannot be measured by conventional techniques and  $L$  is very difficult to obtain experimentally, the application of equation (15) has been severely limited. Nevertheless, by differentiating equation (15) and incorporating equation (13), we get:

$$\frac{d\alpha}{dt} = k L (L - 1) x (1 - x)^{L-1} \quad (16)$$

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

$$f(\alpha) = L(L - 1) x (1 - x)^{L-1} \quad (17)$$

Many kinetic analysis methods involve the fitting of experimental data to a certain kinetic model. This requires the  $f(\alpha)$  functions 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 equation (15), it can be determined that  $\alpha = x^2$ . Therefore, equations (16) and (17) become:

$$\frac{d\alpha}{dt} = 2k(\alpha^{1/2} - \alpha) \quad (18)$$

$$f(\alpha) = 2(\alpha^{1/2} - \alpha) \quad (19)$$

Taking into account that the relationship between  $x$  and  $\alpha$  is established in equation (15), for any given  $L$  and assigning values to  $\alpha$ , from equation (17) it is possible to calculate numerically the corresponding  $f(\alpha)$  conversion functions.

### 3. Experimental

A commercial type of poly(lactic acid) (PLA 2002D, Natureworks®), characterized by a relative density of 1.24, a D-monomer content of 4.25% and a residual monomer content of 0.3% was used. The glass transition temperature and the melting temperature of PLA 2002D are 58°C and 153°C,

respectively. As the filler, an organically modified montmorillonite (OMMT) (Cloisite® 30B, Southern Clay Products) was used. The organic modifier of the OMMT was an organic cation  $[N(CH_3)(C_2H_4OH)_2R]^+$ , where R is an aliphatic radical with 16–18 carbon atoms.

The first step of the compounding process was the production of the masterbatch, which was carried out using a corrotative twin-screw extruder (Collins, ZK 25, Germany) with a screw diameter of 25 mm and length/diameter (L/D) ratio of 36. The screw speed was 80 rpm, the estimated residence time 150 seconds and the temperature profile ranged between 145 and 195°C. Since PLA is susceptible to hydrolytic degradation, the use of a dehumidifier (Piovan, DSN506HE) was necessary (80°C for 3 hours) prior to any type of processing. The PLA pellets and the OMMT powder were put simultaneously into the extruder. After granulation and drying, granulates were subjected to a second extrusion process using the same conditions to homogenize the compound. Subsequently, the exact composition of the masterbatch, nominally 4% (weight) of OMMT, was determined by calcination. The third step consisted of diluting the masterbatch with virgin PLA in the twin-screw extruder, in order to obtain two compounds with nominal compositions of 0.5 and 2.5% (weight) of OMMT.

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 N<sub>2</sub>). Experiments were carried out at various linear heating rate ( $\beta = 1, 2, 4$  and 8 K/min) and by means of a Constant Rate Thermal Analysis (CRTA) at a rate of 0.004 min<sup>-1</sup>. Small samples (of approximately 9 mg) were used in order to minimize heat and mass transfer limitations. They were placed on a 1 cm diameter platinum pan inside a low thermal inertia furnace. Experimental conversion-time curves were differentiated by means of the Origin software (OriginLab) to obtain the differential curves required for the kinetic analysis.

## 4. Results and discussion

Fig. 1 shows the experimental curves conversion curves recorded for the thermal degradation of PLA-OMMT nanocomposite (containing 2.5% of OMMT) under linear heating rate ( $\beta = 1, 2, 4$  and  $8$  K/min) and Constant Rate Thermal Analysis (CRTA at  $0.004 \text{ min}^{-1}$ ) conditions. Moreover, Fig. 2 shows the variation of the conversion derivative ( $d\alpha/dt$ ) with temperature for the same nanocomposite and same operating conditions. From these plots it was possible to obtain various decomposition parameters (conversion, conversion derivative and temperature) at the maximum decomposition rate as well as the onset decomposition temperature ( $T_5$ : temperature at which 5% of mass is lost), as shown in Table 1. The onset decomposition temperature obviously increased when increasing the linear heating rate (from  $270$  to  $309^\circ\text{C}$  for PLA, from  $273$  to  $311$  for 0.5%-nanocomposite and from  $258$  to  $303^\circ\text{C}$  for 2.5%-nanocomposite). In all cases, the 0.5%-nanocomposite was more thermally stable than the polymer matrix whereas the 2.5%-nanocomposite was less stable (note that the thermal stability was quantified by means of  $T_5$  values). For example, at  $4$  K/min, the 0.5%-nanocomposite had an onset temperature  $12^\circ\text{C}$  higher than the polymer matrix (and  $17^\circ\text{C}$  higher than the 2.5%-nanocomposite). On the other hand, the 2.5%-nanocomposite had an onset temperature  $6^\circ\text{C}$  lower than the polymer matrix. Therefore, a higher load of OMMT did not lead to a higher thermal stability. Fig. 3 clearly illustrates the higher thermal stability of the 0.5% nanocomposite all through the conversion range. In our previous work [41], it was shown by transmission electron microscopy (TEM) that the nanocomposite containing 2.5% of OMMT presented more aggregates than the nanocomposite containing 0.5% of OMMT. Clearly these aggregates are responsible for a lower thermal stability. It must be noted that aggregates contain montmorillonite nanoparticles which were not well dispersed and, therefore, they can be more easily volatilized at low temperatures. The variations were not so drastic for the temperature at the maximum decomposition rate. For example, at  $4$  K/min, the 0.5%-nanocomposite had a maximum temperature  $9^\circ\text{C}$  higher than the polymer matrix (and  $4^\circ\text{C}$  higher than the 2.5%-nanocomposite). On

the other hand, the 2.5%-nanocomposite had a maximum temperature 5°C higher than the polymer matrix. By means of the Kissinger equation it was possible to evaluate the activation energy as 171, 140 and 154 kJ/mol for PLA, 0.5%-nanocomposite and 2.5%-nanocomposite, respectively. Conversions at the maximum reaction rate remained almost constant and ranged between 63 and 71%.

Fig. 4a and 4b show the variation of the activation energy with conversion as obtained by isoconversional methods (Friedman and Flynn-Wall-Ozawa) for nanocomposites containing 0.5 and 2.5% of OMMT, respectively. In both cases, there was a notorious variation of activation energy as the decomposition reaction advances. However, the trends are different for the two studied nanocomposites. At 95% confidence level, the intervals for the activation energy were  $137 \pm 6$  kJ/mol (FWO) and  $160 \pm 10$  kJ/mol (Friedman) for the nanocomposite containing 0.5% of OMMT. Taking into account that the activation energy evaluated by the Kissinger equation was 140 kJ/mol, it seems that the value calculated by the Friedman method was overevaluated. On the other hand, the intervals for the activation energy were  $158 \pm 3$  kJ/mol (FWO) and  $154 \pm 3$  kJ/mol (Friedman) for the nanocomposite containing 2.5% of OMMT. Both values are quite similar to that obtained by the Kissinger equation (154 kJ/mol). The trend of variation for PLA was similar to that of nanocomposite containing 0.5% of OMMT (*i.e.* there was a continuous increasing of activation energy with conversion). However, the E vs  $\alpha$  plot for the nanocomposite containing 2.5% of OMMT presented a bell-shape form at low conversions (lower than 20%). This could be due to the presence of aggregates, which are thermally unstable. The dependence of activation energy on conversion is an indication of a complex reaction system with the participation of at least two different mechanisms. It is well known that the thermal decomposition of biodegradable polyesters consists of a competition between the random chain scission via a cis-elimination (generating an acrylic ester unit) and the cyclic rupture via intramolecular transesterification (releasing lactic acid). Chrissafis et al. (2010) [42] reported a continuous increase of activation energy with conversion for PLA (Resorbaid, Cousin Biotech, France) from 118 kJ/mol ( $\alpha = 20\%$ ) to 148 kJ/mol ( $\alpha = 80\%$ ).

Fig. 5 shows the results of the differential kinetic analysis when using  $f(\alpha) = (1 - \alpha)^n$  for the nanocomposite containing 2.5% of OMMT. The value of  $n$  was optimized for the whole set of experimental points for the polymer matrix (PLA) at various linear heating rates and CRTA conditions. The reaction order so calculated was  $n = 0.55$ . The same value was adopted for the nanocomposites in order to adequately compare activation energy values. The fit of the experimental data to the  $n$ -order conversion function was not excellent (*i.e.* there were certain sets of experimental points which presented an important degree of deviation from the straight line). Fig. 6 shows the results of the differential kinetic analysis when using  $f(\alpha) = c(1 - \alpha)^n\alpha^m$ . The values of  $n$  and  $m$  were optimized for the whole set of experimental points for the polymer matrix, as previously stated. The exponents so calculated were  $n = 0.771$  and  $m = 0.244$ . The fit of the experimental data to this conversion function was not excellent, but it was better than that observed for the conversion function  $f(\alpha) = (1 - \alpha)^n$  in Fig. 5. Therefore, the introduction of two parameters ( $n$  and  $m$ ) to the conversion function  $f(\alpha)$  clearly improved the fitting of TG data ( $r^2 = 0.995$  vs  $0.990$ ). Fig. 7 shows the results of the fitting when combining the general analytical solution (GAE), developed by Carrasco (1993) [30], with the conversion function  $f(\alpha) = (1 - \alpha)^n$  ( $n$ -order kinetics). The linear regression of the whole experimental points was not excellent and this plot clearly indicates that the deviations of experimental data from the straight line were still significant. However, the use of the general analytical equation clearly improved the adjustment of the experimental TG data compared to the differential method shown in Fig. 5 and 6. The deviations observed can be minimized by using  $f(\alpha) = c(1 - \alpha)^n\alpha^m$  as the conversion function, as illustrated in Fig. 8. In this case, the fitting was really excellent ( $r^2 = 0.998$  vs  $0.988$ ) and all the experimental points presented minimal errors with respect to the straight line. Therefore, equation (12) is a new enhanced method to determine kinetic parameters which combines the general analytical equation (GAE), developed by Carrasco in 1993 [30] and the conversion function  $f(\alpha) = c(1 - \alpha)^n\alpha^m$ , which is a modified form of the equation developed by Sestak-Berggren in 1971 [29].

Table 2 contains the activation energy values determined for the polymer matrix (PLA) and nanocomposites containing 0.5 and 2.5% of OMMT by using different methods (model-free, differential and integral, and two different  $f(\alpha)$  conversion functions). This table clearly indicates that the activation energy evaluated by using the enhanced general analytical equation is statistically the same than those obtained by Flynn-Wall-Ozawa isoconversional model-free method. Indeed, the best activation energies (found by means of the enhanced general analytical equation) were 161 kJ/mol (156-168 kJ/mol by means of FWO method) for PLA, 140 kJ/mol (131-143 kJ/mol) for the nanocomposite containing 0.5% of OMMT and 154 kJ/mol (155-161 kJ/mol) for the nanocomposite containing 2.5% of OMMT. Even though the activation energy for the nanocomposite containing 0.5% of OMMY was lower, its thermal stability was higher given that the degradation process took place at higher temperatures (as it was illustrated in Fig. 3). It was also possible to evaluate frequency factors through the enhanced general analytical equation:  $A_c = 3.03 \cdot 10^{13}$ ,  $2.82 \cdot 10^{11}$  and  $1.09 \cdot 10^{13} \text{ min}^{-1}$ , respectively. It has to be noted that there was a kinetic compensation effect between the Arrhenius parameters ( $\ln A_c = -4.87 + 0.22 E$ ,  $r^2 = 0.9999$ ), thus indicating that the thermal degradation of PLA and that of its nanocomposites are related processes.

Fig. 9 illustrates the validity of the kinetic parameters evaluated by various methods when the experiments were carried out at 1 K/min. It is clear that the simulated points obtained by means of the enhanced general analytical equation properly reconstructed the experimental values of conversion whereas there were more significant deviations when using the general analytical equation for an n-order kinetics and these divergences were really important when using the differential method for an n-order kinetics. On the other hand, Fig. 10 shows the divergences observed between theoretical and experimental values of temperature as a function of conversion. This plot is suitable to check the validity of the proposed kinetic model. When using our enhanced general analytical equation, the temperature differences ranged from -1 to +1°C. The temperature

divergences were higher when using the general analytical equation for an n-order kinetics (*i.e.* from -1 to +4°C) and they were unacceptable when using the classical differential methods for an n-order kinetics (*i.e.* from -11 to +5°C). Theoretical temperatures were calculated by using the Newton-Raphson method at a given  $\alpha$ , which uses a convergent iterative process to approach one root of a function. The function and its derivative for the enhanced general analytical equation were the following:

$$y(\alpha, T) = \ln \left[ \frac{\beta E}{cAR} \frac{1 - (1 - \alpha)^{1-n} + \frac{\alpha^{1-m}}{1-m}}{T^2 \left(1 - \frac{2RT}{E}\right)} \right] + \frac{E}{RT} = 0 \quad (20)$$

$$\left(\frac{\partial y}{\partial T}\right)_{\alpha} = f'(T) = \frac{2 \left(\frac{3R}{E} - \frac{1}{T}\right)}{1 - \frac{2RT}{E}} - \frac{E}{RT^2} = 0 \quad (21)$$

Fig. 11a shows the comparison of  $f(\alpha)$  conversion function for different models, such as: a modified form of the Sestak-Berggren equation  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (where  $n$  and  $m$  are values optimized for the whole set of experimental points at various heating rates and CRTA conditions as previously stated) and the equations corresponding to conventional solid-state mechanisms (nucleation and growth, geometrical, diffusion and reaction-order) and random scission ( $L = 2$ ). All conversion functions were normalized at  $f(0.5)$  for an easier differentiation in the shape between the different models. This plot shows that the conversion function (*i.e.* modified Sestak-Berggren equation) associated with the thermal degradation of PLA and its nanocomposites (dotted line) had a very close resemblance to the random scission model ( $L = 2$ ), although it did not exactly match it, probably due to the deviation of the real process from the ideal conditions assumed in the model. On the other hand, the experimental points for PLA ( $\beta = 4$  K/min) and the nanocomposite containing 0.5%



of OMMT ( $\beta = 1$  K/min) had also a close resemblance to the random scission model ( $L = 2$ ) (see details in Fig. 11b). As previously reported in this paper, thermal and hydrolysis reactions for biopolymers could be generated by random chain scission reactions of the ester groups. In addition, intra- and intermolecular transesterification reactions could also cause a drop in molecular weight at longer reaction time. Moreover, pyrolysis could be also be considered at high temperatures ( $T > 300^\circ\text{C}$ ). All these phenomena explain the reaction mechanisms found in this work.

Finally, in our study a reaction order  $n = 0.55$  was obtained as the best order by means of linear regression of the differential equation for all the PLA experimental data, as previously stated. It must be taken into consideration that some of the conventional kinetic mechanisms of solid-state processes are based on  $n$ -order reactions ( $F_1$ ,  $F_2$  and  $F_3$  which consider the random nucleation of one, two and three nuclei on the individual particle). This is a simple method often reported in the literature, but clearly an  $n$  value different of 1, 2 or 3 is not considered in the conversion functions representing the reaction-order kinetic mechanisms. It was demonstrated that the fitting of experimental points was not excellent. On the other hand, the fitting of experimental data by using the conversion function  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  was clearly better. This conversion function is more general than that corresponding to an  $n$ -order kinetics and, depending on  $n$  and  $m$  values, can reconstruct all the conversion functions corresponding to the various conventional kinetic mechanisms (nucleation and growth, geometrical, reaction-order and diffusion) as well as the random scission mechanism presented in this work.

## 5. Conclusions

In this work, an enhanced general analytical equation has been used to study the kinetics of the thermal degradation of poly(lactic acid) (PLA) and its nanocomposites with an organomodified montmorillonite (OMMT). This new method consists of including a modified form of the Sestak-

Berggren equation  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  into the general analytical equation (GAE), which is an integral procedure to analyze TG data. The kinetic parameters so calculated were:  $E = 161$  kJ/mol and  $A_c = 3.03 \cdot 10^{13}$  min<sup>-1</sup> for PLA,  $E = 140$  kJ/mol and  $A_c = 2.82 \cdot 10^{11}$  min<sup>-1</sup> for the nanocomposite containing 0.5% of OMMT, and  $E = 157$  kJ/mol and  $A_c = 1.09 \cdot 10^{13}$  min<sup>-1</sup> for the nanocomposite containing 2.5% of OMMT. This method revealed to be better than the often used conversion function  $f(\alpha) = (1 - \alpha)^n$ , which corresponds to an n-order reaction. The exponents  $n = 0.771$  and  $m = 0.244$  were previously optimized for the whole set of experiments carried out at different linear heating rates and at constant reaction rate (CRTA) for the thermal degradation of PLA. These exponents were also used for nanocomposites for comparison purposes. Moreover, the kinetic parameters evaluated by this new method were compared to those obtained by differential and isoconversional methods. Moreover, Simha-Wall equations for the description of random scission mechanism have been used together with the conversion functions for other conventional mechanisms (nucleation and growth, geometrical, reaction-order and diffusion) in order to ascertain the best mechanism. It has been demonstrated the thermal degradation of PLA and its nanocomposites was in a good accordance with a random scission mechanism for  $L = 2$ , which corresponds to the conversion function  $f(\alpha) = 2(\alpha^{1/2} - \alpha)$ . It has been shown that nanocomposites were thermally more stable than the polymer matrix. Moreover, when comparing both types of nanocomposites (with 0.5 and 2.5% of OMMT), the nanocomposite containing the higher amount of nanoparticles was less stable because of the presence of aggregates.

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## Figure Captions

**Fig. 1.** Experimental conversion vs temperature plots for the thermal degradation of the nanocomposite containing 2.5% of OMMT at various linear heating rates and CRTA (Constant Rate Thermal Analysis) conditions.

**Fig. 2.** Experimental conversion derivative vs temperature plots for the thermal degradation of the nanocomposite containing 2.5% of OMMT at various linear heating rates and CRTA (Constant Rate Thermal Analysis) conditions.

**Fig. 3.** Comparison of the thermal stability between PLA and its nanocomposites at a linear heating rate of 4 K/min.

**Fig. 4.** Variation of activation energy with conversion according to isoconversional methods for **(a)** the nanocomposite containing 0.5% of OMMT; **(b)** the nanocomposite containing 2.5% of OMMT;

**Fig. 5.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the conversion differential equation and  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation).

**Fig. 6.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the conversion differential equation and  $f(\alpha) = c(1 - \alpha)^m$  (modified Sestak-Berggren equation).



**Fig. 7.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the general analytical equation (GAE) and  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation).

**Fig. 8.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the general analytical equation (GAE) and  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation).

**Fig. 9.** Comparison between experimental conversion data (solid line) and theoretical conversion values for the thermal degradation of the nanocomposite containing 2.5% of OMMT at a linear heating rate of 1 K/min. The theoretical data were obtained by using two different kinetic equations (differential equation and general analytical equation (GAE)) and two different conversion functions:  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation) and  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation).

**Fig. 10.** Validity of the enhanced general analytical equation and other methods. The theoretical temperature was calculated by using two different kinetic equations (differential equation and general analytical equation (GAE)) and two different conversion functions:  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation) and  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation). Experimental temperatures correspond to the thermal degradation of the nanocomposite containing 2.5% of OMMT at a linear heating rate of 1 K/min.

**Fig. 11. (a)** Comparison of the  $f(\alpha)$  conversion functions (solid lines) normalized at  $\alpha = 0.5$ , corresponding to some of the ideal kinetic models with the curve reconstructed by means of  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation) and experimental points for the

thermal degradation of PLA at  $\beta = 4$  K/min and that of the nanocomposite containing 0.5% of OMMT at  $\beta = 1$  K/min; **(b)** Comparison of the random scission mechanism ( $L = 2$ ) with the curve reconstructed by means of  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren) and experimental points for the thermal degradation of PLA at  $\beta = 4$  K/min and that of the nanocomposite containing 0.5% of OMMT at  $\beta = 1$  K/min.

# ENHANCED GENERAL ANALYTICAL EQUATION FOR THE KINETICS OF THE THERMAL DEGRADATION OF POLY(LACTIC ACID) / MONTMOTILLONITE NANOCOMPOSITES DRIVEN BY RANDOM SCISSION

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## Abstract

An enhanced general analytical equation has been developed in order to evaluate the kinetic parameters of the thermal degradation of nanocomposites, composed of poly(lactic acid) (PLA) and organo-modified montmorillonite (OMMT) nanoparticles. This improvement has consisted of replacing the n-order conversion function by a modified form of the Sestak-Berggren equation  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  that led to a better adjustment of experimental data and also adequately represented the conventional mechanisms for solid-state processes. The kinetic parameters so obtained have been compared to those determined by conventional differential and isoconversional methods. Given that the thermal degradation of PLA has been argued to be caused by random chain scission reactions of ester groups, the conversion function  $f(\alpha) = L(L - 1)x(1 - x)^{L-1}$ , corresponding to a random scission mechanism, has been tested. Once optimized the kinetic model, the thermal degradation kinetics of nanocomposites (0.5 an was compared to that of the polymer

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matrix. Moreover, the thermal stability of nanocomposites was tested and compared to that of the polymer matrix.

**Keywords:** poly(lactic acid); montmorillonite; nanocomposites; thermal degradation; enhanced kinetic model; general analytical equation; random scission

## 1. Introduction

Poly(lactic acid) (PLA) is a thermoplastic, high-strength, high-modulus polymer that can be made from annually renewable resources to yield articles for use in either the industrial packaging field or the biocompatible/bioabsorbable medical device market. It is easily processed on standard plastics equipment to yield molded parts, films, or fibers [1]. Thus, it can be reasonably substituted for certain petroleum-based plastics in high volume applications. In order for PLA to increase its application window and be processed on large-scale production lines such as injection molding, blow molding, thermoconforming, and extrusion, the polymer must possess adequate thermal stability or low thermal degradation during processing and use, and maintain its molecular weight and properties.

Melt degradation of polymers can be defined as molecular deterioration as a result of overheating. At high temperatures the components of the long chain polymer backbone can begin to separate (molecular scission) and react with another molecule to change the polymer properties. It has to be noted that thermal degradation of PLA is very complex and various mechanisms have been postulated, including various non-radical and radical reactions: random chain scission reactions, depolymerization, oxidative degradation, intramolecular and intermolecular transesterifications, hydrolysis, pyrolytic elimination and radical reactions [2-14].

In order to improve the thermal, mechanical, and other properties of the organic polymeric materials, inorganic fillers are added into the polymer formulations to form organic-inorganic composites. The formation of nanocomposites has been studied because of their high interfacial areas and exceptional properties. Nanoscale spherical particles, nanotubes, and layered clay [15-22] are major fillers in preparation of nanocomposites. Considerable efforts have been made to reduce thermal degradation rate and enhance thermal stability so that PLA can have wider applications without a compromise of the product properties prior to the onset of degradation. Among the many methods that can be used to reduce PLA thermal degradation, a promising one is to prepare nanocomposites by adding organo-modified montmorillonite (OMMT) clays in the PLA matrix. Additional advantages would be: 1) the final product cost may be reduced; 2) OMMT can improve physical and mechanical properties; 3) the parameters during melt processing do not need to be changed at low filler loading.

Due to its applicability in the macroscopic scale, the modeling of the thermal decomposition processes in inert or in reactive conditions has been broadly applied by using isoconversional, integral, differential and special methods proposed by different authors with good acceptance because its versatility in different polymeric materials. The kinetic 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 depolymerization processes was 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 analysis was performed by means of the differential kinetic analysis method that 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 [23-28]. The kinetic

parameters thus obtained were 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 first or n-order kinetic models. On the other hand, a modified form of the Sestak-Berggren equation (1971) [29] was introduced, as a conversion function, into the general analytical equation (GAE) developed by Carrasco (1993) [30] in order to improve the calculation of the kinetic parameters, thus resulting in an enhanced general analytical equation.

## 2. Theoretical background

The reaction rate of a solid-state reaction can be described by the following equation:

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

where  $k$  is the kinetic constant,  $A$  is the Arrhenius pre-exponential factor,  $R$  is the gas constant,  $E$  the activation energy,  $\alpha$  the reacted fraction or conversion,  $T$  is the process temperature and  $f(\alpha)$  accounts for the reaction rate dependence on  $\alpha$ . Equation (1) is a general expression that describes the relationship among the reaction rate, conversion 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  $\beta = dT/dt$ , equation (1) can be written as follows:

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

Sample Controlled Thermal Analysis (SCTA) is another alternative approach which is attracting a rising interest for decomposition reactions [31-33]. 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 Thermal Analysis (CRTA). This way, by selecting a decomposition rate that is slow enough, the mass and heat transfer phenomena limitations are minimized. 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 equation (1) becomes:

$$C = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (3)$$

### 2.1. Analysis based on parameters at the maximum reaction rate

The most known method which is based on parameters at the maximum reaction rate was proposed by Kissinger (1957) [34]. Its equation can be formulated as follows:

$$\ln \frac{\beta}{T_m^2} = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T_m} \quad (4)$$

where  $T_m$  is the temperature at the maximum reaction rate.

### 2.2. Isoconversional kinetic analysis

Isoconversional methods (*i.e.* model-free methods) are used for determining the activation energy as a function of the conversion without any previous assumption on the kinetic model fitted by the reaction. The main used methods are those proposed by Friedman (1964) [35] and Flynn-Wall-Ozawa (1966, 1970) [36-37]. These methods provide accurate values of activation energies even if

the activation energy was a function of the conversion. Friedman method is a differential procedure which calculates kinetic parameters at a given  $\alpha$ . Flynn-Wall-Ozawa method is an integral procedure which also determines parameters at a given  $\alpha$ . The two latter methods are useful for evaluating the activation energy as a function of conversion.

Friedman equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[A f(\alpha)] - \frac{E}{R} \frac{1}{T} \quad (5)$$

Flynn-Wall-Ozawa equation:

$$\ln \beta = \left( \ln \frac{AE}{R g(\alpha)} - 5.3305 \right) - \frac{1.05228}{R} \frac{1}{T} \quad (6a)$$

$$\text{where } g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \quad (6b)$$

### 2.3. Differential kinetic analysis

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

$$\ln\left(\frac{\frac{d\alpha}{dt}}{f(\alpha)}\right) = \ln A - \frac{E}{R} \frac{1}{T} \quad (7)$$



As no assumption regarding the thermal pathway is made in equation (7), the kinetic parameters obtained should be independent of the thermal pathway. 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 [25]:

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

This equation is a modified form of the Sestak-Berggren empirical equation [29]. It has been shown that it can fit every function (for the different mechanisms of solid-state reactions) by merely adjusting the parameters  $c$ ,  $n$  and  $m$  by means of the maximize function incorporated in Mathcad software.

From equations (7) and (8), we reach:

$$\ln \left[ \frac{\frac{d\alpha}{dt}}{(1 - \alpha)^n \alpha^m} \right] = \ln(c A) - \frac{E}{R} \frac{1}{T} \quad (9)$$

If  $c = 1$  and  $m = 0$ , the  $n$ -order kinetic equation can be found and then equation (9) becomes:

$$\ln \left[ \frac{\frac{d\alpha}{dt}}{(1 - \alpha)^n} \right] = \ln A - \frac{E}{R} \frac{1}{T} \quad (10)$$

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, parameter n (n-order kinetics) as well as n and m (modified Sestak-Berggren equation) that yield the best linear correlation are obtained, and the corresponding values of activation energy can be calculated.

#### 2.4. The general analytical equation

The general analytical equation (GAE) was developed by Carrasco in 1993 [30,38-39]. The primitive of the kinetic equation (2) contains an infinite number of terms. Often it is possible to truncate the series at the first two terms (when  $RT \ll E$ ) and the solutions are the following for the two models previously described (n-order kinetics and a modified form of the Sestak-Berggren equation):

$$\ln \left[ \beta \frac{1 - (1 - \alpha)^{1-n}}{(1-n) T^2 \left(1 - \frac{2RT}{E}\right)} \right] = \ln \frac{AR}{E} - \frac{E}{R} \frac{1}{T} \quad (11)$$

$$\ln \left[ \beta \frac{\frac{1 - (1 - \alpha)^{1-n}}{1-n} + \frac{\alpha^{1-m}}{1-m}}{T^2 \left(1 - \frac{2RT}{E}\right)} \right] = \ln \frac{cAR}{E} - \frac{E}{R} \frac{1}{T} \quad (12)$$

This latter equation provides a new enhanced method to determine kinetic parameters because it considers the general analytical equation and the general expression  $f(\alpha) = c(1 - \alpha)^n \alpha^m$ , which represents all the reaction mechanisms (random scission, nucleation and growth, geometrical, diffusion and reaction-order).

### 2.5. Random scission kinetic analysis

According to Simha and Wall (1952) [40], the cleavage of bonds in random scission processes follows a first order kinetics and the following expressions hold true:

$$\frac{dx}{dt} = k (1 - x) = A \exp\left(-\frac{E}{RT}\right) (1 - x) \quad (13)$$

$$1 - \alpha = (1 - x)^{L-1} \left[1 + x \frac{(N - L)(L - 1)}{N}\right] \quad (14)$$

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  $N$  is usually negligible in comparison to  $L$ , equation (14) can be simplified to:

$$\alpha = 1 - (1 - x)^{L-1} [1 + x (L - 1)] \quad (15)$$

Given that  $x$  cannot be measured by conventional techniques and  $L$  is very difficult to obtain experimentally, the application of equation (15) has been severely limited. Nevertheless, by differentiating equation (15) and incorporating equation (13), we get:

$$\frac{d\alpha}{dt} = k L (L - 1) x (1 - x)^{L-1} \quad (16)$$

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

$$f(\alpha) = L(L - 1) x (1 - x)^{L-1} \quad (17)$$

Many kinetic analysis methods involve the fitting of experimental data to a certain kinetic model. This requires the  $f(\alpha)$  functions 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 equation (15), it can be determined that  $\alpha = x^2$ . Therefore, equations (16) and (17) become:

$$\frac{d\alpha}{dt} = 2k(\alpha^{1/2} - \alpha) \quad (18)$$

$$f(\alpha) = 2(\alpha^{1/2} - \alpha) \quad (19)$$

Taking into account that the relationship between  $x$  and  $\alpha$  is established in equation (15), for any given  $L$  and assigning values to  $\alpha$ , from equation (17) it is possible to calculate numerically the corresponding  $f(\alpha)$  conversion functions.

### 3. Experimental

A commercial type of poly(lactic acid) (PLA 2002D, Natureworks®), characterized by a relative density of 1.24, a D-monomer content of 4.25% and a residual monomer content of 0.3% was used. The glass transition temperature and the melting temperature of PLA 2002D are 58°C and 153°C,

respectively. As the filler, an organically modified montmorillonite (OMMT) (Cloisite® 30B, Southern Clay Products) was used. The organic modifier of the OMMT was an organic cation  $[N(CH_3)(C_2H_4OH)_2R]^+$ , where R is an aliphatic radical with 16–18 carbon atoms.

The first step of the compounding process was the production of the masterbatch, which was carried out using a corrotative twin-screw extruder (Collins, ZK 25, Germany) with a screw diameter of 25 mm and length/diameter (L/D) ratio of 36. The screw speed was 80 rpm, the estimated residence time 150 seconds and the temperature profile ranged between 145 and 195°C. Since PLA is susceptible to hydrolytic degradation, the use of a dehumidifier (Piovan, DSN506HE) was necessary (80°C for 3 hours) prior to any type of processing. The PLA pellets and the OMMT powder were put simultaneously into the extruder. After granulation and drying, granulates were subjected to a second extrusion process using the same conditions to homogenize the compound. Subsequently, the exact composition of the masterbatch, nominally 4% (weight) of OMMT, was determined by calcination. The third step consisted of diluting the masterbatch with virgin PLA in the twin-screw extruder, in order to obtain two compounds with nominal compositions of 0.5 and 2.5% (weight) of OMMT.

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 N<sub>2</sub>). Experiments were carried out at various linear heating rate ( $\beta = 1, 2, 4$  and 8 K/min) and by means of a Constant Rate Thermal Analysis (CRTA) at a rate of 0.004 min<sup>-1</sup>. Small samples (of approximately 9 mg) were used in order to minimize heat and mass transfer limitations. They were placed on a 1 cm diameter platinum pan inside a low thermal inertia furnace. Experimental conversion-time curves were differentiated by means of the Origin software (OriginLab) to obtain the differential curves required for the kinetic analysis.

## 4. Results and discussion

Fig. 1 shows the experimental curves conversion curves recorded for the thermal degradation of PLA-OMMT nanocomposite (containing 2.5% of OMMT) under linear heating rate ( $\beta = 1, 2, 4$  and  $8$  K/min) and Constant Rate Thermal Analysis (CRTA at  $0.004 \text{ min}^{-1}$ ) conditions. Moreover, Fig. 2 shows the variation of the conversion derivative ( $d\alpha/dt$ ) with temperature for the same nanocomposite and same operating conditions. From these plots it was possible to obtain various decomposition parameters (conversion, conversion derivative and temperature) at the maximum decomposition rate as well as the onset decomposition temperature ( $T_5$ : temperature at which 5% of mass is lost), as shown in Table 1. The onset decomposition temperature obviously increased when increasing the linear heating rate (from  $270$  to  $309^\circ\text{C}$  for PLA, from  $273$  to  $311$  for 0.5%-nanocomposite and from  $258$  to  $303^\circ\text{C}$  for 2.5%-nanocomposite). In all cases, the 0.5%-nanocomposite was more thermally stable than the polymer matrix whereas the 2.5%-nanocomposite was less stable (note that the thermal stability was quantified by means of  $T_5$  values). For example, at  $4$  K/min, the 0.5%-nanocomposite had an onset temperature  $12^\circ\text{C}$  higher than the polymer matrix (and  $17^\circ\text{C}$  higher than the 2.5%-nanocomposite). On the other hand, the 2.5%-nanocomposite had an onset temperature  $6^\circ\text{C}$  lower than the polymer matrix. Therefore, a higher load of OMMT did not lead to a higher thermal stability. Fig. 3 clearly illustrates the higher thermal stability of the 0.5% nanocomposite all through the conversion range. In our previous work [41], it was shown by transmission electron microscopy (TEM) that the nanocomposite containing 2.5% of OMMT presented more aggregates than the nanocomposite containing 0.5% of OMMT. Clearly these aggregates are responsible for a lower thermal stability. It must be noted that aggregates contain montmorillonite nanoparticles which were not well dispersed and, therefore, they can be more easily volatilized at low temperatures. The variations were not so drastic for the temperature at the maximum decomposition rate. For example, at  $4$  K/min, the 0.5%-nanocomposite had a maximum temperature  $9^\circ\text{C}$  higher than the polymer matrix (and  $4^\circ\text{C}$  higher than the 2.5%-nanocomposite). On

the other hand, the 2.5%-nanocomposite had a maximum temperature 5°C higher than the polymer matrix. By means of the Kissinger equation it was possible to evaluate the activation energy as 171, 140 and 154 kJ/mol for PLA, 0.5%-nanocomposite and 2.5%-nanocomposite, respectively. Conversions at the maximum reaction rate remained almost constant and ranged between 63 and 71%.

Fig. 4a and 4b show the variation of the activation energy with conversion as obtained by isoconversional methods (Friedman and Flynn-Wall-Ozawa) for nanocomposites containing 0.5 and 2.5% of OMMT, respectively. In both cases, there was a notorious variation of activation energy as the decomposition reaction advances. However, the trends are different for the two studied nanocomposites. At 95% confidence level, the intervals for the activation energy were  $137 \pm 6$  kJ/mol (FWO) and  $160 \pm 10$  kJ/mol (Friedman) for the nanocomposite containing 0.5% of OMMT. Taking into account that the activation energy evaluated by the Kissinger equation was 140 kJ/mol, it seems that the value calculated by the Friedman method was overevaluated. On the other hand, the intervals for the activation energy were  $158 \pm 3$  kJ/mol (FWO) and  $154 \pm 3$  kJ/mol (Friedman) for the nanocomposite containing 2.5% of OMMT. Both values are quite similar to that obtained by the Kissinger equation (154 kJ/mol). The trend of variation for PLA was similar to that of nanocomposite containing 0.5% of OMMT (*i.e.* there was a continuous increasing of activation energy with conversion). However, the  $E$  vs  $\alpha$  plot for the nanocomposite containing 2.5% of OMMT presented a bell-shape form at low conversions (lower than 20%). This could be due to the presence of aggregates, which are thermally unstable. The dependence of activation energy on conversion is an indication of a complex reaction system with the participation of at least two different mechanisms. It is well known that the thermal decomposition of biodegradable polyesters consists of a competition between the random chain scission via a cis-elimination (generating an acrylic ester unit) and the cyclic rupture via intramolecular transesterification (releasing lactic acid). Chrissafis et al. (2010) [42] reported a continuous increase of activation energy with conversion for PLA (Resorbaid, Cousin Biotech, France) from 118 kJ/mol ( $\alpha = 20\%$ ) to 148 kJ/mol ( $\alpha = 80\%$ ).

Fig. 5 shows the results of the differential kinetic analysis when using  $f(\alpha) = (1 - \alpha)^n$  for the nanocomposite containing 2.5% of OMMT. The value of  $n$  was optimized for the whole set of experimental points for the polymer matrix (PLA) at various linear heating rates and CRTA conditions. The reaction order so calculated was  $n = 0.55$ . The same value was adopted for the nanocomposites in order to adequately compare activation energy values. The fit of the experimental data to the  $n$ -order conversion function was not excellent (*i.e.* there were certain sets of experimental points which presented an important degree of deviation from the straight line). Fig. 6 shows the results of the differential kinetic analysis when using  $f(\alpha) = c(1 - \alpha)^n\alpha^m$ . The values of  $n$  and  $m$  were optimized for the whole set of experimental points for the polymer matrix, as previously stated. The exponents so calculated were  $n = 0.771$  and  $m = 0.244$ . The fit of the experimental data to this conversion function was not excellent, but it was better than that observed for the conversion function  $f(\alpha) = (1 - \alpha)^n$  in Fig. 5. Therefore, the introduction of two parameters ( $n$  and  $m$ ) to the conversion function  $f(\alpha)$  clearly improved the fitting of TG data ( $r^2 = 0.995$  vs  $0.990$ ). Fig. 7 shows the results of the fitting when combining the general analytical solution (GAE), developed by Carrasco (1993) [30], with the conversion function  $f(\alpha) = (1 - \alpha)^n$  ( $n$ -order kinetics). The linear regression of the whole experimental points was not excellent and this plot clearly indicates that the deviations of experimental data from the straight line were still significant. However, the use of the general analytical equation clearly improved the adjustment of the experimental TG data compared to the differential method shown in Fig. 5 and 6. The deviations observed can be minimized by using  $f(\alpha) = c(1 - \alpha)^n\alpha^m$  as the conversion function, as illustrated in Fig. 8. In this case, the fitting was really excellent ( $r^2 = 0.998$  vs  $0.988$ ) and all the experimental points presented minimal errors with respect to the straight line. Therefore, equation (12) is a new enhanced method to determine kinetic parameters which combines the general analytical equation (GAE), developed by Carrasco in 1993 [30] and the conversion function  $f(\alpha) = c(1 - \alpha)^n\alpha^m$ , which is a modified form of the equation developed by Sestak-Berggren in 1971 [29].



Table 2 contains the activation energy values determined for the polymer matrix (PLA) and nanocomposites containing 0.5 and 2.5% of OMMT by using different methods (model-free, differential and integral, and two different  $f(\alpha)$  conversion functions). This table clearly indicates that the activation energy evaluated by using the enhanced general analytical equation is statistically the same than those obtained by Flynn-Wall-Ozawa isoconversional model-free method. Indeed, the best activation energies (found by means of the enhanced general analytical equation) were 161 kJ/mol (156-168 kJ/mol by means of FWO method) for PLA, 140 kJ/mol (131-143 kJ/mol) for the nanocomposite containing 0.5% of OMMT and 154 kJ/mol (155-161 kJ/mol) for the nanocomposite containing 2.5% of OMMT. Even though the activation energy for the nanocomposite containing 0.5% of OMMY was lower, its thermal stability was higher given that the degradation process took place at higher temperatures (as it was illustrated in Fig. 3). It was also possible to evaluate frequency factors through the enhanced general analytical equation:  $A_c = 3.03 \cdot 10^{13}$ ,  $2.82 \cdot 10^{11}$  and  $1.09 \cdot 10^{13} \text{ min}^{-1}$ , respectively. It has to be noted that there was a kinetic compensation effect between the Arrhenius parameters ( $\ln A_c = -4.87 + 0.22 E$ ,  $r^2 = 0.9999$ ), thus indicating that the thermal degradation of PLA and that of its nanocomposites are related processes.

Fig. 9 illustrates the validity of the kinetic parameters evaluated by various methods when the experiments were carried out at 1 K/min. It is clear that the simulated points obtained by means of the enhanced general analytical equation properly reconstructed the experimental values of conversion whereas there were more significant deviations when using the general analytical equation for an n-order kinetics and these divergences were really important when using the differential method for an n-order kinetics. On the other hand, Fig. 10 shows the divergences observed between theoretical and experimental values of temperature as a function of conversion. This plot is suitable to check the validity of the proposed kinetic model. When using our enhanced general analytical equation, the temperature differences ranged from -1 to +1°C. The temperature

divergences were higher when using the general analytical equation for an n-order kinetics (*i.e.* from -1 to +4°C) and they were unacceptable when using the classical differential methods for an n-order kinetics (*i.e.* from -11 to +5°C). Theoretical temperatures were calculated by using the Newton-Raphson method at a given  $\alpha$ , which uses a convergent iterative process to approach one root of a function. The function and its derivative for the enhanced general analytical equation were the following:

$$y(\alpha, T) = \ln \left[ \frac{\beta E}{cAR} \frac{1 - (1 - \alpha)^{1-n} + \frac{\alpha^{1-m}}{1-m}}{T^2 \left(1 - \frac{2RT}{E}\right)} \right] + \frac{E}{RT} = 0 \quad (20)$$

$$\left(\frac{\partial y}{\partial T}\right)_{\alpha} = f'(T) = \frac{2 \left(\frac{3R}{E} - \frac{1}{T}\right)}{1 - \frac{2RT}{E}} - \frac{E}{RT^2} = 0 \quad (21)$$

Fig. 11a shows the comparison of  $f(\alpha)$  conversion function for different models, such as: a modified form of the Sestak-Berggren equation  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (where  $n$  and  $m$  are values optimized for the whole set of experimental points at various heating rates and CRTA conditions as previously stated) and the equations corresponding to conventional solid-state mechanisms (nucleation and growth, geometrical, diffusion and reaction-order) and random scission ( $L = 2$ ). All conversion functions were normalized at  $f(0.5)$  for an easier differentiation in the shape between the different models. This plot shows that the conversion function (*i.e.* modified Sestak-Berggren equation) associated with the thermal degradation of PLA and its nanocomposites (dotted line) had a very close resemblance to the random scission model ( $L = 2$ ), although it did not exactly match it, probably due to the deviation of the real process from the ideal conditions assumed in the model. On the other hand, the experimental points for PLA ( $\beta = 4$  K/min) and the nanocomposite containing 0.5%

of OMMT ( $\beta = 1$  K/min) had also a close resemblance to the random scission model ( $L = 2$ ) (see details in Fig. 11b). As previously reported in this paper, thermal and hydrolysis reactions for biopolymers could be generated by random chain scission reactions of the ester groups. In addition, intra- and intermolecular transesterification reactions could also cause a drop in molecular weight at longer reaction time. Moreover, pyrolysis could be also be considered at high temperatures ( $T > 300^\circ\text{C}$ ). All these phenomena explain the reaction mechanisms found in this work.

Finally, in our study a reaction order  $n = 0.55$  was obtained as the best order by means of linear regression of the differential equation for all the PLA experimental data, as previously stated. It must be taken into consideration that some of the conventional kinetic mechanisms of solid-state processes are based on  $n$ -order reactions ( $F_1$ ,  $F_2$  and  $F_3$  which consider the random nucleation of one, two and three nuclei on the individual particle). This is a simple method often reported in the literature, but clearly an  $n$  value different of 1, 2 or 3 is not considered in the conversion functions representing the reaction-order kinetic mechanisms. It was demonstrated that the fitting of experimental points was not excellent. On the other hand, the fitting of experimental data by using the conversion function  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  was clearly better. This conversion function is more general than that corresponding to an  $n$ -order kinetics and, depending on  $n$  and  $m$  values, can reconstruct all the conversion functions corresponding to the various conventional kinetic mechanisms (nucleation and growth, geometrical, reaction-order and diffusion) as well as the random scission mechanism presented in this work.

## 5. Conclusions

In this work, an enhanced general analytical equation has been used to study the kinetics of the thermal degradation of poly(lactic acid) (PLA) and its nanocomposites with an organomodified montmorillonite (OMMT). This new method consists of including a modified form of the Sestak-

Berggren equation  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  into the general analytical equation (GAE), which is an integral procedure to analyze TG data. The kinetic parameters so calculated were:  $E = 161$  kJ/mol and  $A_c = 3.03 \cdot 10^{13}$  min<sup>-1</sup> for PLA,  $E = 140$  kJ/mol and  $A_c = 2.82 \cdot 10^{11}$  min<sup>-1</sup> for the nanocomposite containing 0.5% of OMMT, and  $E = 157$  kJ/mol and  $A_c = 1.09 \cdot 10^{13}$  min<sup>-1</sup> for the nanocomposite containing 2.5% of OMMT. This method revealed to be better than the often used conversion function  $f(\alpha) = (1 - \alpha)^n$ , which corresponds to an n-order reaction. The exponents  $n = 0.771$  and  $m = 0.244$  were previously optimized for the whole set of experiments carried out at different linear heating rates and at constant reaction rate (CRTA) for the thermal degradation of PLA. These exponents were also used for nanocomposites for comparison purposes. Moreover, the kinetic parameters evaluated by this new method were compared to those obtained by differential and isoconversional methods. Moreover, Simha-Wall equations for the description of random scission mechanism have been used together with the conversion functions for other conventional mechanisms (nucleation and growth, geometrical, reaction-order and diffusion) in order to ascertain the best mechanism. It has been demonstrated the thermal degradation of PLA and its nanocomposites was in a good accordance with a random scission mechanism for  $L = 2$ , which corresponds to the conversion function  $f(\alpha) = 2(\alpha^{1/2} - \alpha)$ . It has been shown that nanocomposites were thermally more stable than the polymer matrix. Moreover, when comparing both types of nanocomposites (with 0.5 and 2.5% of OMMT), the nanocomposite containing the higher amount of nanoparticles was less stable because of the presence of aggregates.

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## Figure Captions

**Fig. 1.** Experimental conversion vs temperature plots for the thermal degradation of the nanocomposite containing 2.5% of OMMT at various linear heating rates and CRTA (Constant Rate Thermal Analysis) conditions.

**Fig. 2.** Experimental conversion derivative vs temperature plots for the thermal degradation of the nanocomposite containing 2.5% of OMMT at various linear heating rates and CRTA (Constant Rate Thermal Analysis) conditions.

**Fig. 3.** Comparison of the thermal stability between PLA and its nanocomposites at a linear heating rate of 4 K/min.

**Fig. 4.** Variation of activation energy with conversion according to isoconversional methods for **(a)** the nanocomposite containing 0.5% of OMMT; **(b)** the nanocomposite containing 2.5% of OMMT;

**Fig. 5.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the conversion differential equation and  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation).

**Fig. 6.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the conversion differential equation and  $f(\alpha) = c(1 - \alpha)^m$  (modified Sestak-Berggren equation).

**Fig. 7.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the general analytical equation (GAE) and  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation).

**Fig. 8.** Kinetic analysis of experimental data for the thermal degradation of the nanocomposite containing 2.5% of OMMT by using the general analytical equation (GAE) and  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation).

**Fig. 9.** Comparison between experimental conversion data (solid line) and theoretical conversion values for the thermal degradation of the nanocomposite containing 2.5% of OMMT at a linear heating rate of 1 K/min. The theoretical data were obtained by using two different kinetic equations (differential equation and general analytical equation (GAE)) and two different conversion functions:  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation) and  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation).

**Fig. 10.** Validity of the enhanced general analytical equation and other methods. The theoretical temperature was calculated by using two different kinetic equations (differential equation and general analytical equation (GAE)) and two different conversion functions:  $f(\alpha) = (1 - \alpha)^n$  (n-order reaction equation) and  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation). Experimental temperatures correspond to the thermal degradation of the nanocomposite containing 2.5% of OMMT at a linear heating rate of 1 K/min.

**Fig. 11. (a)** Comparison of the  $f(\alpha)$  conversion functions (solid lines) normalized at  $\alpha = 0.5$ , corresponding to some of the ideal kinetic models with the curve reconstructed by means of  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren equation) and experimental points for the

thermal degradation of PLA at  $\beta = 4$  K/min and that of the nanocomposite containing 0.5% of OMMT at  $\beta = 1$  K/min; **(b)** Comparison of the random scission mechanism ( $L = 2$ ) with the curve reconstructed by means of  $f(\alpha) = c(1 - \alpha)^n \alpha^m$  (modified Sestak-Berggren) and experimental points for the thermal degradation of PLA at  $\beta = 4$  K/min and that of the nanocomposite containing 0.5% of OMMT at  $\beta = 1$  K/min.

Table 1. Onset decomposition temperature and temperature at the maximum rate for raw material (PLA) and nanocomposites (0.5 and 2.5% of MMT).

$\beta$ (K/min)	$T_5$ (°C)			$T_m$ (°C)		
	PLA	Nano 0.5%	Nano 2.5%	PLA	Nano 0.5%	Nano 2.5%
1	270.3	273.4	258.5	311.9	312.3	312.4
2	283.2	290.2	270.8	322.5	328.9	326.2
4	290.7	302.7	285.7	330.5	339.4	335.9
8	309.3	310.9	303.3	346.4	343.8	351.6

Table 2. Activation energies obtained by different methods for the thermal degradation of PLA and PLA/OMMT nanocomposites containing 0.5 and 2.5% of OMMT.

Method	Equation	E (kJ/mol)		
		PLA	NC (0.5%)	NC (2.5%)
Kissinger	(4)	171	140	154
Friedman	(5)	168 ± 4	160 ± 10	154 ± 3
Flynn-Wall-Osawa	(6)	162 ± 6	137 ± 6	158 ± 3
Differential + $f(\alpha) = (1 - \alpha)^n$	(10)	165	162	155
Differential + $f(\alpha) = c(1 - \alpha)^n \alpha^m$	(9)	166	161	155
General analytical equation + $f(\alpha) = (1 - \alpha)^n$	(11)	168	150	164
General analytical equation + $f(\alpha) = c(1 - \alpha)^n \alpha^m$	(12)	161	140	157

Figure 1

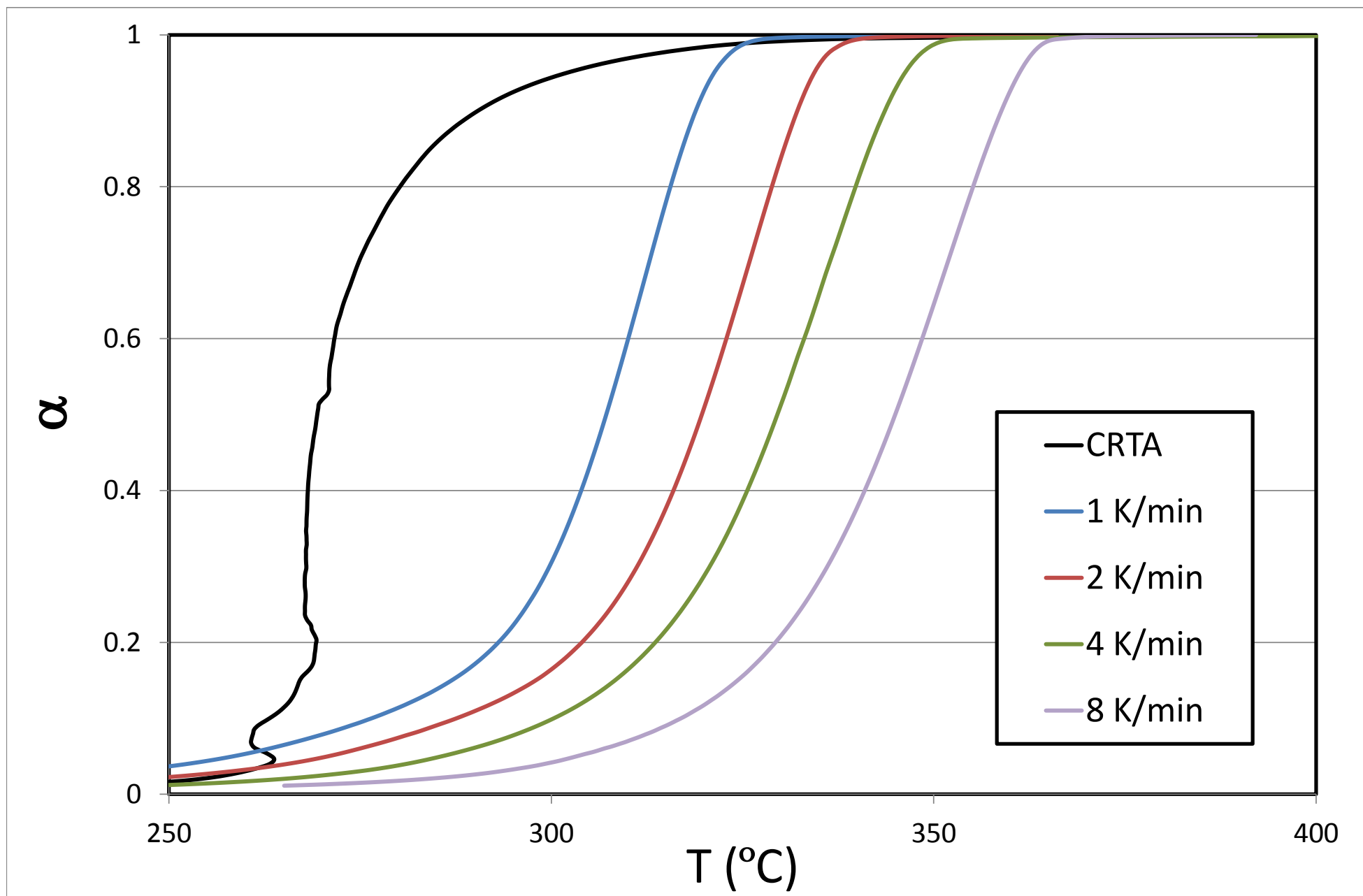


Figure 2

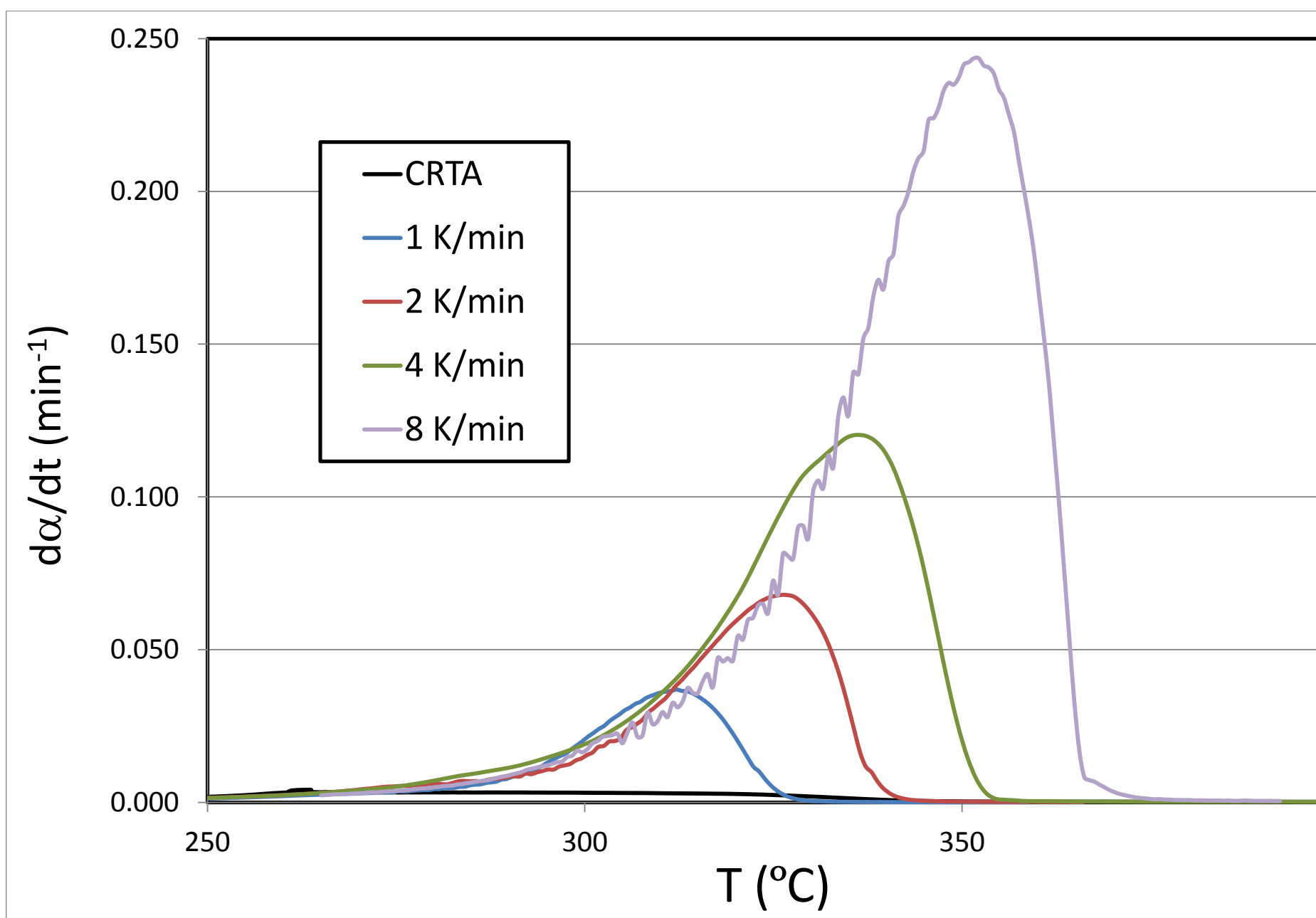




Figure 3

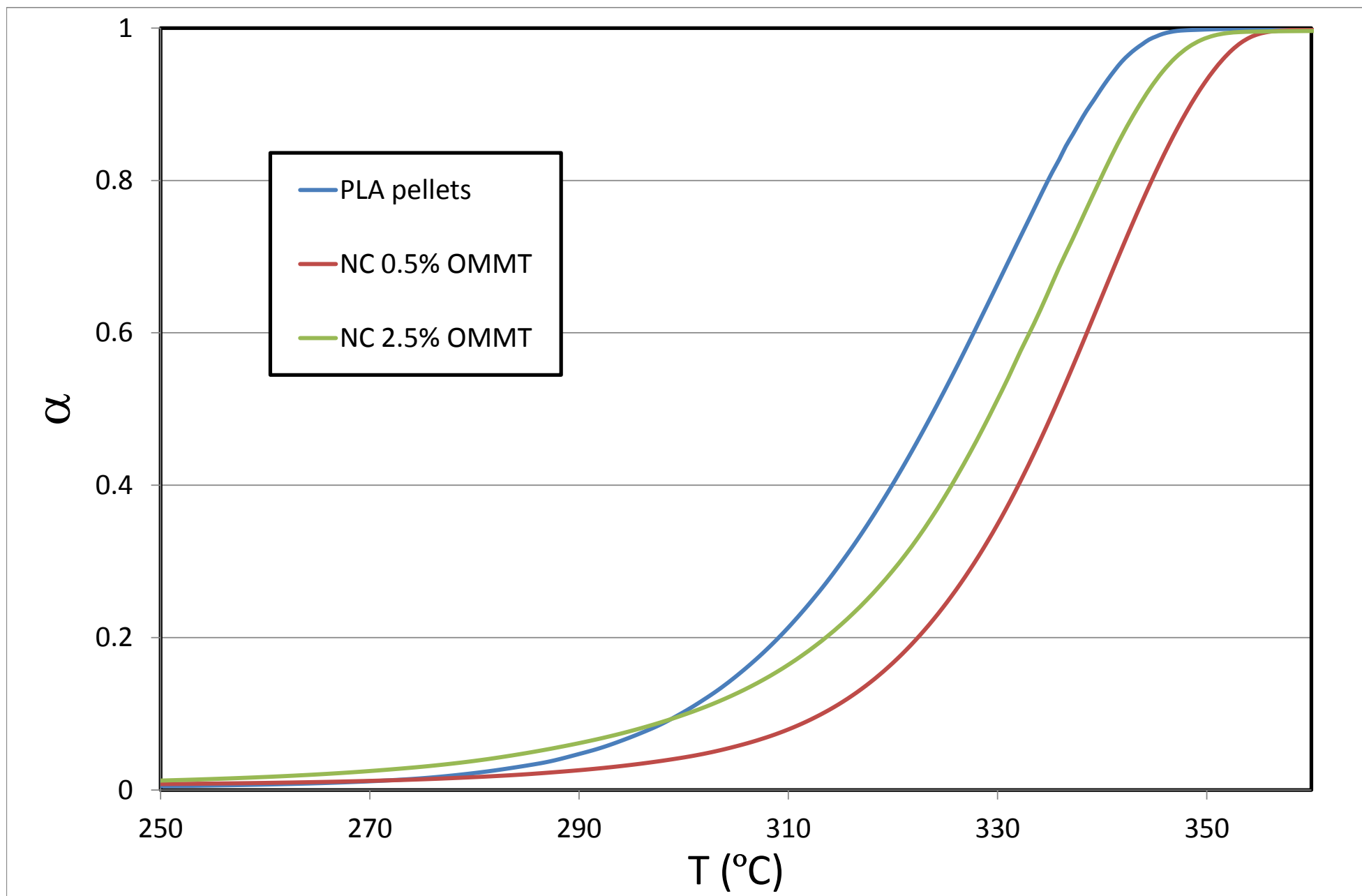


Figure 4a

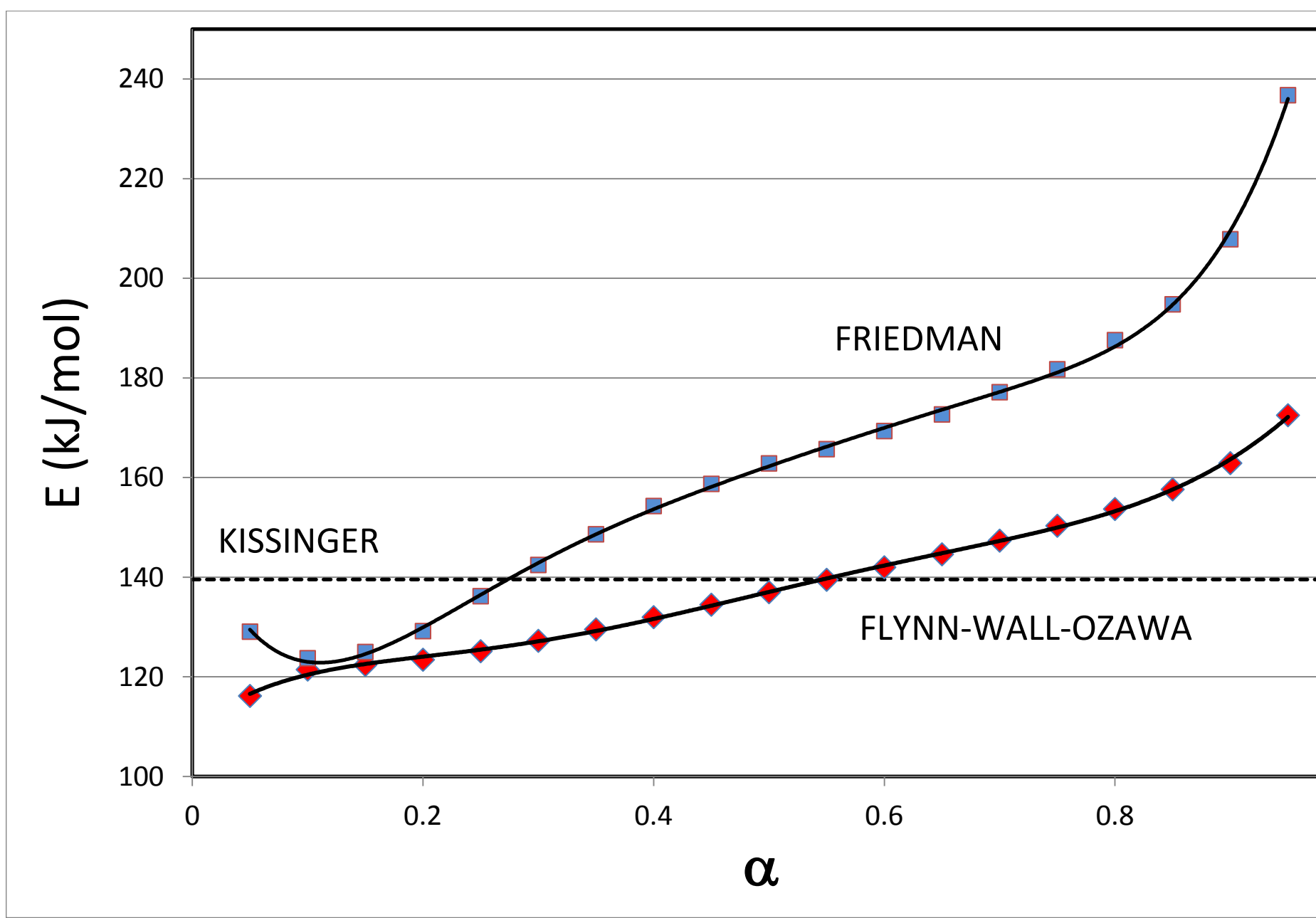


Figure 4b

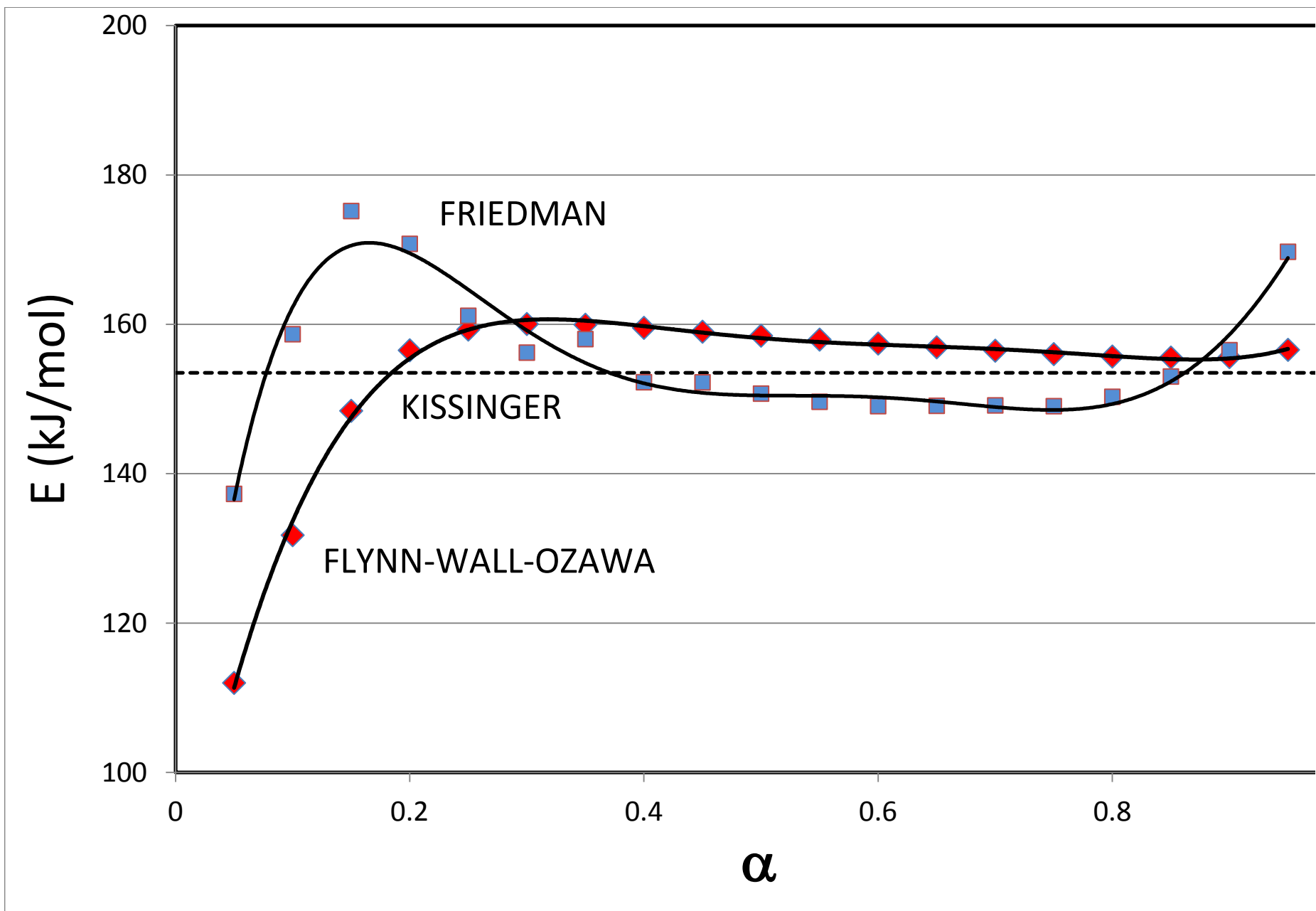


Figure 5

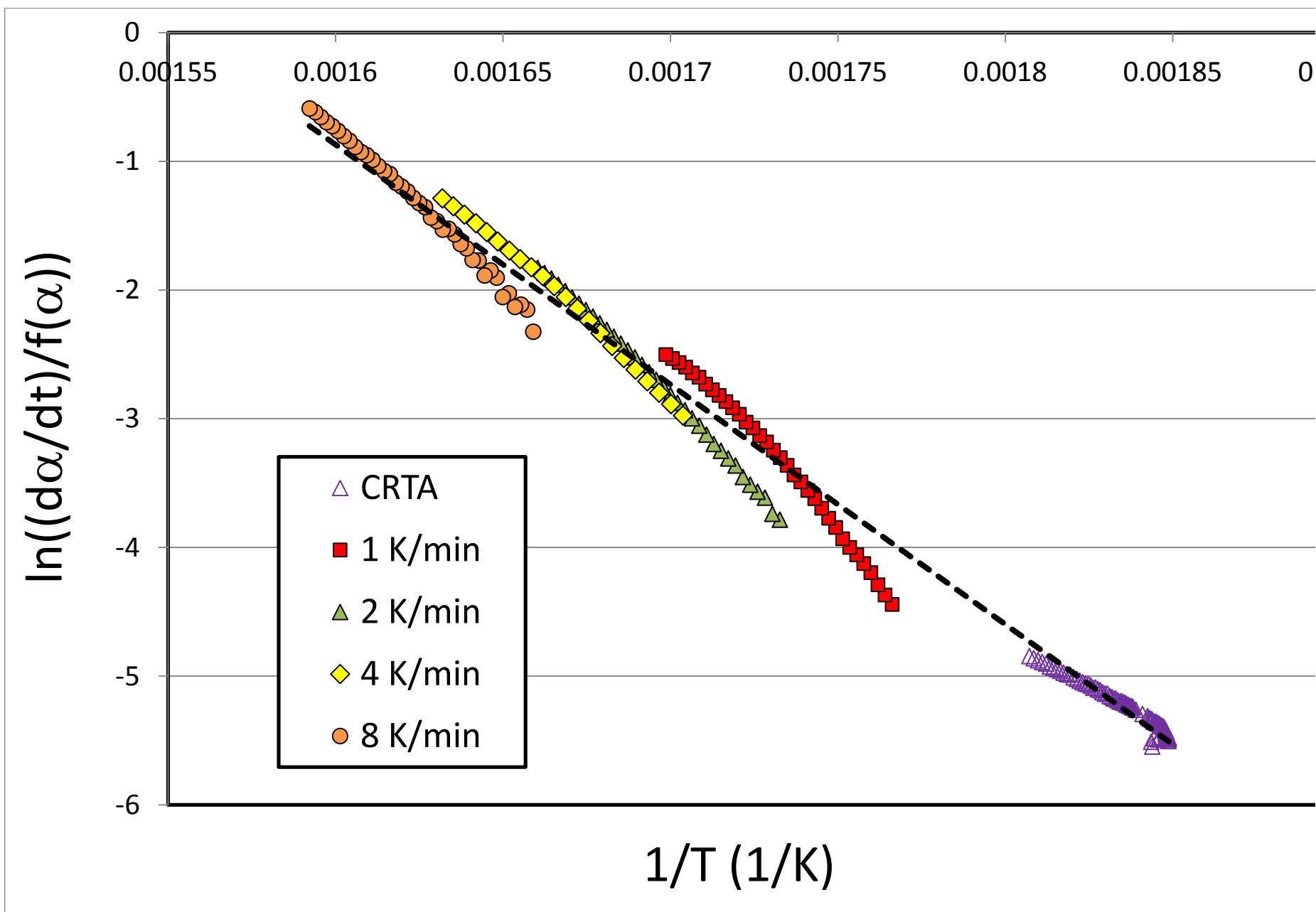


Figure 6

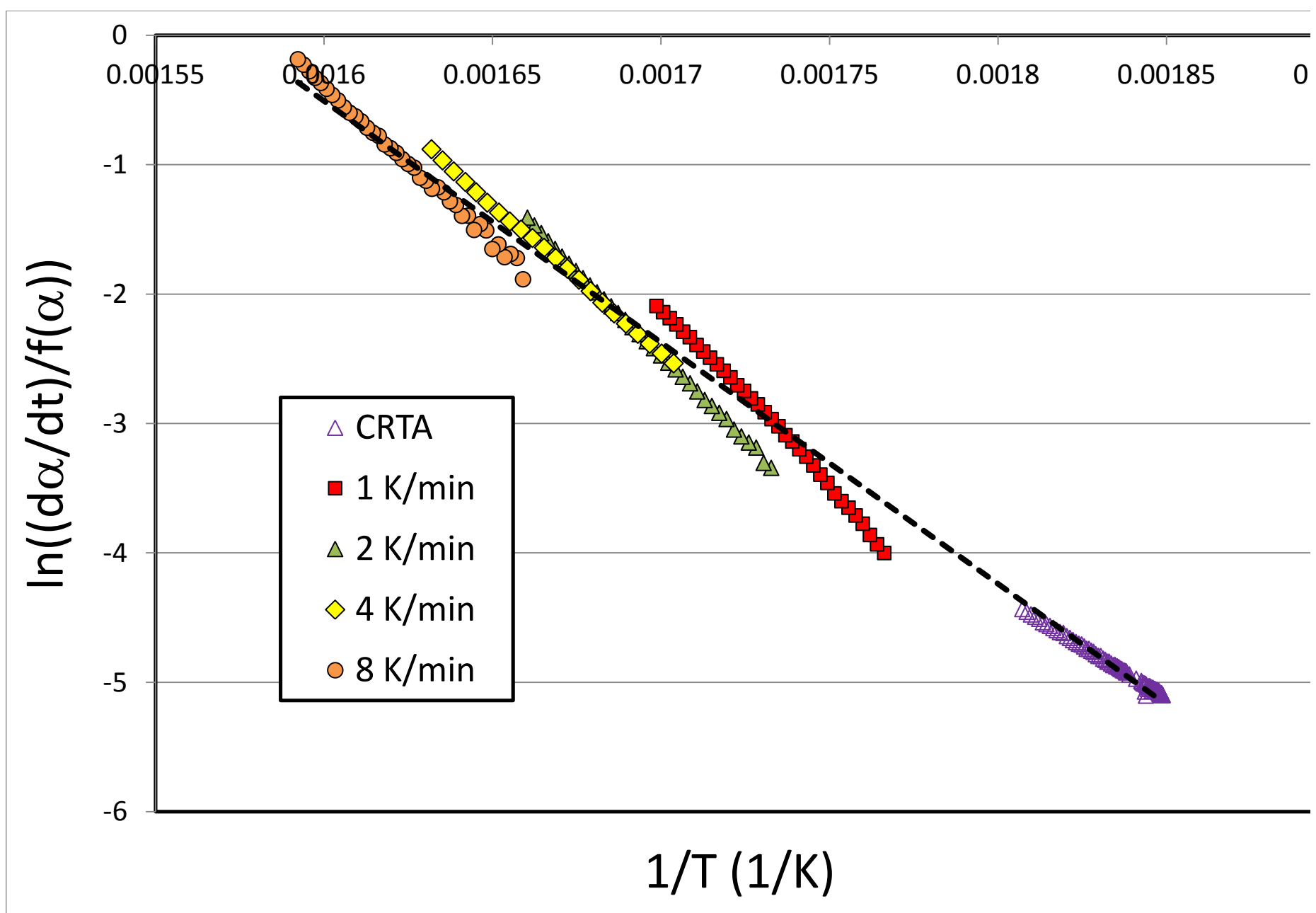


Figure 7

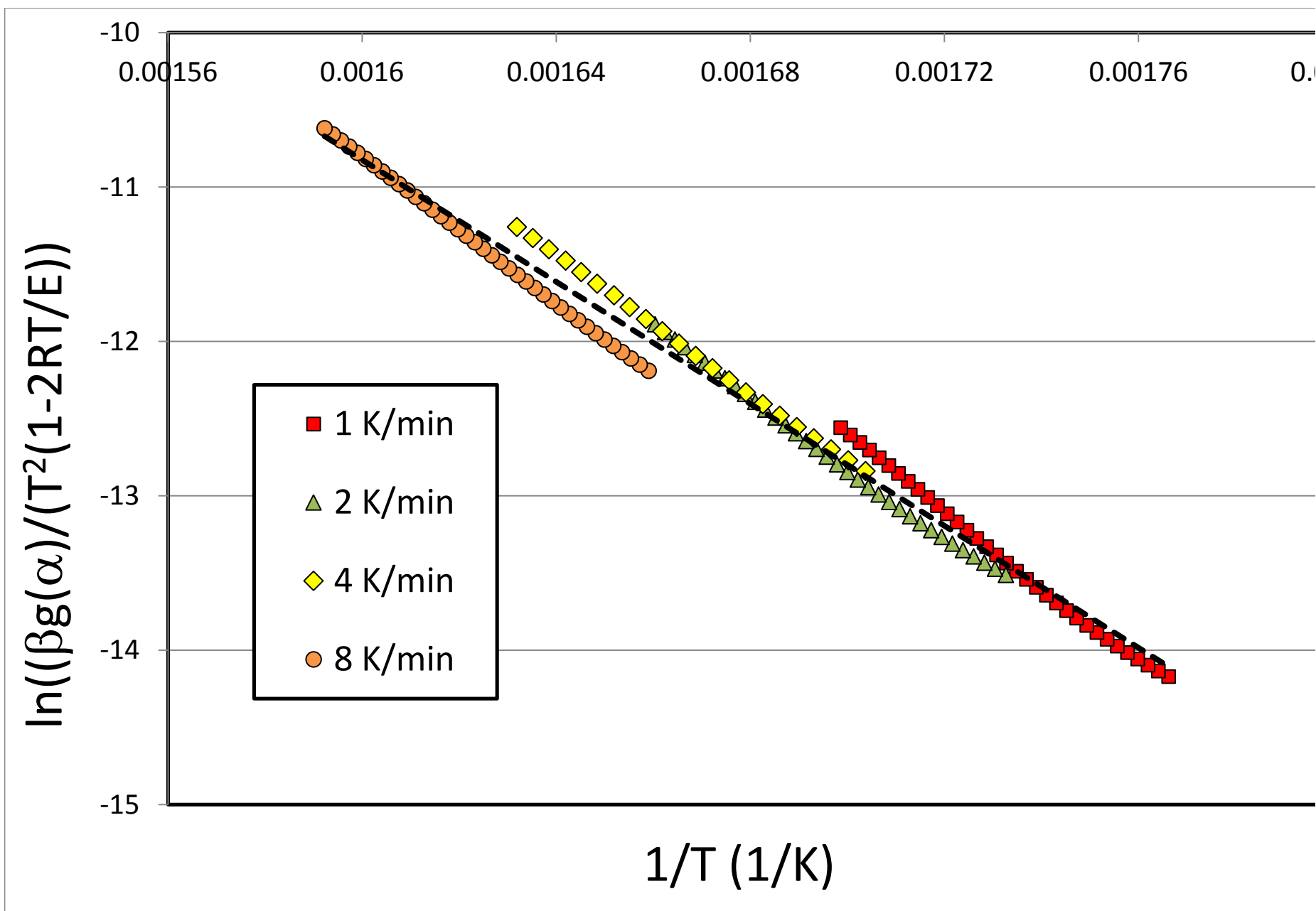


Figure 8

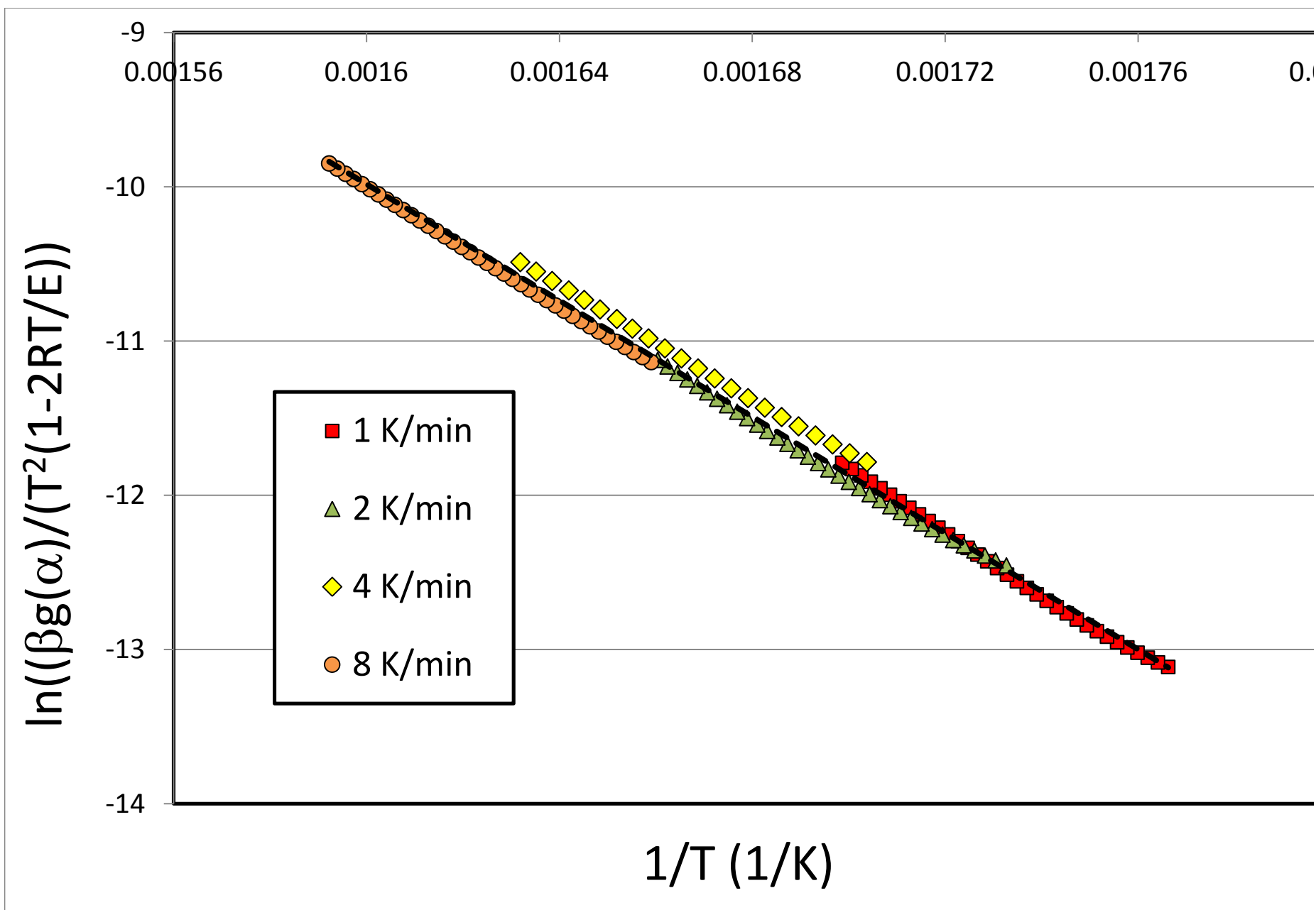


Figure 9

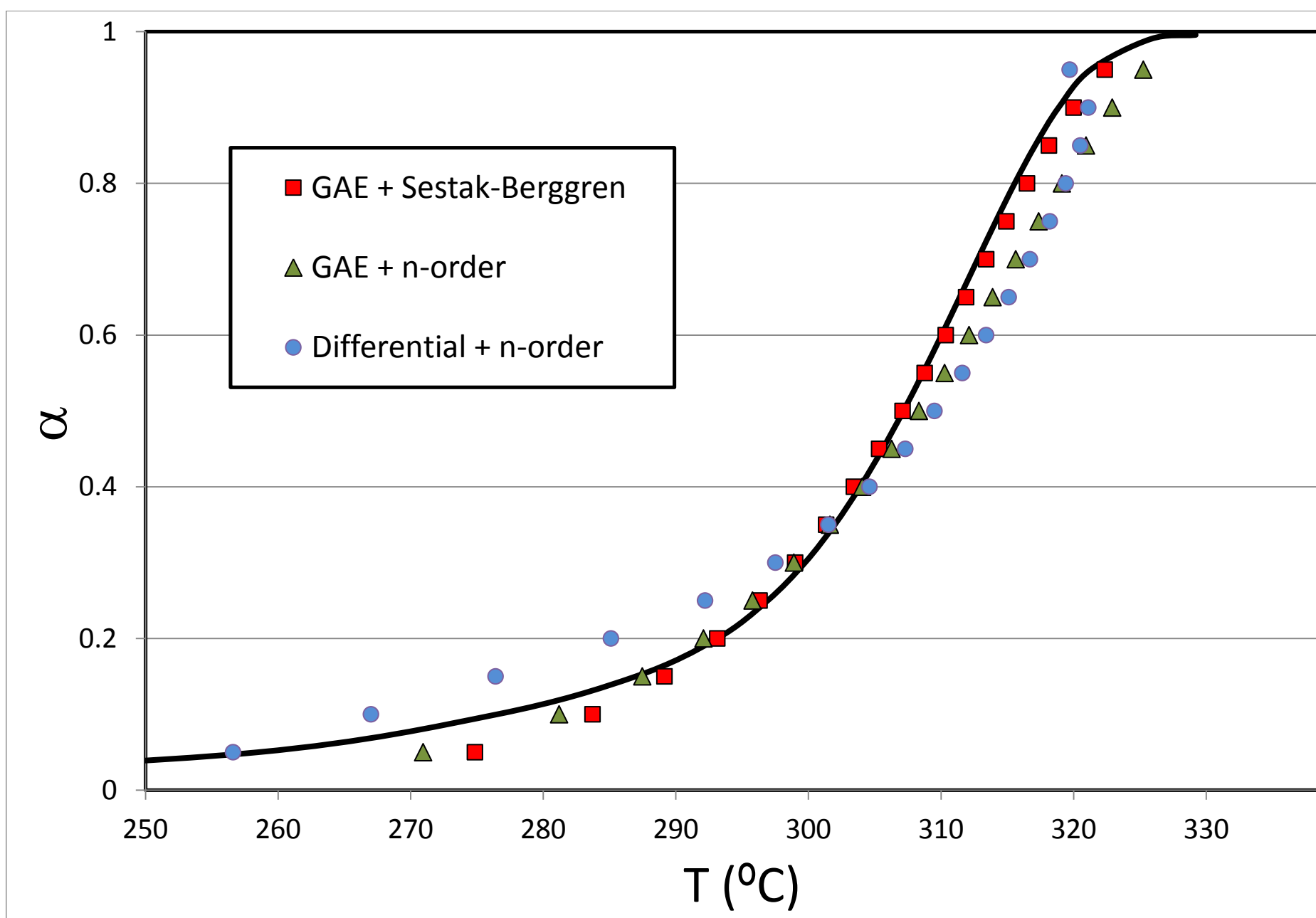




Figure 10

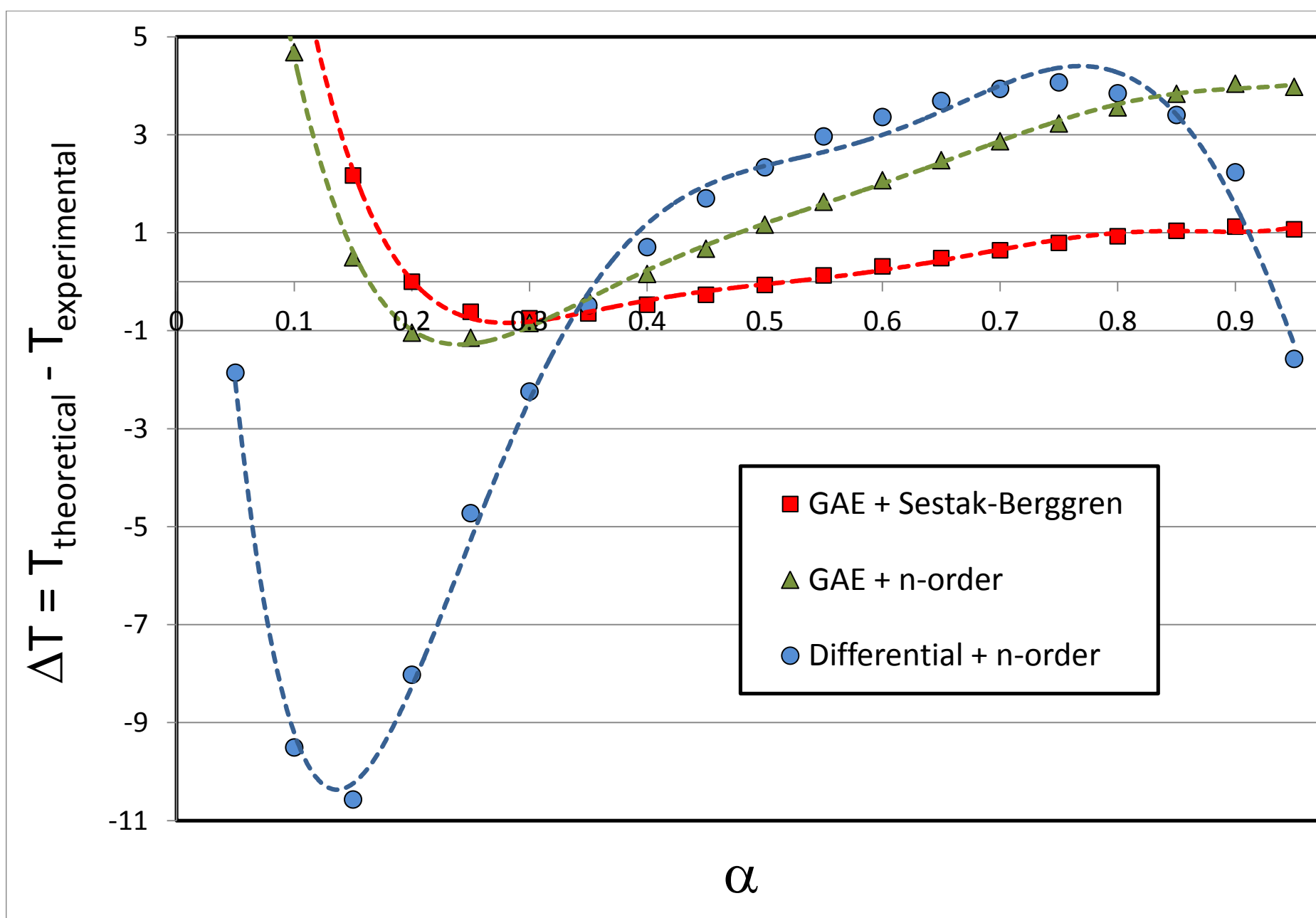


Figure 11a

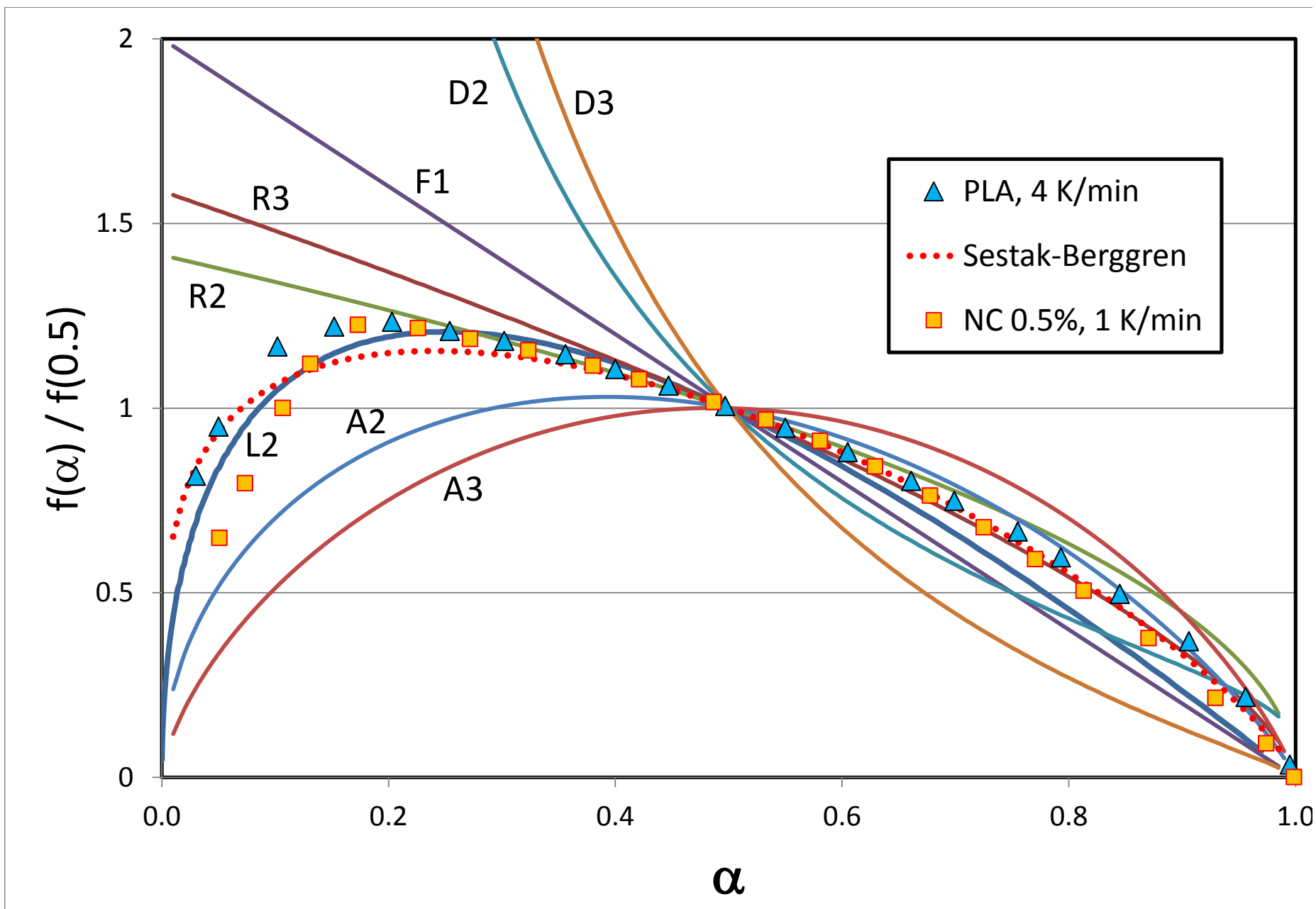


Figure 11b

