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**Experiments based analysis of thermal decomposition kinetics model.  
Case of carbon fibers PolyPhenylene Sulfide composites**

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**Keywords:** thermal decomposition kinetics; Thermoplastic composites; pyrolysis kinetics models; thermogravimetry; fire exposure

**Highlights**

- This study allows a better understanding of the thermal decomposition of composite structures during critical events such as aircraft engine fires
- The most physically consistent approach to model the isothermal decomposition kinetics of C/PPS composites was identified
- The predictive capabilities of three types of approaches (modelistic, model free/isoconversional model, isoconversional model) have been discussed based on statistical analyses (Fisher's test).
- These approaches are virtually statistically equivalent.
- Model-fitting methods result in relatively accurate prediction of the TGA curves at a given temperature.
- The model-free approach is the most predictive, from a physical point of view, to account for the thermal decomposition of C/PPS composites under isothermal conditions.

# Experiments based analysis of thermal decomposition kinetics model. Case of carbon fibers PolyPhenylene Sulfide composites

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## Abstract

Considering their increasing use in high-temperature aeronautical applications, thermoplastic-based laminates have to meet certification requirements in terms of critical service conditions (e.g. aircraft engine's fire). This work is aimed at identifying the most relevant approach to model the isothermal decomposition of C/PPS composites. The first step in the understanding of the thermal decomposition of these materials relies on TGA and MT-TGA tests. They can be conducted in isothermal and anisothermal conditions to characterize the thermal decomposition kinetics taking place in a fire scenario. The experimental database obtained from these tests is of major importance to identify input parameters of pyrolysis kinetics models. The predictive capabilities of three different approaches (model-fitting, isoconversional/model-fitting and model-free) is discussed based on statistical analyses (Fisher's test). For C/PPS laminated composites, these approaches are virtually statistically equivalent. Model-fitting methods result in relatively accurate predictions of the TGA curves at a given heating rate. However, this type of approaches is not fully satisfactory especially when it is used to predict the thermal decomposition of polymer-matrix composites under anisothermal conditions. Finally, the model-free approach is identified as the most relevant from a physical point of view to account for the thermal decomposition of C/PPS composites under isothermal conditions.

**Keywords:** thermal decomposition kinetics; thermoplastic composites; pyrolysis kinetics models; thermogravimetry; fire exposure

## 1. Introduction

Over the past 40 years, the use of polymer matrix composite materials in aeronautics has been confronted with ever more demanding safety standards to which it is imperative to provide reliable and measurable answers [1]. Therefore, it is essential to enable manufacturers to understand/predict the thermal decomposition of composite materials in different configurations of use.

During the last decades, carbon fiber reinforced polymer (CFRP) composites have been widely used in the aerospace and aeronautics sectors due to their superior strength and stiffness. Carbon/thermosetting polymers (epoxy) are the most common CFRP used in aircraft's structure. Indeed, these composites have an excellent endurance and resistance to corrosion besides high mechanical properties. However, epoxy resin matrix is highly inflammable. If these composites are exposed to high temperature environment, it can result in thermal damage, thermal decomposition, mechanical performance degradation, and damage to an aircraft's structure. Which creates highly uncertain conditions of an emergency earth or water landing.

High-performance thermoplastic polymers provide an alternative solution to thermosetting polymers. Polyphenylene sulfide (PPS) is one of the candidates to substitute thermosetting resins in structural parts that would potentially be exposed to fire. Previous studies have focused on characterization of thermal and mechanical behavior of carbon fibres reinforced PPS composite (C/PPS) composites under very high temperature conditions [2–6]. Results have shown that PPS has excellent properties, including high melting temperature, high glass transition temperature and a very good retention of their mechanical properties under fire conditions.

Moreover, thermal analysis allowed studying the pyrolysis behavior of both pure PPS thermoplastic resin and C/PPS laminates composites, and the assessment of the decomposition mechanisms as well as their kinetics [7]. Analyses were conducted at different testing conditions (heating rate, isothermal and anisothermal, inert or oxidizing atmosphere) by means of thermogravimetric (TGA) analysis and modulated TGA (MT-TGA). MT-TGA developed by Blaine et al. [8] was used to calculate the activation energy related to the main decomposition mechanisms [7]. It was demonstrated that the atmosphere influences the decomposition in a manner similar to what is conventionally observed on high-temperature polymers, which is also corroborated by other studies on the PPS (high amount of char formation under anaerobic atmosphere, oxidization of char and carbon fibers in atmospheres with oxygen) [9–11]. For anisothermal conditions, it was noticed that the temperature of the decomposition onset ( $T_{d,onset}$ ) shifts to higher temperature with increasing the heating rate, whether the testing atmosphere is oxidizing or not. Regarding C/PPS composites, it was reported that the presence of carbon fibres delays the onset of pyrolysis under oxidizing atmosphere, in agreement with conclusions presented in the literature on PPS and PPS-based composites [12]. The activation energy calculated from MT-TGA suggests the existence of three different mechanisms during pyrolysis

under inert atmosphere: depolymerization, random chain scission and ultimately cyclisation (char formation) [7,10].

Different factors are known to be prominent in the thermal decomposition of polymers. Among them, the heating rate (the rate of temperature increase) is of major importance, especially concerning applications of structural parts exposed to fire. In this situation, the composite laminate is exposed to one-sided heating from the fire, leading to a high gradient of heating rate in the thickness of the plate: it is the highest on the exposed face and decreases dramatically towards the cold face [4], mainly because of the low thermal diffusivity of the material. Other factors also contribute to reducing the heating rate, including the convective cooling from the outward flow of combustion gases and the absorption of heat by the decomposition reactions of the polymer matrix, which are mainly endothermic [13].

Figure 1 shows an example of temperature evolutions measured on C/PPS laminates subjected to a heat flux of 50 kW/m<sup>2</sup>. One can note the two-step evolution: a transient phase characterized by a high temperature increase (at rates of about 400 and 150 °C/min at the centers of the front and back faces resp.) followed by a stabilization at a constant temperature (in average, 550° and 300° resp.).

This stabilization occurs as the balance in the heat transfers is reached between the heating source (radiation from the heat source) and the cooling mechanisms (radiation of the material, convection and thermal decomposition). This steady-state equilibrium is characterized by a difference of the order of 200 to 300°C between the exposed and the back faces of the composite plate. This very high thermal gradient is at the origin of various thermal decomposition kinetics throughout the thickness of the sample, which cannot be characterized experimentally in an exhaustive way. This motivates the development of a pyrolysis kinetics model that could reproduce the evolution of the extent of conversion  $\alpha$  (also referred as degree of decomposition) under different conditions, with a particular emphasis on isothermal experiments. Indeed, for the characterization under isothermal conditions, conventional protocols consist in imposing first a rapid increase of the temperature then a stabilization at the target temperature, which actually corresponds the thermal conditions a composite laminate encounters in the case of a fire.

As far as the authors know, most of the studies published in the literature about the modelling of the decomposition kinetics of CFRP composites are considering anisothermal conditions [14,15]. Very few concern the analysis of the decomposition kinetics under isothermal

conditions. For instance, in the case of PPS, only one study dealing with isothermal decomposition could be found [11]. The considered temperatures were ranging from 366 and 415°C and the induced decompositions were lasting for tens of hours, which does not correspond to the characteristic temperatures and times encountered during a fire exposure.

In this study, the original problem of decomposition kinetics modelling for isothermal conditions at temperatures ranging up to 550°C is at stake. To address it, we first provide in Section 2 an analysis of decomposition kinetics models presented in the literature. This enables to establish in section 3 the detailed objectives of this study. The presentation of the inputs for the evaluation of decomposition kinetics models is proposed in section 4: respectively the material, the reference experimental data and the evaluated models. Results and discussions on the performed analyses are presented in section 5.

## 2. Literature review on the pyrolysis kinetics modelling

The analysis of solid-state decomposition kinetics is usually based on a single step equation which describes the extent of decomposition ( $\alpha$ ) [16]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Where  $k(T)$  is the temperature dependent rate factor of the pyrolysis reaction;  $f(\alpha)$  is the reaction model (or conversion function) and depends on the extent of conversion.

The rate factor  $k(T)$  can be expressed using the Arrhenius equation:

$$k(T) = Ae^{\left(\frac{-E}{RT}\right)} \quad (2)$$

Where  $A$  (the pre-exponential factor) and  $E$  (the activation energy) represent the Arrhenius parameters and  $R$  is the gas constant. The Arrhenius parameters and the reaction model  $f(\alpha)$  constitute the so-called kinetic triplet.

Under conditions of temperature increase at a constant rate  $\beta$ , the explicit time dependence in Eq.(1) can be replaced by a temperature dependence:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E}{RT}\right)} \cdot f(\alpha) \quad (3)$$

Assuming  $A$  is independent on T, Eq.(3) leads to:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \int_0^{T_\alpha} e^{\left(\frac{-E}{RT}\right)} dT = \frac{A}{\beta} I(E, T) \quad (4)$$

Where  $T_\alpha$  is the temperature corresponding to the extent of conversion  $\alpha$  and  $I(E, T)$  is the so-called temperature integral.

Since 1960s, considerable progress has been made in the development of mathematical techniques dedicated to the modelling of kinetics. Two main approaches were developed to determine the kinetic triplet from TGA (for both isothermal or anisothermal data): model-fitting (or modelistic) approach and isoconversional approach.

A model-fitting approach consists in determining the Arrhenius parameters ( $E$  and  $A$ ) by assuming *a priori* the form of  $f(\alpha)$ . Several reaction models have been proposed for  $f(\alpha)$  (nucleation models, geometrical contraction models, diffusion models, and reaction-order models) [17]. The method of Coats Redfern [17] is one of the most commonly adopted for anisothermal conditions (see e.g. [18,19]). It is based on a proposal of approximation in the expression of the temperature integral in eq. (4), which enables to describe the evolution of the kinetics according to closed-form expressions.

Model-fitting methods can result in accurate predictions of the decomposition kinetics at a given heating rate  $\beta$ . Yet, the physical relevance of predictions obtained from such approaches should be considered with caution, especially for anisothermal experiments [18]: as shown in [19], one may reproduce correctly given decomposition kinetics from many different reaction models relying on very different values of Arrhenius parameters, which raises doubts about the physical meaning of these values. This may happen particularly for anisothermal experiments because, as opposed to isothermal decomposition where  $k(T)$  is kept constant, the reaction rates depend simultaneously on  $k(T)$  and  $f(\alpha)$ . The variation of  $f(\alpha)$  with  $\alpha$  being less important than the variation of  $k(T)$  with  $T$ , errors on the conversion function can be compensated by errors on the rate factor.

In order to exclude any loss of objectivity, one of the parameter of the kinetic triplet can be calculated separately. In contrast to the model-fitting methods, the isoconversional methods propose to calculate the activation energy of the decomposition mechanisms as a function of the extent of conversion and without considering any particular reaction model [20]. These methods are based on the determination of characteristic temperatures  $T_{\alpha i}$  (or times  $t_{\alpha i}$ ) corresponding to a given conversion rate  $\alpha$  (from which the term isoconversional), measured in tests at different heating rates  $\beta_i$  (or temperatures  $T_i$ ). For isoconversional methods, the activation energy and the pre-exponential factor will be noted  $E_\alpha$  and  $A_\alpha$  respectively to avoid any confusion with the parameters computed in a model fitting method.

A large number of isoconversional methods were presented in the literature. Starink has proposed a review of different methods for determining  $E_{\alpha}$ , and classified them into two main groups: rate-isoconversional methods (type A) and  $p(y)$ -isoconversional methods (type B) [21]. The first one (type A) does not resort to any mathematical approximation but instead is based on the knowledge of the reaction rates at an equivalent stage of the reaction for various heating rates. One may refer to Friedman *et al.* [22] as an example of type A method. The main limits of this technique come from the experimental measure it is based on: the higher the heating rate the higher the perturbations on the signals and more difficult it is to obtain good-quality measures of the decomposition rate. The other set of methods (type B), relies on the approximation of the “temperature integral” in Eq. (4). This set of methods includes Kissinger [23], Ozawa-Flynn–Wall [24,25] and Starink methods [21].

Apart from these two main families, there are methods that are specifically formulated to avoid any approximation of the temperature integral. One of them, proposed by Vyazovkin and referred to as “model free method” will be used in this study [26].

### **3. Objectives of the study**

This study is a contribution to the more general study of the thermo-mechanics of C/PPS composites under very high temperature conditions such as a fire exposure. In this situation, large thermal gradients occur which induce a heterogeneous decomposition of the constituents in the laminate and consequently a heterogeneous degradation of the mechanical properties. The knowledge on the decomposition kinetics can only be obtained from modelling because of the heterogeneous character of the material and of its temperature field. This study is thus aimed at evaluating the suitability of different approaches to model the pyrolysis kinetics of the considered material. The analysis of the literature shows that the majority of the publications on polymer decomposition modelling concern anisothermal heating. But in the case of a fire exposure, the temperature of the material rapidly reaches a steady-state, which in experimental analyses of thermal decomposition should be considered as an isothermal condition of study. In studies referring to this situation, the kinetic parameters are very often identified with a model fitting method. In this study, the computation is realized by means of three approaches: model fitting, mixed isoconversional/model fitting (based on Starink’s isoconversional method [21]) and model-free, developed by Vyazovkin [26]. Their principles are explained in detail in section 4.3. The evaluation of the models is made by comparison to experimental data provided by the thermo-gravimetry analyses presented in a previous study [7]. The adopted methodology for analysing and evaluating each approach is based on a F-Test as proposed by Vyazovkin [27].

## 4. Materials and methods

### 4.1. Materials

The carbon fibres reinforced PPS composite have already been used in [2–6]. As for previous studies, the composite material was manufactured using a woven-ply prepreg (T300, 3K, 5HS) supplied by SOFICAR and a semi-crystalline high-performance PPS marketed by the Ticona company. The prepreg plates were hot pressed according to a quasi-isotropic stacking sequence [(0,90)/(±45)/(0,90)/(±45)/(0,90)/ (±45)/(0,90)]. Resulting composites are characterized by a fiber weight fraction of 58 %, a glass transition temperature ( $T_g$ ) at 98 °C and a melting temperature ( $T_m$ ) of the order of 280 °C. The degree of crystallinity of PPS matrix is close to 30% and the porosity ratio is less than 2%.

### 4.2. Experimental tests

In the TGA and MT-TGA presented in [7], thermal decomposition was studied for three different atmospheres: nitrogen, air and dioxygen. Analyses were conducted on samples whose initial mass is about 8mg. It was shown that the decomposition occurs according to a single step (matrix pyrolysis) in the inert atmosphere ( $N_2$ ) whereas it unfolds in several steps (matrix pyrolysis, char oxidation and fibre oxidation) for the oxidizing atmospheres (air and  $O_2$ ). The interplays between the involved mechanisms in the oxidizing atmospheres and their dependences to temperature and heating rate are sources of complexity and uncertainty in the interpretation of results. Furthermore, these experiments are not representative of the thermal aggression in the core of the material and even less so at its surface if the flame is not oxidizing. Therefore, for the present study, only the kinetics of anaerobic pyrolysis –taken from [7]- are examined.

Both isothermal and anisothermal conditions have been considered (the second ones were only considered to compute  $E_\alpha$  in isoconversional methods). For isothermal conditions, seven temperatures were considered: 465, 475, 485, 500, 515, 530 and 545 °C. For anisothermal conditions, samples were heated continuously from room temperature to 700 °C. The heating rates were either constant (5, 10, 20 or 35 °C.min<sup>-1</sup>) or sinusoidally increasing (modulated TGA). This last technique is interesting as it allows to determine the activation energy  $E_\alpha$  from a single experiment with the following formula [28]:

$$E_{\alpha} = \frac{R (T^2 - A^2) \ln \left( \frac{d\alpha_p}{d\alpha_v} \right)}{2B} \quad (5)$$

Where  $T$  is the average value of oscillatory temperature;  $B$  is the amplitude of the temperature oscillation; and  $\left( \frac{d\alpha_p}{d\alpha_v} \right)$  is the ratio for adjacent peaks and valleys of the periodic rate of reaction.

### 4.3. Pyrolysis kinetic model

#### 4.3.1. Model fitting method

For model fitting methods, Arrhenius parameters are determined by assuming *a priori* the form of the reaction model  $f(\alpha)$ . Some of the most common reaction models proposed in the literature and used for this study are listed in Table 1 [29].

For isothermal experiments, the determination of the Arrhenius parameters is based on the integration of Eq.(1) which gives:

$$G_i(\alpha, T_j) = k_i(T_j) \cdot t \quad (6)$$

$i$  and  $j$  are the indexes of the considered reaction model and temperature respectively. By substituting a given reaction model into Eq.(6),  $k_i(T_j)$  can be evaluated from the slope of the function  $G_i(\alpha, T_j)$  versus  $t$ . Then,  $k_i(T_j)$  being evaluated for all the considered temperatures  $T_j$ , the Arrhenius parameters ( $E_i$  and  $A_i$ ) can be determined from Eq. (7), which is the logarithmic expression of the Eq.(2):

$$\ln \left( k_i(T_j) \right) = \ln(A_i) - \frac{E_i}{RT_j} \quad (7)$$

Eq.(7) indeed indicates that the plot of  $\ln \left( k_i(T_j) \right)$  versus  $1/T_j$  (also known as an Arrhenius plot) leads to a straight line from which one can easily deduce  $E_i$  and  $A_i$ .

#### 4.3.2. Isoconversional method: evaluation of $E_{\alpha}$

Using data from isothermal experiments to evaluate  $E_{\alpha}$  from isoconversional methods can be inappropriate when the test temperatures are slightly above the decomposition onset. For instance, for a TGA performed at 545°C (one of the temperatures considered in this study), 30% of the matrix is decomposed before reaching the test temperature [7]. Thus, the use of such

data to determine  $E_\alpha$  may generate erroneous results. Since the involved chemical mechanisms are supposed to be the same in isothermal and anisothermal experiments, it is proposed here to use anisothermal data to evaluate  $E_\alpha$ . A literature review shows that whether the use of activation energies determined from anisothermal experiments can lead to a good prediction for isothermal experiments is not consensual [27,30]. In this study, two isoconversional methods based on anisothermal experiments are used to evaluate  $E_\alpha$  : Starink [21] and Vyazovkin [26] approaches.

#### 4.3.2.1. Starink approach

The Starink method consists in approximating the temperature integral of Eq. (4). Assuming that  $E_\alpha$  is independent on T, Eq.(4) can be written as follows:

$$G(\alpha) = \frac{A_\alpha E_\alpha}{\beta R} \int_{x_\alpha}^{\infty} \frac{e^{-x}}{x^2} dx = \frac{A_\alpha E_\alpha}{\beta R} P(x_\alpha) \quad (8)$$

Where  $x = E/RT$  and  $x_\alpha = E_\alpha/RT_\alpha$ .

Starink proposes to approximate the integral by setting:

$$P(x) \approx \frac{\exp(1.0008x - 0.312)}{x^{1.92}} \quad (9)$$

Introducing this expression into Eq. (8) and taking the natural logarithm of both sides yields:

$$\ln\left(\frac{\beta}{T_\alpha^{1.92}}\right) = -1.0008 \frac{E_\alpha}{RT_\alpha} + C \quad (10)$$

For a given value of  $\alpha$ , the plot of  $\left(\frac{1}{T_\alpha}\right)$  versus  $\ln\left(\frac{\beta}{T_\alpha^{1.92}}\right)$  results in a straight line whose slope is used to calculate the corresponding  $E_\alpha$ .

#### 4.3.2.2. Vyazovkin approach

In order to avoid using an approximation, although it enables to result in a linear equations and to facilitate the modelling, Vyazovkin has proposed an exact equation (non-linear) based on the general assumption that the reaction model (i.e.  $G(\alpha)$ ) is independent on the heating rate. On this basis, for a given  $\alpha$ , the ratio  $\frac{I(E_\alpha, T_{\alpha,i})}{\beta_i}$  is a constant whatever the heating rate  $\beta_i$ . Considering a set of  $n$  experiments performed at different heating rates, Vyazovkin proposed to calculate the activation energy for a given  $\alpha$  by minimizing the function  $\Phi$  defined in eq. 11:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i})\beta_j}{I(E_\alpha, T_{\alpha,j})\beta_i} \quad (11)$$

### 4.3.3. Using $E_\alpha$ values to model isothermal decomposition: Isoconversional/model fitting and “model-free” methods

The Vyazovkin and Starink methods presented above are meant to provide only the evaluation of the activation energy as a function of the extent of conversion. To complete the isothermal decomposition kinetics model with  $f(\alpha)$  and  $A_\alpha$ , two methods can be used.

The first one consists in determining  $f(\alpha)$  and  $A_\alpha$  by using the Starink equation (Eq.10). It can be transformed to yield :

$$A_{\alpha i} = \left[ G_i(\alpha) \left( \frac{E_\alpha}{R} \right)^{0.92} \right] e^{C+0.312} \quad (12)$$

Where  $C$  is the intercept of the curve  $\ln \left( \frac{\beta}{T_\alpha^{1.92}} \right) = f \left( \left( \frac{1}{T_\alpha} \right) \right)$ . As this approach requires the choice of a particular reaction model, it is referred to as isoconversional/model fitting method.

As shown by Vyazovkin, the sole knowledge of  $E_\alpha$  can be used to compute the isothermal decomposition from the data of one anisothermal experiment carried out at a given heating rate  $\beta$  [27]. The time  $t_\alpha$  at which a given extent of conversion  $\alpha$  is reached at an arbitrary temperature  $T_i$  is given by:

$$t_\alpha = \frac{\int_0^{T_\alpha} e^{\left( \frac{-E_\alpha}{RT} \right)} dT}{\beta e^{\left( \frac{-E_\alpha}{RT_i} \right)}} \quad (13)$$

As this method does not require choosing a reaction model, it is referred to as “model-free”.

## 5. Result and discussions

### 5.1. Limits of the TGA tests

When composite laminates are exposed to one-sided fire (most studied configuration in the literature and a very often-occurring event in real in-service conditions), it leads to high temperature and heating rates gradients through the thickness and on the exposed surface of the laminates. These large thermal gradients induce a heterogeneous decomposition of the

constituents in the laminates, and data coming from these tests is thus very difficult to use as is to develop a kinetic model. It is worth noticing that the studies trying to follow this path [31,32] usually find a single value for the activation energy  $E$  and the pre-exponential factor  $A$ , which does not fully reproduce the mechanisms of the decomposition process.

Considering that the decomposition is only temperature and time-dependent and in order to identify the evolution of  $E$  and  $A$  along with decomposition, reference data should be extracted from experiments with an accurate control on temperature time evolution (enabling a uniform temperature in the whole sample) and a high-precision mass measurement. As long as these two conditions are met, it is possible to access representative values for the parameters of a kinetic model. To our knowledge, the TGA is currently the best approach to this end. Remains the question of whether the TGA can be representative of a flame exposure. As described by Mouritz et al., in case of fire exposure [1], the thermal decomposition is (1) anaerobic within the material – (2) oxidative on the outer surfaces (more or less depending on the flame stoichiometry).

The results presented in our study are obtained in inert conditions ( $N_2$ ) and are thus at least representative of the thermal decomposition “inside” the sample. The representativity of these tests concerning the “surface” decomposition of the sample depends on the type of flame (more or less oxidizing). Supplementary analyses with an oxidizing atmosphere ( $O_2$  or air) are necessary to find values for  $E$  and  $A$  accounting for the oxidative decomposition at the surface.

## **5.2. Determination of the activation energies ( $E_\alpha$ ) by means of isoconversional methods**

The isoconversional methods are applied for a set of three experiments performed at four heating rates (5, 10, 20 and  $35^\circ\text{C}\cdot\text{min}^{-1}$ ).

For the Starink method,  $E_\alpha$  are obtained from the slopes of the curves derived from Eq. 10 (see Figure 2).

Figure 3 shows the evolution of the activation energies obtained by means of isoconversional methods (Vyazovkin and Starink) as a function of the extent of conversion  $\alpha$  superimposed with those determined experimentally by means of MT-TGA.

It can be observed that the activation energies obtained from isoconversional methods increase slightly during the pyrolysis reaction, while those determined experimentally show higher

fluctuations, especially during the beginning and the end of the pyrolysis reaction. This might be explained by the significant scattering of the temperature during these steps of the reaction, which may lead to some uncertainty in the values of  $E_\alpha$ . The mean values of activation energy for each method are compared in Table 2.

The Vyazovkin method yields mean values for activation energy closer to MT-TGA values than the ones obtained from the Starink method. Indeed, this method is based on a mathematical minimization and it is not as sensitive to experimental noise that could default the Starink method.

The discrepancies between the experimental values and the computed ones may be associated to the conditions of the experiments. MT-TGA were performed with a sinusoidal heating rate corresponding to 5°C/min in average. For technical reasons, it has not been possible to set a heating ramp with a higher mean value.

### 5.3. Pyrolysis kinetic modelling under isothermal conditions

#### 5.3.1. Model fitting method

Figure 4 shows the plot of  $\ln(k(T))$  as a function of  $1/T$  for the different reaction models  $F_i$ . The Arrhenius parameters  $E_i$  and  $A_i$  are respectively determined from the slopes and the intercepts of the curves. The obtained values are summarized in Table 3. It can be noticed that the variations of  $E$  according to the adopted reaction model are slight (standard deviation  $\sigma = 9 \text{ kJ.mol}^{-1}$ ). This can be compared to what has been obtained in [33] calling upon the Coats-Redfern approximation in the model-fitting method for anisothermal data:  $E$  were varying between 21 and 328  $\text{kJ.mol}^{-1}$  and the standard deviation was  $\sigma = 105 \text{ kJ.mol}^{-1}$ . This illustrates the weaker mathematical flexibility of the model-fitting when applied to an isothermal case. It is worth emphasizing that the mean value of the activation energy  $E$  obtained for the different reaction models (154  $\text{kJ.mol}^{-1}$ ) is fairly close to that measured by means of MT-TGA (180  $\text{kJ.mol}^{-1}$ ), especially considering the scattering of results. Using these parameters, the evolution of the extent of conversion  $\alpha$  with time is determined for each reaction model. A comparison with the experimental data at 485°C is presented in Figure 5. From the plots of Figure 5, one can define the best reaction model to reproduce the isothermal decomposition of C/PPS. However, whereas several temperatures are considered, a statistical analysis is necessary to classify the reaction models. In this study, the quality of the fit is estimated for each reaction

model by using the residual sum of squares method proposed by Vyazovkin. To this aim, at first, all curves are normalized by the time  $t_f$  corresponding to the final (or maximal) extent of conversion considered in the analyses. The residual sum of squares is then calculated as follows:

$$S_i^2 = \frac{1}{n-1} \sum_{j=1}^n \left( \frac{t_j(\text{experimental})}{t_f(\text{experimental})} - \frac{t_j(\text{computed})}{t_f(\text{computed})} \right)^2 \quad (14)$$

For each model  $i$ , the test statistics  $\beta_i$ , calculated as follow :

$$\beta_i = \frac{S_i^2}{S_{min}^2} \quad (15)$$

with  $S_{min}^2$  is the minimum value among all  $S_i^2$  values, has an F-distribution. The values of  $\beta_i$  calculated for each model are summarized in Table 3. According to the Fisher test, can be considered as giving a standard deviation  $S_i^2$  significantly different than  $S_{min}^2$  only the reaction models for which  $\beta_i > F_{1-p, n-1, n-1}$  (percentile of the Fisher distribution for a  $(1-p)$  confidence level). All the other reaction models can be considered as accurate as the model that yields  $S_{min}^2$ .

Due to the form of the equations of the reaction models, the difference between computed and experimental values can increase very significantly at the very end of the decomposition. The kinetic model which will be identified from this study is intended to be included in the thermo-mechanical modelling of the composite material exposed to fire [33,34]. It is therefore chosen to set a maximal considered extent of conversion at  $\alpha = 0.90$ . Above this value, there is no more influence of the matrix decomposition on the thermo-mechanical behavior of the material.

Within the 95% confidence interval ( $F_i = 2.27$ ), three models ( $F_1$ ,  $F_{10}$  and  $F_{11}$ ) are identified as statistically more representative of the reaction kinetics of C/PPS isothermal decomposition. These results are in agreement with those of Day *et al.* who studied the isothermal decomposition of PPS between 365 and 415°C and showed that the best models were the 2D and 3D diffusion ( $F_{10}$  and  $F_{11}$ ) [11]. Nonetheless, for the next-to-come approaches, which require to set a particular reaction model for the computation of the evolution of  $\alpha$ , three more reaction models will also be considered, those at the 4<sup>th</sup> to 6<sup>th</sup> rank in the Fisher classification, viz.  $F_2$ ,  $F_7$  and  $F_9$ . It is worth noting that extending the statistical analysis to  $\alpha = 0.95$  would not modify the top-6 list but it would change their ranking (which would become :  $F_{11} = 1.00$ ,  $F_{10} = 1.70$ ,  $F_1 = 1.80$ ,  $F_9 = 3.87$ ,  $F_7 = 5.19$ ,  $F_2 = 7.31$ ).

### 5.3.2. Isoconversional/model fitting method

As presented in Paragraph 0, another way to model the isothermal decomposition kinetics is to take the values of  $E_\alpha$  from an isoconversional technique (here, Starink approach), as an input of a model-fitting method. Once the activation energies for a given  $\alpha$  is determined from the slopes of the curves, a reaction model  $i$  is chosen and the corresponding pre-exponential factor  $A_{\alpha i}$  is obtained from the intercept of the linear curves shown in Figure 2 using Eq. 12. The obtained results are summarized in Table 4.

### 5.3.3. Model-free

For the model-free approach, the knowledge of the activation energy is sufficient to compute the anisothermal decomposition kinetics (see Eq. 13). The two sets of  $E_\alpha$  values calculated in Section 5.2 (Figure 3) are used, as well as those obtained experimentally with modulated TGA.

Figure 6 presents the evolution of the extent of conversion as a function of time at 545°C. Experimental data and results obtained from the different approaches presented in this paper (model-fitting, isoconversional/model-fitting, model free) are superimposed for comparison purpose.

The computed values are in satisfactory agreement with the experimental results. Examining in more details, it is noticed that the curve based on the model-free method with Starink  $E_\alpha$  values is closest to the curve based on isoconversional/M-F method than to the other model-free curve (with Vyazovkin's  $E_\alpha$  values). This seems to show that in isoconversional/M-F methods, the  $E_\alpha$  values has much more influence on the computed kinetics than the reaction model.

### 5.3.4. Evaluation of the models

In order to discuss the best approach to model the isothermal decomposition kinetics of C/PPS, the accuracy of each fitting function is estimated by using the residual sum of squares method proposed by Vyazovkin and described in Eq. 14 and 15. In order for the results from the different methods to be comparable, the value considered for  $S_{min}^2$  to calculate the test statistics  $T_i$  is taken among the values of  $S_i$  in all the approaches described in this study. For the same reasons as exposed in Section 5.3.1, the statistical analysis is performed up to  $\alpha = 0.90$ .

The results established with this modus operandi of the Fisher classification on two approaches (model-fitting and isoconversional/model-fitting) are presented in Table 5. They show that in model-fitting method, only two models, F<sub>10</sub> and F<sub>11</sub>, are suitable to correctly represent the experimental data. Let us remind that three models were considered as statistically equivalent if the statistical analysis is performed only on the model-fitting results (see Paragraph 5.3.1). The top-2 models are the same as those identified by Day *et al.* for the isothermal decomposition kinetics of PPS [11]. These reaction models lead to almost the same pairs of Arrhenius parameters ( $E_{\alpha}$ =161 and 164 kJ.mol<sup>-1</sup>; log A =9 and 8.8 min<sup>-1</sup>). Values of the activation energy are in good agreement with results from modulated TGA (mean value: 174 kJ.mol<sup>-1</sup>). Thus, model fitting method may be seen as a correct method to model isothermal experiments. Nevertheless, it is limited to a single value of the Arrhenius law parameters ( $E$  and  $A$ ), which does not allow to fully represent the complexity of the decomposition process.

For the isoconversional/model fitting method, the six considered models are shown to correctly represent experimental data and present very close values of Fisher indicators. The six computations are indeed based on the same set of  $E_{\alpha}$  values. As a result, the values for  $A_{\alpha}$  are less dispersed than in the model-fitting method. In this latter, the values of  $A_i$  vary by a factor of 80 whereas this factor is 25 in the mixed approach. An interesting finding is that, even if the pre-exponential factor exhibits a strong dependence on the chosen reaction model, the curves  $A_{\alpha} = f(\alpha)$  present the same evolution regardless of the model, as featured in Figure 7. In addition to better representing the physics of the decomposition phenomenon, the isoconversional/model-fitting method results in a more accurate prediction of the experimental data than the model-fitting method. More than that, since the activation energy varies during the decomposition, it authorizes the use of up to six reactions models without degrading the quality of the prediction. If this can be seen as an advantage, it leaves open the question of which reaction model should be privileged to model the decomposition. The model-free approach enables to avoid this problem.

One of the advantages of the model-free method is that it does not require the use of isoconversional curves (such as presented in Figure 2). Therefore, any set of activation energy values can be used. The Fisher indicators for this method are given in Table 6, based on the values of  $E_{\alpha}$  taken from modulated TGA, and calculations made with the Vyazovkin and Starink methods (see Paragraph 5.2). The analysis shows that the use of isoconversional methods as an input of the model-free approach yields very good results, as good as those obtained with isoconversional/model-fitting. Although the Fisher statistics indicates an

equivalence of the two methods, it is interesting to note that the lowest values are obtained wherever the Vyazokin's formula (Eq. 13) is used. It is possible to imagine that would the statistical analysis be carried out on more points (reducing the value of  $F_{1-p,n-1,n-1}$  considered), then Vyazovkin isoconversional method would come out as the best method. The use of modulated TGA yields less accurate results than isoconversional methods. A possible explanation is that the mean value of the heating rate during the experiments is quite low ( $5^{\circ}\text{C}\cdot\text{min}^{-1}$ ). For such a heating rate, the decomposition of C/PPS might be a mix of isothermal and anisothermal decomposition, lowering the value of the measured activation energy. Unfortunately, the mean heating rate cannot be increased in the experiment because of a technical limitation: the number of periods of the sinusoidal thermal ramp should be above a minimum during the decomposition.

Based on the above observations, it can be concluded that the activation energy is the most important parameter to model the decomposition. In order to determine the most appropriate approach to represent isothermal TGA experiments conducted on C/PPS laminates, it has to be based on an accurate determination of  $E$ . Therefore, the model-fitting approach can be excluded, which brings us to focus on isoconversional methods. In this study, two of these methods are compared: one based on isoconversional curves (Starink), and another based on a mathematical minimization (Vyazovkin). Regardless of the approach, it is more relevant to use anisothermal data as input of the isothermal decomposition kinetics model. Beyond the use of this data (any heating rate can be used in anisothermal tests, whereas test temperatures higher than the onset decomposition temperature should be avoided), the use of data different from those modelled is recommended. Although the Vyazovkin method is more accurate with respect to physics (it uses only the activation energies) and might thus produce a priori more accurate results (further investigations should be carried out to confirm this hypothesis), it has two main drawbacks. On the one hand, it is not sure that the mathematical minimization leads to a curve that reflects all the physics of the decomposition. On the other hand, since the method is not based on isoconversional curves, it is incompatible with the choice of reaction model.

In the particular case of the C/PPS isothermal decomposition, the model-free method based on the Vyazovkin's isoconversional method is promising. However, if one needs a model can deal with both isothermal and anisothermal decompositions, the isoconversional/model-fitting method should be preferred. To use the Vyazovkin, it is necessary in a first step to check if it yields a curve  $E_{\alpha} = f(\alpha)$ , which is meaningful from a physical point of view.

## 6. Conclusion

This work was aimed at identifying the most physically consistent approach to model the isothermal decomposition kinetics of C/PPS composites to be used in aeronautics, therefore allowing a better understanding of the thermal decomposition of composite structures during critical events such as aircraft engine fires. Thermal decomposition under isothermal conditions represents the majority of the practical cases encountered with respect to the fire response of Polymer Matrix Composites (PMCs). However, this problem is rarely addressed in the literature. The predictive capabilities of three types of approaches (modelistic, model free/isoconversional model, isoconversional model) have been discussed based on statistical analyses (Fisher's test). For C/PPS laminated composites, these approaches are virtually statistically equivalent (at least for several reaction models). Model-fitting methods result in relatively accurate prediction of the TGA curves at a given temperature. However, many criticisms have been raised concerning this type of approaches especially when they are used to predict the thermal decomposition of PMCs under anisothermal conditions. Finally, the model-free approach is the most predictive, from a physical point of view, to account for the thermal decomposition of C/PPS composites under isothermal conditions.

As an immediate perspective to this work, the model-free approach does not allow simulating thermal decomposition under both isothermal and anisothermal conditions. In this case, a mixed (model free/isoconversional model) approach could be relevant because the activation energy is determined by an isoconversional approach.

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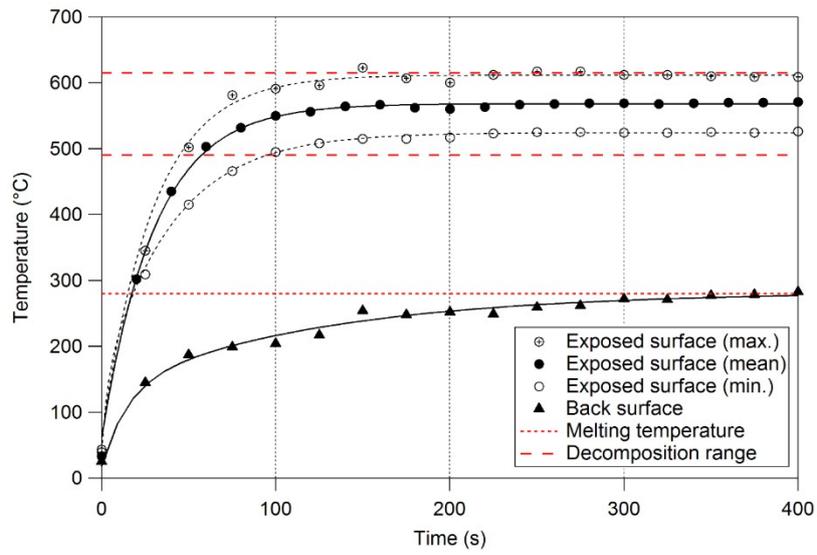


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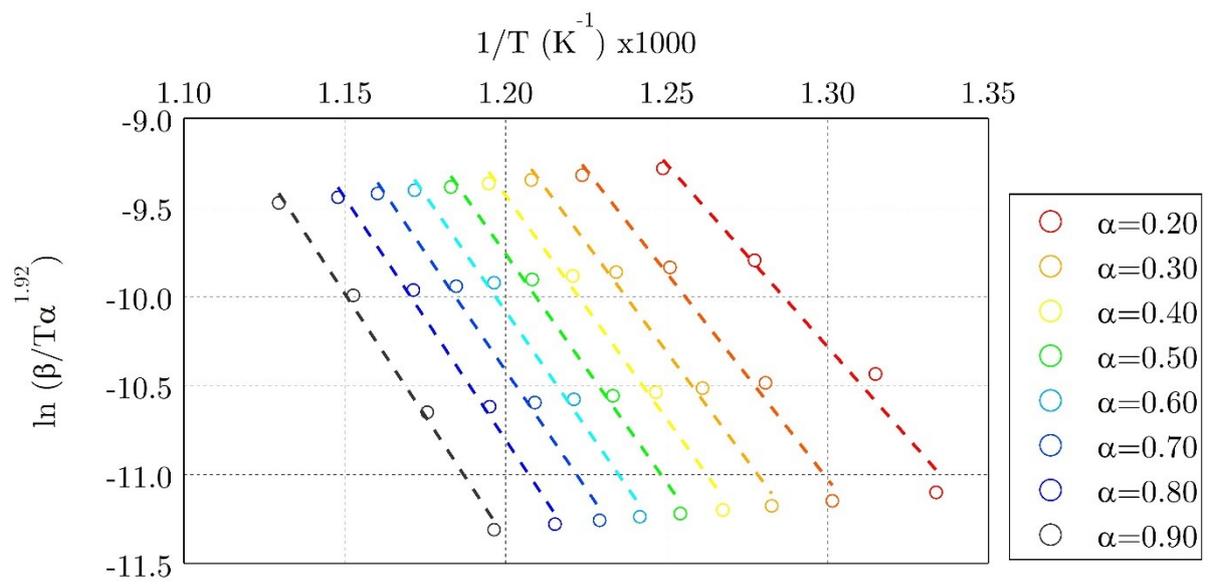


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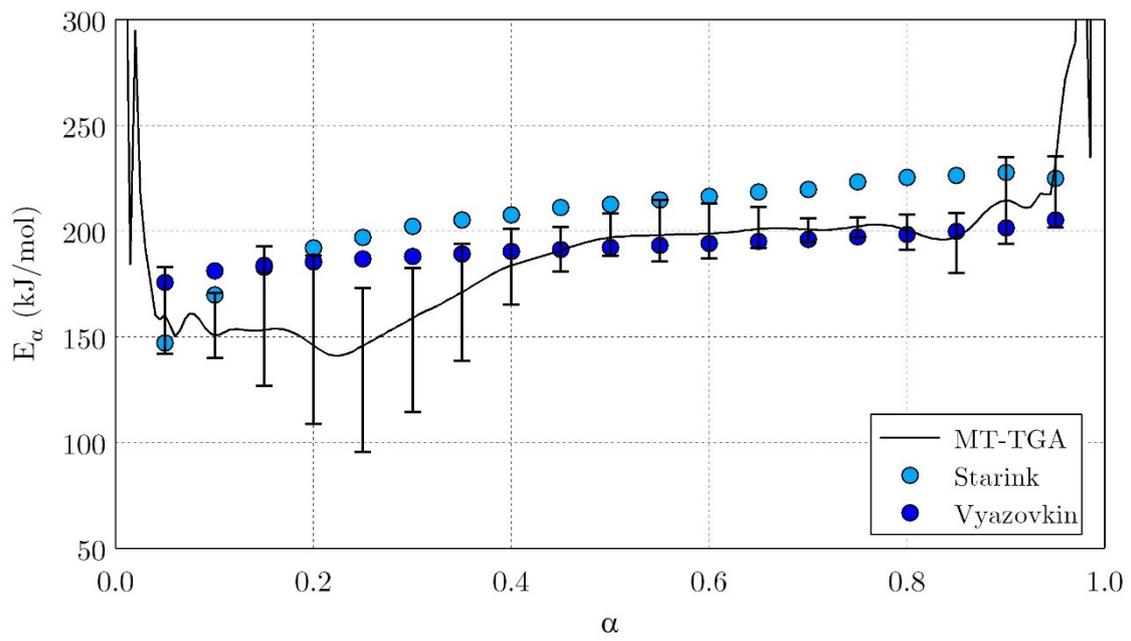


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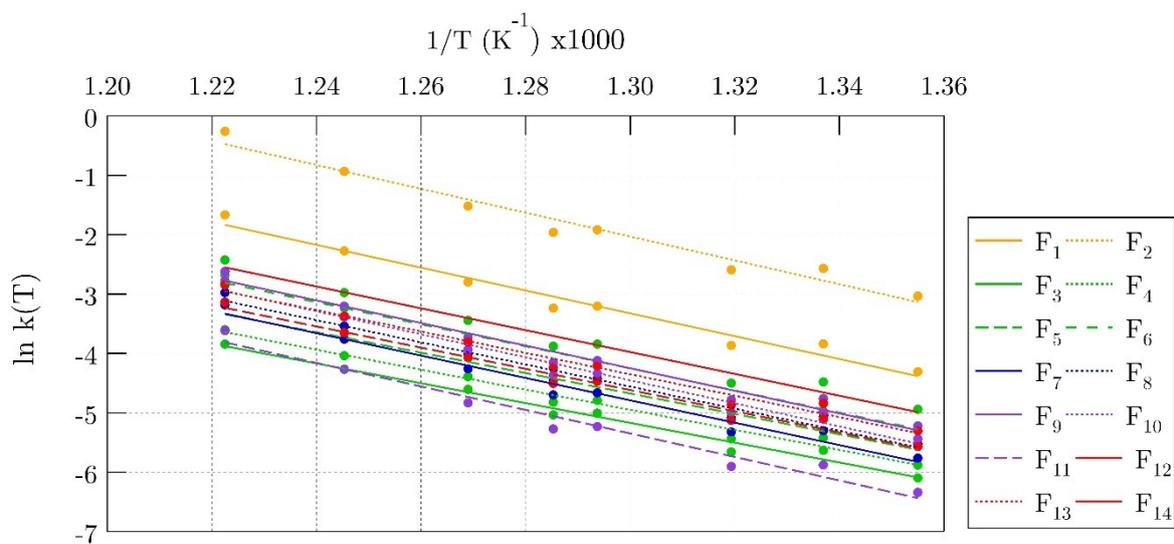


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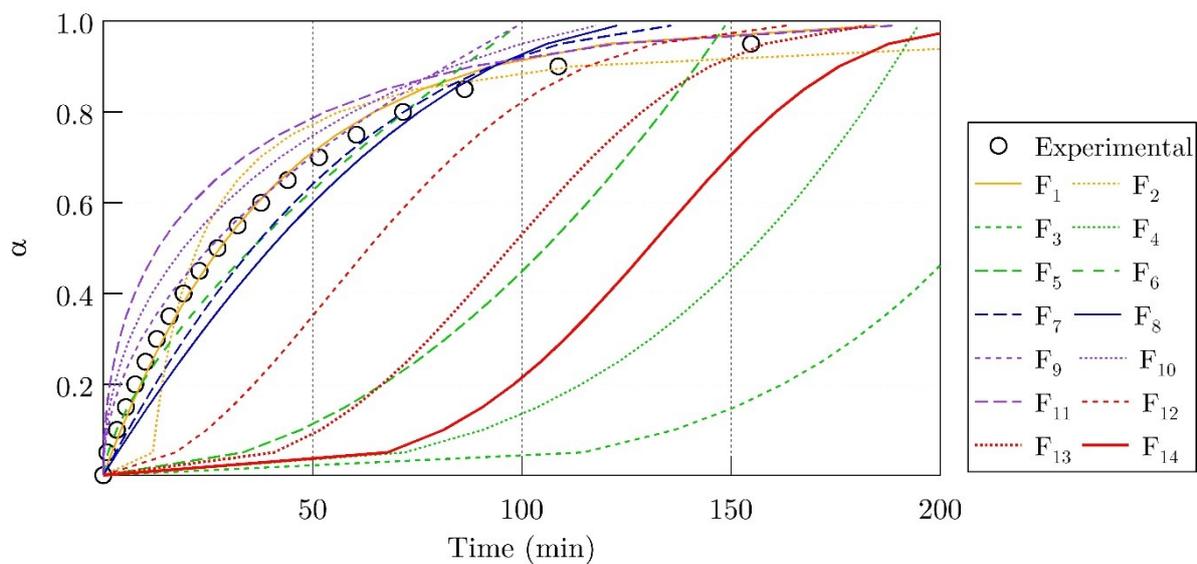


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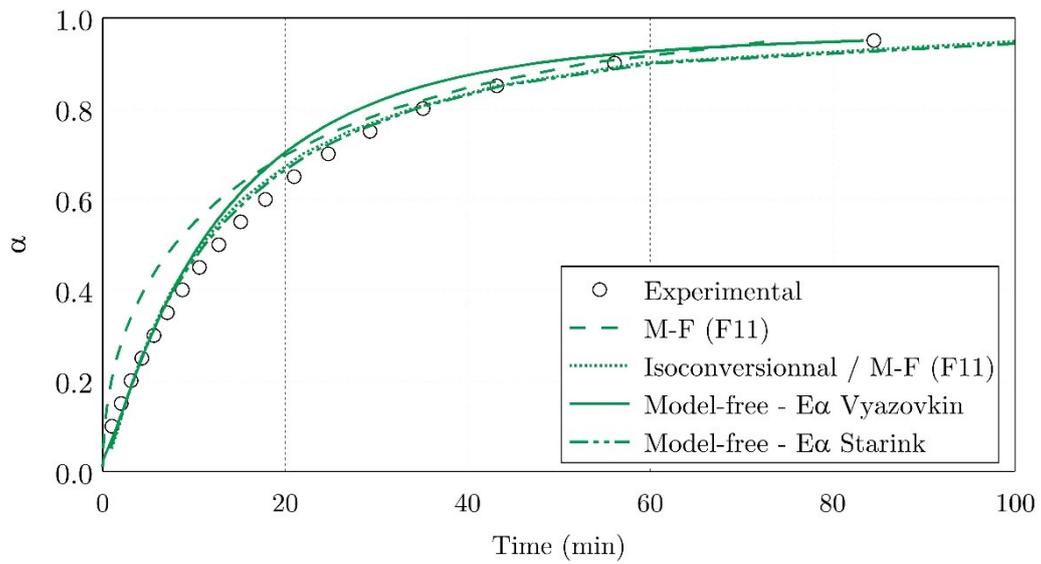


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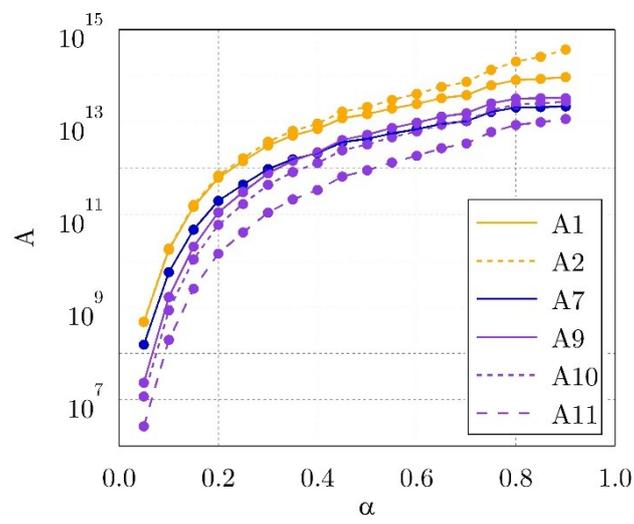


Figure 7 : Evolution of  $A_\alpha$  in the isoconversional/model-fitting method

Table 1 : Reaction models used to compute the decomposition kinetics of C/PPS

Reaction model		$f(\alpha)$	$G(\alpha) = \int \frac{d\alpha}{f(\alpha)}$
F1	First-order	$1 - \alpha$	$-\ln(1 - \alpha)$
F2	Second-order	$(1 - \alpha)^2$	$1/(1 - \alpha) - 1$
F3	Power law (P= 1/4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
F4	Power law (P=1/3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
F5	Power law (P=1/2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
F6	Power law (P=3/2)	$2/3(\alpha^{2/3})$	$\alpha^{3/2}$
F7	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
F8	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
F9	1D diffusion	$1/2\alpha$	$\alpha^2$
F1	2D diffusion	$1/\ln(1 - \alpha)$	$\alpha + \ln(1 - \alpha)(1 - \alpha)$
0			
F1	3D diffusion	$3(1 - \alpha)^{2/3}(1 - (1 - \alpha)^{1/3})^{-1}$	$(1 - (1 - \alpha)^{1/3})^2$
1			
F1		$2(1 - \alpha)(\ln(1 - \alpha))^{1/2}$	$(-\ln(1 - \alpha))^{1/2}$
2			
F1	Avrami-Erofeev	$3(1 - \alpha)(\ln(1 - \alpha))^{2/3}$	$(-\ln(1 - \alpha))^{1/3}$
3			
F1		$4(1 - \alpha)(\ln(1 - \alpha))^{3/4}$	$(-\ln(1 - \alpha))^{1/4}$
4			

Table 2 : Comparison of the mean value of the activation energy

Method	MT-TGA [7]	Vyazovkin	Starink
$E_\alpha$	174	191	205

*Table 3 : Arrhenius parameters and Fisher's statistic*

Model	$E$ (kJ.mol <sup>-1</sup> )	log $A$ (min <sup>-1</sup> )	$F_i(\alpha \leq 0.90)$
F <sub>1</sub>	160	9.4	2.02
F <sub>2</sub>	167	10.5	4.31
F <sub>3</sub>	139	7.2	99.03
F <sub>4</sub>	140	7.4	82.12
F <sub>5</sub>	143	7.7	57.65
F <sub>6</sub>	155	8.6	8.74
F <sub>7</sub>	157	8.6	6.20
F <sub>8</sub>	155	8.5	9.32
F <sub>9</sub>	158	8.9	3.41
F <sub>10</sub>	161	9	1.00
F <sub>11</sub>	164	8.8	1.22
F <sub>12</sub>	153	8.7	23.44
F <sub>13</sub>	150	8.3	46.46
F <sub>14</sub>	148	8.1	65.01

Table 4 : Pre-exponential factor  $A_\alpha$  computed with Starink method

$\alpha$	$E_\alpha$ (kJ.mol-1)	$A_{\alpha i}$ (min <sup>-1</sup> )					
		F <sub>1</sub>	F <sub>2</sub>	F <sub>7</sub>	F <sub>9</sub>	F <sub>10</sub>	F <sub>11</sub>
0.10	170	1.8E+10	1.9E+10	5.7E+09	1.7E+09	8.6E+08	2.0E+08
0.20	192	6.2E+11	7.0E+11	2.0E+11	1.1E+11	6.0E+10	1.4E+10
0.30	202	3.1E+12	3.7E+12	9.7E+11	7.9E+11	4.4E+11	1.1E+11
0.40	208	7.1E+12	9.2E+12	2.2E+12	2.2E+12	1.3E+12	3.4E+11
0.50	213	1.5E+13	2.1E+13	4.4E+12	5.4E+12	3.3E+12	9.1E+11
0.60	216	2.5E+13	4.1E+13	7.1E+12	9.7E+12	6.3E+12	1.9E+12
0.70	220	3.8E+13	7.4E+13	1.0E+13	1.6E+13	1.1E+13	3.4E+12
0.80	225	8.1E+13	2.0E+14	2.1E+13	3.2E+13	2.4E+13	8.7E+12
0.90	228	9.4E+13	3.7E+14	2.2E+13	3.3E+13	2.7E+13	1.2E+13
Mean value		2.7E+13	6.8E+13	7.0E+12	1.0E+13	7.5E+12	2.7E+12

Table 5 : Fisher statistic obtained with the model-fitting and the isoconversional/model-fitting methods

Approach Model	M-F $F_i$	Isoconversional/M-F $F_i$
F1	2.47	1.41
F2	5.95	1.37
F7	8.44	1.4
F9	4.61	1.37
F10	1.15	1.41
F11	1.5	1.41

Table 6 : Fisher statistic obtained with the model-free approach

$\beta$ (C°/min)	Model free		
	$F_i(E_\alpha \text{ Vyazvokin})$	$F_i(E_\alpha \text{ Starink})$	$F_i(E_\alpha \text{ TGA-MT})$
5	1.08	1.87	2.66
10	1.00	1.51	2.56
20	1.05	1.87	3.11
35	1.12	1.50	3.11