



# On the determination of thermal degradation effects and detection techniques for thermoplastic composites obtained by automatic lamination



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## ARTICLE INFO

### Keywords:

Polymer-matrix composites (PMCs)  
Automated fibre placement (AFP)  
Process modelling

## ABSTRACT

Automatic lay-up and in-situ consolidation with thermoplastic composite materials is a technology under research for its expected use in the profitable manufacturing of structural aeronautical parts. This study is devoted to analysing the possible effects of thermal degradation produced by this manufacturing technique.

Rheological measurements showed that there is negligible degradation in PEEK for the temperatures reached during the process. Thermogravimetric analysis under linear heating and constant rate conditions show that thermal degradation is a complex process with a number of overlapping steps. A general kinetic equation that describes the degradation of the material with temperature has been proposed and validated. Attenuated total reflectance Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy confirmed that there is no remarkable degradation. The use of a combination of in-situ and ex-situ experimental techniques, including kinetic modelling, not only provides reliable information about degradation but also allows setting optimal processing conditions.

## 1. Introduction

With the goal of industrial application of thermoplastic composite materials in aeronautics, similar techniques to those used with thermosets (automatic tape placement, fibre placement) should be fine-tuned taking into account their demonstrated success in aircraft [1]. Current automatic lamination with thermoplastic composite materials attempts to reach full consolidation in only one-step, avoiding the secondary use of an autoclave. However, the lack of tackiness in the material forces the use of heat sources that apply a punctual or surficial heating that lasts only several seconds.

The operating principle of these machines is the sequential heating of individual layers before being placed in contact with the pre-positioned layer for the production of laminates of different shapes and ply orientations. Different heating sources have been used, with diode laser being a preferred solution [2]. After heating to the melting temperature of the polymer, the layers are compacted by a deformable roller.

Establishing the proper limits for the parameters interacting in the control loop of automatic lay-up and in-situ consolidation is a

complicated task, owing to their coupling. Mathematical models defining the responses of the material to these specific effects are needed. These models depend on the way the specific effects are described, and the property used for their calculation. Diverse effects should be estimated in advance, creating models that contemplate thresholds whilst reaching the required power and speed, for acceptable levels of degradation, crystallization, bonding, and so on [3]. Finally, the control system should implement all of them, giving proper impact ranges and estimating the degree of deviation from the ideal result.

Owing to the elevated requirements imposed by aeronautics, high-performance thermoplastics such as those in the poly-aryl-ether-ketone (PAEK) family are the focus of most of the lamination endeavours to set up this manufacturing technology [4–9], with the exception of some works devoted to the application of PPS (poly-phenylene-sulphide) [5,10,11], PEI (polyetherimide) [12], and current works with PA (polyamide) [13,14]. Poly-ether-ether-ketone (PEEK) is a linear, aromatic, semi-crystalline thermoplastic polymer with excellent thermal stability, chemical resistance, and mechanical properties. Its glass transition temperature appears at around 416 K and its melting point is

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616 K. Moreover, above 723 K, 4-phenoxyphenol and 1,4-diphenoxybenzene are detected, showing chain scission thermal degradation [15]. Other authors suggest that the degradation produces cross-linking in the matrix structure, especially under an oxidative atmosphere, which affects the viscosity and the ability to crystallize [16,17]. The atmosphere has an important effect on the degradation, with differences in the time required for degradation at the same temperature as high as 16% in either inert or oxidative atmospheres [18].

For the automatic lamination processes of carbon fibre/PEEK composites (CF/PEEK), temperatures in the range from 623 K to 673 K, or even higher, should be applied to achieve melting and bonding among layers. Thus, the processing temperature is very close to the onset of degradation [18]. Moreover, considering that the temperature control is manual, instances of overheating could discretely appear, thereby changing the material elementary structure.

Considering the normal trends in automatic lamination with carbon fibre-reinforced thermoplastics, the relevant speeds of lamination differ from consulted groups of study. As a parameter still under analysis, it is possible to find values as low as 10 mm/s [19] and as high as 400 mm/s [20], which imply times of maximum temperature stabilization in the range of seconds, depending on the heating spot. Additionally, there is an important effect of polymer molecular weight, which affects the capacity of chains to move and, therefore, the maintenance time needed to reach full healing. Thus, for the sake of establishing comparisons, all these parameters should be carefully considered. Owing to the fact that thermal degradation is not only affected by temperature but, also by the dwell time at this temperature, both parameters should be considered in any degradation model. For a proper kinetic model, a specific monitoring parameter (mass loss, linkage% content, molecular weight, or viscosity) should be considered.

Degradation kinetics permit one to obtain a mathematical formula that relates the extension of conversion (degradation by means of different parameters) to time–temperature profiles. Kinetic thermal analysis is a powerful tool, which is widely employed to estimate in advance the behaviour of a material subjected to a specific thermal process condition. It is a valuable tool in many scientific branches and has already been used with PEEK [15,21,22].

In particular, for the PAEK family, several studies have tried to obtain information about the degradation mechanisms. Most of them focused on the detection and explanation of the degradation mechanism from a physical–chemical point of view [16,23–26] and a low number of works elucidate the kinetic model. Some of them, related to kinetics, are focused on pyrolytic tests [27], oxidative atmosphere tests [28], or both. In the particular case of oxidative degradation, the authors consider that there are only two mechanisms interacting from the beginning (0% mass loss) to the end (100% mass loss). Nevertheless, the great dispersion observed in activation energies, even for the first 30% of mass loss, suggests the presence of more than one mechanism in this small range.

Furthermore, there are many works reporting that, before the appearance of any kind of measurable degradation by mass loss, PEEK already experiences modifications that affect its structure. This effect is related to the unstable behaviour of ether and carbonyl groups, which is mainly detectable by rheological testing and by appreciable changes in the crystallization behaviour [17,29]. Other authors consider that mass loss fails when one tries to associate its appearance with detrimental mechanical properties [30].

This study aims to analyse several effects in PEEK degradation and CF/PEEK composites. It includes different experimental measurements for the determination of possible degradation effects after diode-laser-irradiation processing of the composite material. Moreover, a simplified kinetic equation is proposed that predicts the behaviour of neat resin under any heating profile by considering two monitoring parameters independently: mass loss and viscosity changes.

## 2. Theoretical background of thermal degradation kinetics

Eq. (1) is commonly used for studying the kinetics of solid-state reactions [31]:

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

where  $A$  is the pre-exponential Arrhenius factor,  $E_a$  the activation energy,  $\alpha$  the reacted fraction or conversion,  $d\alpha/dt$  the reaction rate, and  $f(\alpha)$  the kinetic model.

This equation can be rewritten considering the evolution of conversion with temperature instead of its time dependency, by means of the reaction rate,  $\beta$ .

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

From Eq. (2), it follows that it is necessary to obtain the values of the kinetic triplet ( $A$ ,  $E_a$ ,  $f(\alpha)$ ) in order to complete the information that properly describes the kinetics of a reaction.

The use of the so-called ‘isoconversional’ methods facilitates this task, because the reaction rate at a constant extent of conversion is considered to be only a function of temperature. Thus, the activation energy values can be extracted without any consideration of the reaction model. One of the most used differential isocoverisional methods is that of Friedman [31], which for nonisothermal heating programs, has the form (3):

$$\ln \left[ \beta_i \left( \frac{d\alpha}{dT} \right)_{\alpha,i} \right] = \ln[(f(\alpha)A_\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (3)$$

The index ‘ $i$ ’ represents each of the set of dynamic heating programs used for the analysis. The left-hand side of the equation is plotted against  $\frac{1}{RT}$ ; the plot consists of straight lines linked to each conversion value and with a number of points that depends on the number of heating programs used. The slope of the lines gives the value of the activation energy  $E_\alpha$ .

Polymer thermal degradation is usually described by complex mechanisms depending on the number of reactions implied [32]. The presence of multiple reactions complicates the application of isoconversional methods in order to obtain the activation energy, whose evolution is highly dependent on conversion. For this reason, it is not realistic to determine the corresponding activation energy values for each stage using the isoconversional methodology. It is important to clarify that the interaction of simple individual mechanisms is not certified by the fact that a constant activation energy with respect to conversion was obtained, because in any case, a deeper analysis is needed [33].

Attempting to overcome the difficulties when more than one stage is involved in the overall process, several solutions have been suggested. One of these solutions considers the deconvolution of the experimental curves of the reaction rate  $\left(\frac{d\alpha}{dt}\right)$  into different subcurves that represent each stage individually [34,35]. This methodology is applied in the present work in an attempt to obtain the equation that describes the thermal degradation of PEEK.

Thus, after deconvoluting the experimental curves for each heating rate, they are analysed independently for each degradation stage [36]. The calculus of the kinetic triplet is based on the combined kinetic analysis method [37]. For the combined kinetic analysis methodology, the general kinetic equation is converted into the linear form shown in Eq. (4):

$$\ln \left[ \frac{d\alpha}{dt} \frac{1}{f(\alpha)} \right] = \ln(cA) - \frac{E}{RT} \quad (4)$$

However, the plot of the left-hand side of this equation versus the inverse of the temperature yields a straight line only if the correct kinetic function,  $f(\alpha)$  is considered. Moreover, the proposed kinetic

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