

# Curing kinetics analysis of carbon/epoxy prepreg for solid rocket motor casings application

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## Abstract

This paper presents a study about cure kinetics of HXE23<sup>®</sup> resin system; this material has been developed by AVIO S.p.A. for the next generation of solid rocket motor (SRM) cases for VEGA and P120C. Only a complete knowledge of the curing mechanism allows to benefit of all the distinctive advantages of the developed resin system.

Characterization of the resin is one of the prerequisites for optimizing the process parameters, therefore this paper presents a study of HXE23 prepreg in terms of cure kinetic, whose understanding is essential especially when on-line cure monitoring is not possible due to constraints deriving from a combination of part complexity, process needs and tooling peculiarity; this is the situation experienced in SRM cases manufacturing. Moreover, the big size of the parts limits the number of trial items for process setup, and a complete knowledge of the material properties is essential.

As a result, a kinetic cure model was developed giving the possibility to develop a method to optimize the cure cycle for different SRM cases. Differential Scanning Calorimetry (DSC) method was taken into account in order to develop a curing kinetic model. The developed cure model has a fundamental importance from an industrial point of view, since it can be implemented in a dedicated Finite Element Method (FEM) software for the simulation of curing process of SRM casings, thus allowing to predict the degree of conversion and the mechanical and thermal properties on the real part. This approach gives also the opportunity to optimize the curing process in order to obtain the maximum achievable homogeneity of the final properties on the various parts of the casing.

## 1. Introduction

In the last decades, the development of carbon composite materials with excellent mechanical properties, capable of withstanding considerable mechanical loads at high temperatures, has led the Space Industry towards the manufacturing of SRM cases with these new materials instead of traditional metals, giving a clear advantage in terms of weight savings, which are directly translated in higher payload capacity. By using composite materials for producing SRM cases, cost saving and performance increase are achievable by opportunely selecting raw materials and optimizing manufacturing processes. These were the main drivers that induced AVIO S.p.A. to develop its own prepreg for the next generation of solid rocket motors for VEGA and P120C. This prepreg is based on the proprietary resin system HXE23<sup>®</sup> and hot melt impregnation process, with tailored characteristics for SRM case manufacturing [1,2,3,4].

Some full-scale cases have already been manufactured with HXE23 prepreg; the production of these composite cases allowed to validate the cure cycle on large scale items, the processability of materials, i.e. the suitability for filament winding (tow) and the good tack level for manual or automatic tape application (UD tape), and the ability to withstand proof mechanical loads, thanks to a very low defect density.

The technique used to process the resin kinetic equation uses the enthalpy values of the polymer curing reaction under isothermal conditions. In this way, measurements are made in which the maximum heat generated by the reactions at the various temperatures is evaluated ( $H_T$ ), while the total enthalpy of reaction ( $H_U$ ) is estimated as the amount of heat generated during a dynamical scan, that can reach the maximum conversion. This is independent by the sample thermal history and it is calculated with the following equation:

$$H_U = \int_0^{t_f} \left( \frac{dQ}{dt} \right)_f dt \quad (1)$$

where  $(dQ/dt)$  is the generated reaction flow, while  $t_f$  is the time amount for the reaction completion. By making the ratio between the maximum heat developed in an isothermal cure  $H_{(T)}$  and the maximum heat  $H_U$ , you can define the conversion degree to the various isothermal temperatures:

$$\alpha_{(T)} = \frac{H_{(T)}}{H_U} \quad (2)$$

where  $\alpha_{(T)}$  is conversion degree at a defined temperature. The real reaction rate  $(d\alpha/dt)$  can be calculated using the equation:

$$\frac{d\alpha}{dt} = \frac{1}{H_U} \left( \frac{dQ}{dt} \right)_T \quad (3)$$

When the material glass transition is examined, the relationship between  $\alpha$  and  $T_g$  of the semi-crosslinked polymer is used. In fact because of the increase in molecular weight, which at low conversion is due to polymerization, and after the gel point is due to the increase in branching and the density of the crosslinking, the resin  $T_g$  varies from a minimum, corresponding  $T_{g0}$  unreacted monomers, until reaching a maximum value for the completely crosslinked resin. The correlation between these two quantities can be expressed according to several models [5], although the most commonly used is the relationship:

$$\alpha = \frac{T_g - T_{gr}}{T_{g\infty} - T_{gr}} \quad (4)$$

where  $T_{gr}$  and  $T_{g\infty}$  are respectively, the glass transition of the uncured resin and the fully crosslinked polymer, while  $\alpha$  is the conversion degree [6,7,8].

Kinetic models for curing can be classified into two categories: mechanistic and phenomenological. Purely mechanistic models, able to consider all the reactions that take place during crosslinking and to evaluate the influence for thermosetting materials, are difficult to identify and complex to handle mathematically; so in the industrial field, phenomenological or semi-empirical models are often used, which are also simpler to use, from an engineering point of view, and are more easily implemented in numerical modeling software for simulating the process. Furthermore, in the literature, there are many examples in which these models are applied successfully [9]. To explain the kinetic pattern obtained it is necessary to formulate the premises. The reaction can follow three pathways, the first is catalyzed by the accelerator, the second is auto catalytically promoted by the hydroxyls during the reaction and another is a non-catalytic process, with higher activation energy due to the reaction between epoxies. The latter should occur at any temperature, but its contribution becomes significant only above at high temperature, that will not be considered for this work. In the catalytic reaction, the primary amine can react in two consecutive steps with two epoxides, but the activation energy and the enthalpy of the two reactions are similar and so they are therefore considered to be the same. The contribution of catalytic and autocatalytic reactions varies with temperature, changing the ratio between activation energies. However, in the kinetic model processing, reaction orders will be considered constant in all the temperature range analyzed.

For purely catalytic systems [10] the function that best describes the reaction rate as a function of the conversion is:

$$\frac{d\alpha}{dt} = K_1(1 - \alpha)^n \quad (5)$$

where  $K_1$  is the kinetic constant of the catalytic reaction, while  $n$  is the reaction order of the catalytic reaction, typically close to 2 for this kind of systems.

The equation that describes in which there both the contributions (catalytic and auto catalytic) is the Kamal-Sourour equation [11]:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \quad (6)$$

Where  $K_2$  is the kinetic constant of the auto catalytic reaction, while  $m$  is its reaction order.

This is the most widely used kinetic equation in literature for epoxy resin systems, and is particularly suitable for reactions where the initial velocity is not equal to zero [12].

An additional extension of the kinetic equation, proposed by Fournier [13] provides the introduction of a diffusive factor ( $f_d$ ):

$$f_d(\alpha) = \left[ \frac{2}{1 + \exp[(\alpha - \alpha_f)/b]} - 1 \right] \quad (7)$$

where  $\alpha_f$  is the maximum conversion degree reachable at every temperature and  $b$  is the diffusion coefficient. This is linked to macromolecules free volume; in fact, if the reactivity of the molecules initially regulates the curing rate, after the gelation or glassification the reaction is in diffusion control. In that case the catalytic mechanism becomes much more important than non-catalytic and the reaction rate decreases strongly due to the difficulty of formation of the intermediates, due to the diffusive effect restriction. In any case at high values of  $\alpha$ , the rate decreases due to diffusive effect and the entry into the glass transition region; the reaction then stops before the complete conversion, precisely as a result of the glassification. However, despite the importance of diffusive effects, experimental data seems to say that a single kinetic equation can cover the entire conversion range. The most complex equation that takes into account all these parameters is:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1-\alpha)^n f_d(\alpha) \quad (8)$$

In the development of a phenomenological model describing the kinetics of the HXE23 resin curing, the equation 8 was widely used in literature in epoxy systems.

Since all of the constants present in the equation 8 are proportional to the cure temperature, the identification of 6 parameters ( $K_1$ ,  $K_2$ ,  $m$ ,  $n$ ,  $\alpha_f$  and  $b$ ), that can't be identified simultaneously with a single fitting, the iterative approach developed by N. Rabearison [12] is applied.

## 2. Materials and Methods

The material analyzed in this study is the HXE23<sup>®</sup> resin system (AVIO proprietary epoxy resin system) and its carbon fiber reinforced prepreg.

A DSC was employed to study resin and prepreg kinetic behavior. DSC tests were performed by using a TA Instruments Q2000 MDSC under nitrogen flow.

Tests were initially executed in dynamic conditions: in the first part of this work a temperature ramp in a very wide range of temperatures is applied, which includes both  $T_{gr}$  and  $T_{g\infty}$ , and so as to achieve maximum possible polymerization without leading to the resin degradation. The analysis is led with a heating rate of 10 °C/min. The  $T_g$  of the uncured resin and the total enthalpy are evaluated in the first scan, which integrating describes the  $H_U$  value, while  $T_{g\infty}$  is obtained from the second run.

Thereafter, five isothermal temperatures ( $T_1 < T_2 < T_3 < T_4 < T_5$ ) were carried out for a period of time each time adequate and sufficient to allow maximum polymerization at that temperatures. From these tests, the reaction enthalpy at that temperature cure was obtained. By integrating the exothermic peaks, it was possible to know the conversion degree and the reaction rate. Finally, samples treated under isothermal conditions were subjected to a modulated scan at a temperature ramp, with a heating of 5 °C/min overlapping a periodically oscillating temperature of 0.8 °C/min. In this way, the glass transition temperature of the semi-crosslinked polymer and the residual crosslinking heat for the samples previously cured were evaluated.

### 3. Results and Discussion

In the first part of the study are presented all the DSC tests and the elaboration of thermograms to calculate the  $\Delta H$  of dynamical and isothermal run (inclusive of residual after the isothermal cure). In Figure 1 there is synthetic representation of the results.

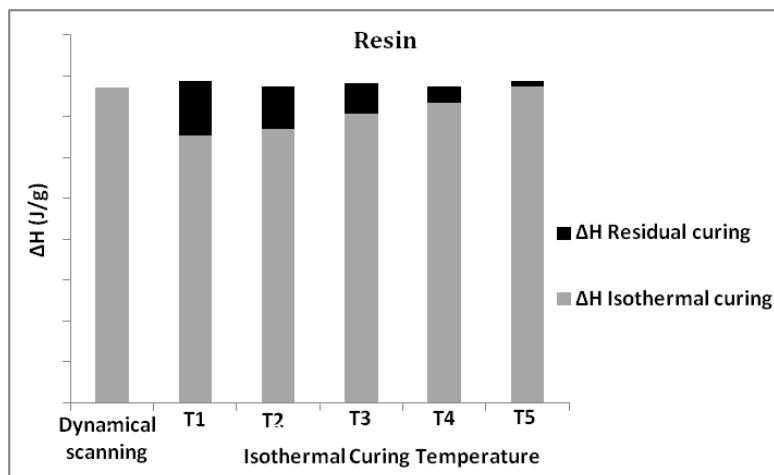


Figure 1: curing enthalpy (isothermal + residual) at several temperatures

By analyzing curing enthalpy it can be seen that the values increase as the cure temperature, since this raises the temperature at which the glassification occurs, that stops the reaction development. By adding the dynamical scanning values after the cure, it can be concluded that the maximum heat generated in the reaction of complete crosslinking is constant, regardless of the thermal treatment. This feature could be used to calculate the conversion degree, particularly in specimens whose thermal history or ageing period is not known, making the difference between the maximum and the value got in isothermal conditions.

It exists a correlation between the polymer  $T_g$  and its conversion degree  $\alpha$ , expressible through various mathematical models. In particular, among the most commonly used, there is the equation 4. The Table 1 shows the glass transition temperature obtained in isothermal conditions and the  $\alpha$  calculated with the equation 4.

Analyzing the data the obtained values  $T_g$  are always close to the temperature test. This is because crosslink concentration within a polymer increases the  $T_g$  from a minimum, corresponding to unreacted resin, up to a maximum value for the fully cured resin. However, when the cure process leads the polymer with a  $T_g$  higher than the isothermal crosslinking temperature, or slightly higher, the macromolecules undergoes the glassification phase and this stops the polymer network growth: for this reason the reaction passes from a kinetic to a diffusive control and the rate decreases considerably. All this justifies the existing correlation between isothermal cure temperature, its  $T_g$  and its conversion degree.

Table 1:  $T_g$  and  $\alpha$  after isothermal cure

Test Temperature	Isothermal Cure $T_g$ ( $^{\circ}\text{C}$ )	Conversion Degree via $T_g$
T1	T1 + 22.3	0.82
T2	T2 + 13.5	0.85
T3	T3 + 33.8	0.91
T4	T4 + 32.1	0.97
T5	T5 + 10.3	0.99

To find all the parameters of the equation 8, it was calculated the evolution of  $\alpha$  as a function of time, using the equation 2. In this way it is possible to obtain  $\alpha$  and performing incremental relationships also the reaction rate ( $d\alpha/dt$ ).

In Figure 2 the heat flow over time has been plotted for the various isothermal reactions, while in Figure 3 the time conversion is reported.

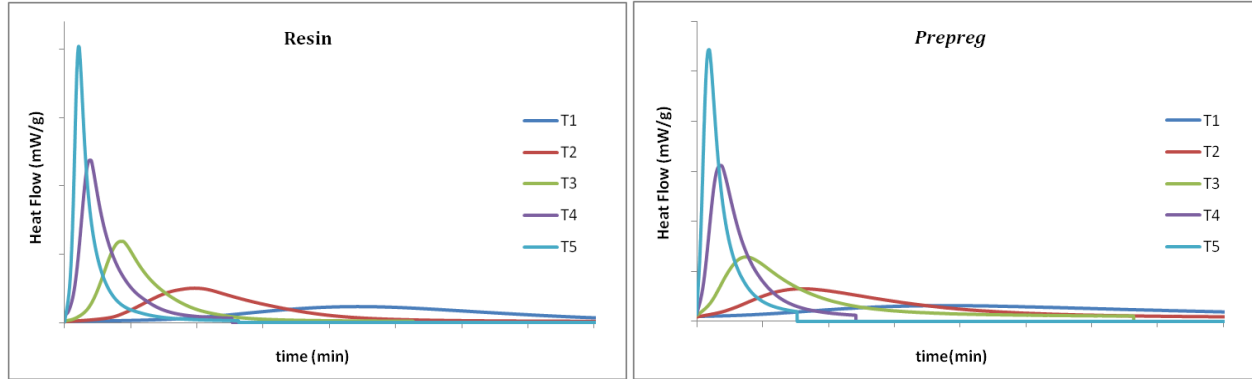


Figure 2: Heat flow developed by isothermal curing cycles

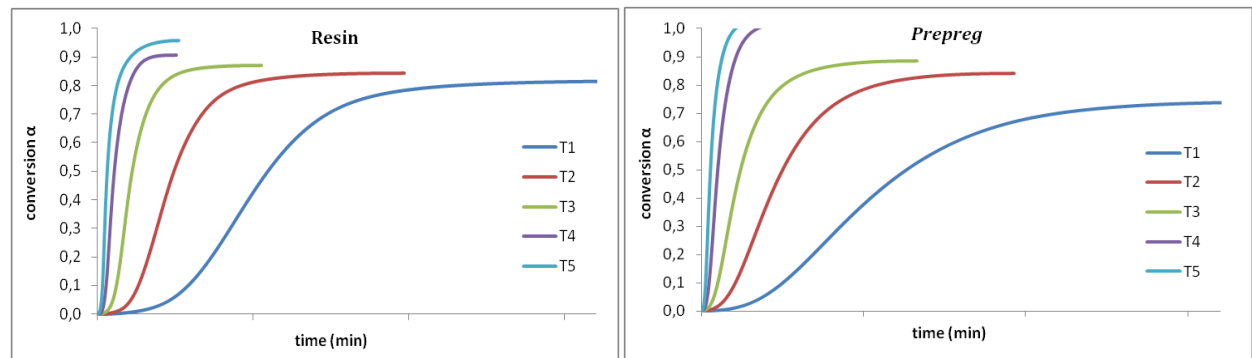


Figure 3: Calculated conversion  $\alpha$  for isothermal curing cycles

Now, it is necessary to write equation 6 in other mathematical form, (temporarily neglecting the diffusive factor):

$$\frac{d\alpha}{dt} = K_1 + K_2 \alpha^m \quad (9)$$

The variation of the exponents as a function of the temperature indicates that reaction mechanism is dependent by temperature itself. In particular the various reactions that characterize epoxy resin curing have a different incidence on the overall kinetics by varying the temperature and chemical composition: for example, the non-catalytic reaction takes place only considerably at temperatures higher than those experienced, while the autocatalytic reaction has a greater importance when the hardener blend is exhausted. There are, however, temperature ranges where  $m$  or  $n$  although they are not strictly linear to temperature, change slowly enough to not lead to errors too significant if considered constant in that temperature range. It should also be noted that the kinetic law obtained in these cases is strictly phenomenological, usable only for descriptive purposes but without absolute kinetic meaning. Considering these reasons, although  $m$  and  $n$  in the present study vary by temperature, it is logical and more consistent to try to assign fixed values to them. To do this, a first fitting was made using Equation 6, but not using the whole polymerization curve, but only the range of values not influenced by the diffusion parameter, excluded from the equation here considered. Figure 4 shows the curing rate as function of the conversion degree. The beginning of the diffusion condition, that brings the polymerization rate at values close to zero, occurs at different conversions for each temperature.

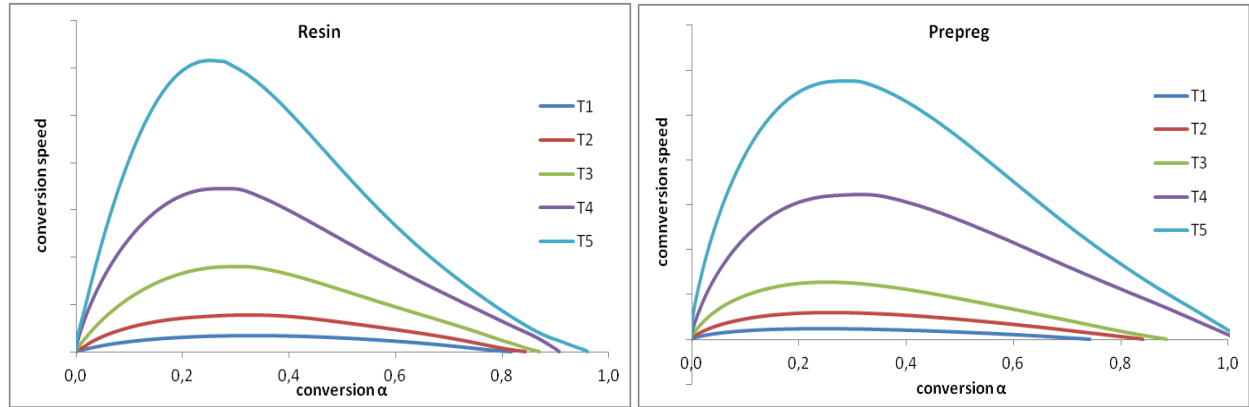


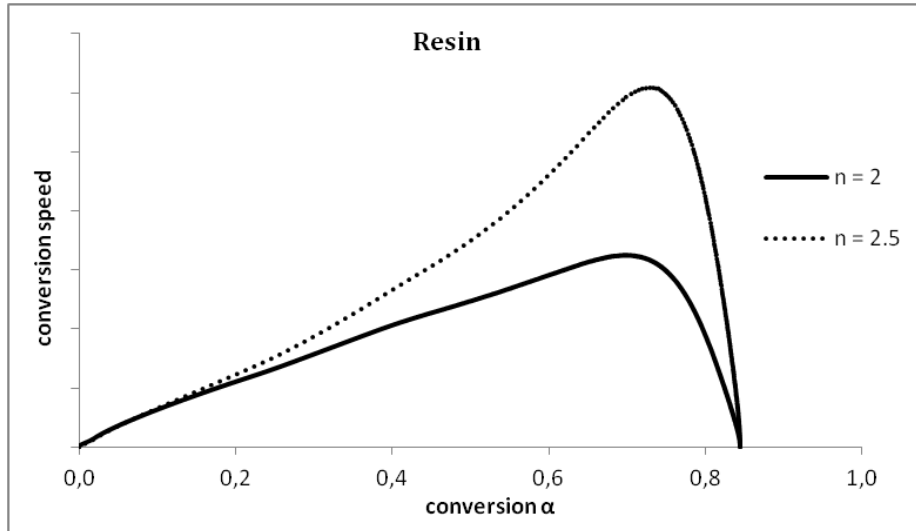
Figure 4: curing rate as function of the conversion

For each isothermal temperature, through a fitting with the equation 6 are obtained  $m$  and  $n$ . The values at each temperature is report in the Table 3.

Table 2:  $m$  and  $n$ 

Test Temperature	$m$	$n$
T1	1.28	2.74
T2	1.12	2.56
T3	0.90	2.12
T4	0.87	2.15
T5	0.78	1.96
average	0.99	2.30

For  $m$ , a value close to 1 is obtained. To find out the value of  $n$ , which from the experimental data is oscillating between 2 and 2.5, the equation 9 is graphed. To  $n$  is assigned predetermined values, in this case exactly 2 and 2.5; since  $m$  is equal to one, it must try to plot the experimental data to obtain a straight line in the first part of the graph (the one that represent the process before the gelation or glassification phenomena). This will be considered the partial order of the catalytic reaction.

Figure 5: plot example to obtain  $K_1$  and  $K_2$  values

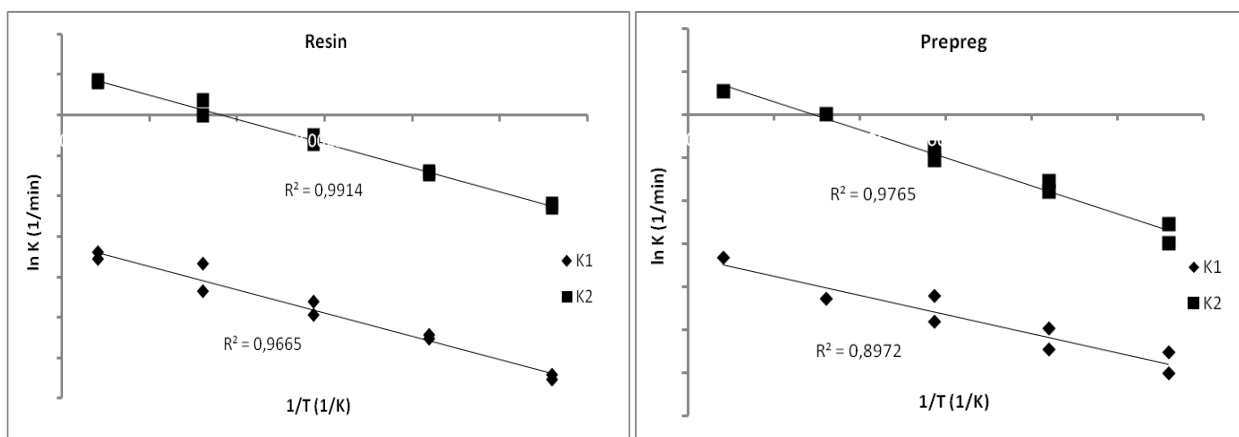
Taking as example (at T2) the Figure 5, which represents the values obtained in an isothermal test carried out on the resin; the curve where  $n$  has been imposed as 2 has a trend linear (in the first part). If, on the other hand,  $n = 2.5$  the fitting is less linear. Therefore, it is decided to assign a value equal to 2. This means that the total order of the curing reaction ( $m + n$ ) is 3, in accordance with the values present in the literature [14,15]. So the empirical equation is:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1 - \alpha)^2 \quad (10)$$

from whose diagram a linear trend is obtained for conversion values below levels where the diffusion contribution becomes relevant before gelation or glassification occurs.

From the first linear part of plot it is possible to obtain the values of  $K_1$  and  $K_2$ , respectively equivalents to intercept and slop of the linear part. After, a second method to find the kinetics constant is applied, taking into account the whole curve, with a not linear fitting, imposing to  $m$  and  $n$  the previous values.

$K_1$  and  $K_2$  are kinetics constant that keep the Arrhenius equation. These parameters contain information on the reagents concentrations and their reactivity, as well as a linear dependence on temperature, as can be seen in Figure 5. It is so possible to extrapolate an indication of the activation energy and pre-exponential factor  $A$  of the two reactions from the linear fitting.

Figure 6: Arrhenius plot for  $K_1$  and  $K_2$ , extrapolated from the linear fitting

From these values some experimental observations are obtained: in particular, if the initial rate tends to zero in all tests and the reaction begins with a certain delay, graphically  $K_1$  (constant of the catalytic reaction and intercepted in Figure 5) will tend to zero. Empirically, this means that in these curing cycles the predominant reaction is the autocatalytic one.

The mathematical information obtained is exploited to perform a second nonlinear fitting of the data on Equation 8, in this case taking into account the whole polymerization curve.

Of the six parameters present in the equation,  $m$  and  $n$  are assigned values obtained from the previous fitting, while  $\alpha_f$  is calculated by dividing  $H_U$  for the maximum enthalpy obtained. In the Figure 7 is possible to observe how the conversion increases linearly as the temperature increases.

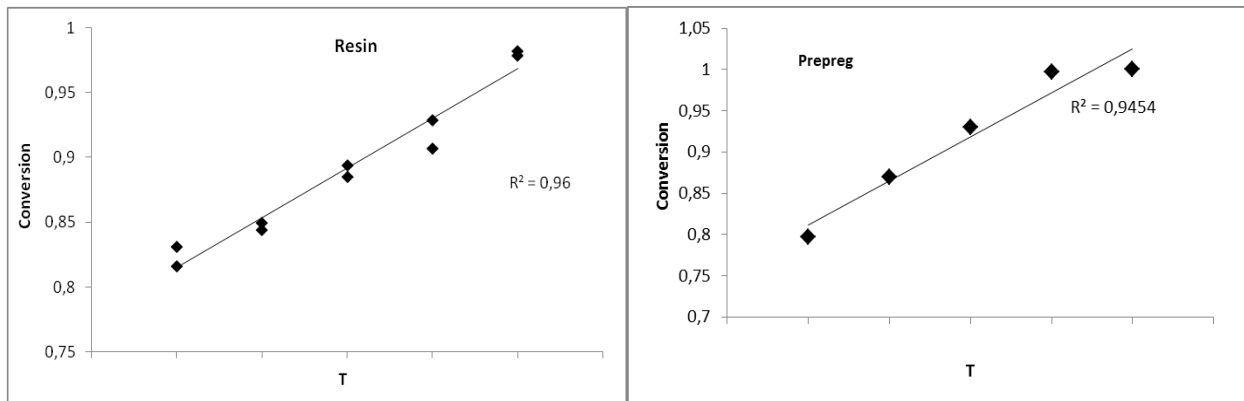


Figure 7:  $\alpha_f$  in isothermal tests

There are thus three unknown parameters, identified at the same time with the not linear fitting of the curve. To help calculate the program,  $K_1$  and  $K_2$  start-up values are specified as previously determined.

From the new values of  $K_1$  and  $K_2$  thus obtained it is possible to obtain the activation energy and the pre-exponential factor for the cure. These values are in agreement with the order quantities found in literature for epoxy resin; however, they differ from those previously calculated with the linear fitting, since they also taken into account the final part of the reaction, governed by the diffusion phenomena.

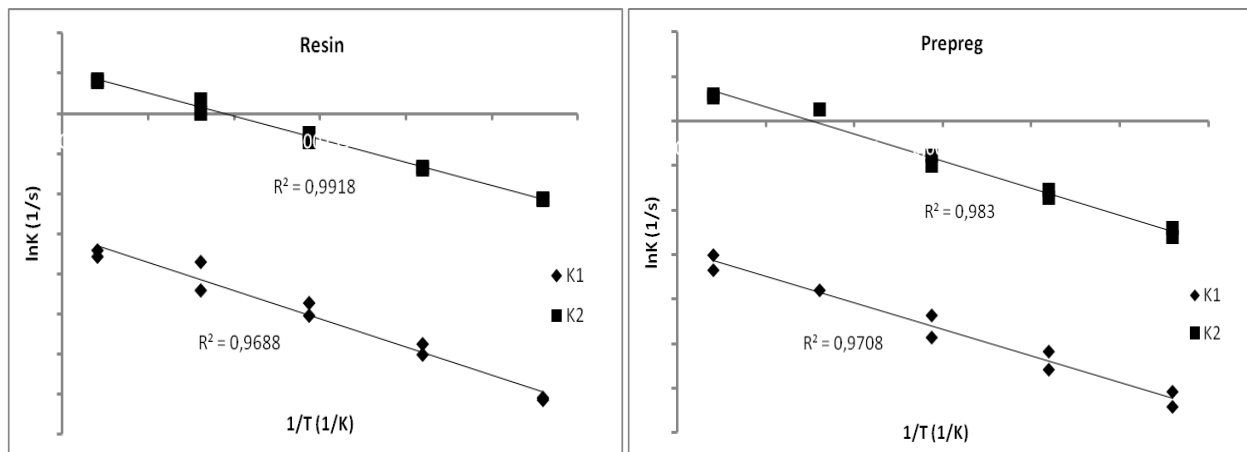
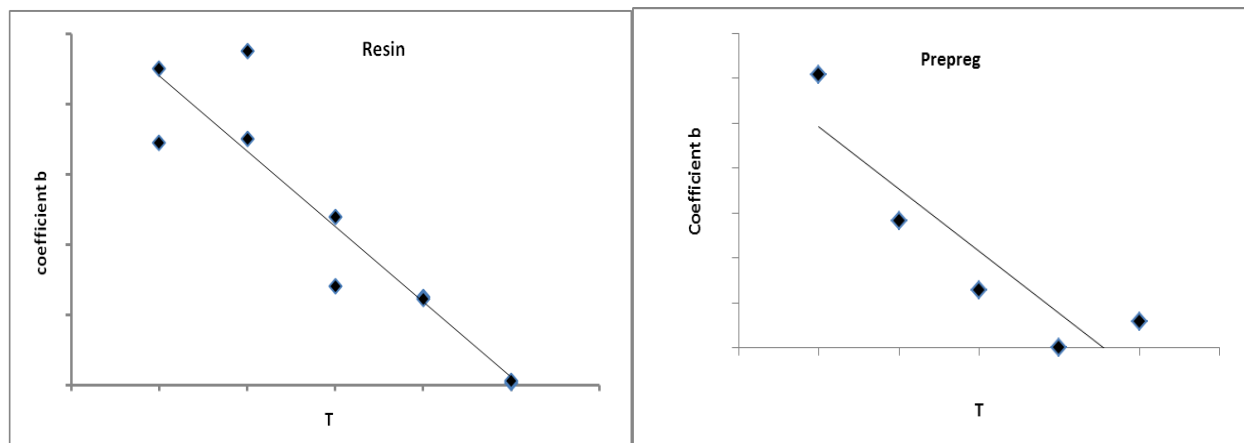


Figure 8: Arrhenius plot for  $K_1$  and  $K_2$ , extrapolated from the not linear fitting

From the not linear fitting it is possible to obtain the values of diffusive coefficient  $b$ . Figure 9 shows how this parameter is proportional to the temperature.



Figure 9: coefficient  $b$  in the diffusion factor

#### 4. Conclusion

In this study, applying a simple and fast technique, such as differential scanning calorimetry, it was possible to derive all the kinetic constants of the material used to produce big dimensions items. The constant values obtained from this study will be implement in a dedicated Finite Element Method (FEM) software for simulation of the curing process of SRM casings, thus allowing to predict the degree of conversion and the mechanical and thermal properties on the real part.

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