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Monitoring of cure kinetic prepreg and cure cycle modeling

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Cure kinetic model is an integral part of composite process simulation, which is used to predict the degree of curing and the amount of the generated heat. The parameters involved in kinetic models are usually determined empirically from isothermal or dynamic differential scanning calorimetry (DSC) data. In this work, DSC and rheological techniques were used to investigate some of the kinetic parameters of cure reactions of carbon/*F161* epoxy prepreg and to evaluate the cure cycle used to manufacture polymeric composites for aeronautical applications. As a result, it was observed that the *F161* prepreg presents cure kinetic with total order 1.2–1.9.

1. Introduction

Curing of the matrix resin is a determining step in manufacturing of fiber-reinforced thermoset composites. The quality of composites is controlled to a great extent by the cure cycle parameters such as time, temperature, pressure and their sequence of combination. Traditionally a composite manufacturer just follows the cure schedule suggested by the prepregger or the resin supplier. This schedule is usually determined in an ideal situation where the resin is still "fresh" and may not be representative to the actual curing state of the resin in a composite manufacturing facility. The composite manufacturer has to study the curing behavior of the matrix resin just prior to autoclave or press curing. This is necessary to verify the processability and to optimize the cure cycles especially if the resin has been shelved several times [1–3].

Laboratory tests for processability aims to determine how a sample performs during a simulated manufacturing curing cycle. These tests use small quantities of material, are fully equipped, and are operated by programmed temperature scanning at a constant heating rate. The role of processability testing is to define the kinetics of curing,the limits of thermal stability, and the optimum curing cycle, which leads to high performance and durability of the manufactured component. Very often, procedures of chemical analysis are implemented to verify thermoanalytical data and to define the mechanism of curing. Matrix resins are commonly classified in terms of their processing temperature range or their service temperature looking for environmental stability. DSC and rheology are among the most important tools of processability testing [1–6].

These combined tests characterize the degree of curing and its effect on the melting temperature and glass temperature transition. The function of processability testing is to find the optimum processing "window", which is a combination of processing time, temperature, pressure for consolidation, resin flow, and chemical curing of the composite laminate. These processability studies should always be accompanied by appropriate chemical analysis [1, 7–15].

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The principles of the autoclave curing process and the constraints of its operation, which were derived from the curing model prediction, are the underlying criteria for decision-making. Major refinements of input interpretation and decision-making to the existing expert systems are needed before they will become more acceptable for real curing environments [1–6, 16–20].

Accurate curing kinetic model is crucial to identify correctly the generated heat in the composite processing. In the present work, curing kinetic model for the carbon fiber/epoxy resin *F161* prepreg was studied and an appropriate curing cycle was proposed. The kinetics of curing and the curing cycle were based on an autocatalytic kinetic model for the proposed method, which uses dynamic and isothermal DSC and rheological data to determine these parameters.

2. Experimental

The prepreg material used in this work was the carbon fabric/epoxy *F161* prepreg supplied by *Hexcel Composites*. *F161* is a structural, heat resistant and electrical grade formulation designed for autoclave curing. It is a high temperature, laminate grade epoxy resin with a 177°C cure. *F161* is unique in that it was the first resin system to meet all types and classes of MIL-R-9300 B [20].

2.1. Rheological test

Rheometry data was obtained in a rheometer from Rheometric Scientific, model SR-5, with parallel plates and controlled stress. Three heating rates were applied: 2.5, 5.0 and 10.0 $K\cdot min^{-1}$, with a constant frequency 1 $rad\cdot s^{-1}$ and stress 1000 Pa, to identify the changes in the viscosity profiles and gel temperatures of the studied prepreg system. In order to obtain an appropriate cure cycle, three isotherms were investigated at: 100, 110 and 120°C.

2.2. Differential scanning calorimetry (DSC)

The uncured prepreg samples (*F161*), weighing about 5 mg, were placed in aluminum crucibles with a sealed lid and placed opposite the empty reference pan in the oven chamber. The DSC testing was performed in both dynamic and isothermal heating modes. The equipment used here was a Perkin Elmer DSC Pyris module. For dynamic testing, four linear heating rates (β) of 2.5; 5.0; 8.0, 10.0 $K\cdot min^{-1}$ were used along the temperature range of 30–300°C for also to determine the curing kinetics of prepreg. Isothermal experiments were conducted at five temperatures (120, 125, 130, 135, 140 and 145°C) in order to obtain both the rate of curing and the extent of curing *versus* time. The reaction was considered complete when the signal returned to the baseline.

3. Results

The processability of the epoxy resins requires the knowledge of the rheological behaviour to determine the properties of the final product and the kinetic of the crosslinked reaction in order to calculate the apparent kinetic constant and activation energy [22].

The curing reaction of epoxy resins usually involves the reaction of epoxide ring with the amine group of the amine. In amine curing agents, each hydrogen on an amine nitrogen is reactive and can open the epoxide ring to form a covalent bond [5]. When the nitrogen of amine contains two hydrogens, each reacts with a different epoxide ring. The network was developing in this way. This mechanism applies to both aliphatic and aromatic amine curing agents. The reaction between epoxide and amine produces a C–N bond, which environmental resistance is good, but their stability to elevated temperature is highly dependent on the adjacent molecular structure.

3.1. Rheological analyses

The correlation between viscosity and temperature or viscosity and time of thermoset resins or prepreg systems has shown effectiveness for the composite processing. The viscosity control during the autoclave processing allows the optimization of the infiltration of the resin inside the reinforcement, allowing consequently a larger densification of the composite materials in a shorter time.

The time of gel formation, i.e., gel time or temperature is an important factor to take into account on the industrial level because from that time and temperature onwards the thermosetting system decreases its processability. In the literature, it is difficult to find measurements concerning the rheological properties of the thermosetting systems due to the increase of the reaction rate caused by the generated heat during the crosslinking process.

Table I and Fig. 1 present the complex viscosimetric parameters for carbon fabric/epoxy *F161* prepreg analyzed at 2.5, 5 and 10 $K\cdot min^{-1}$ heating rates. As it can be observed, at the beginning, the increase of the temperature causes a small effect in the complex viscosity. After this, a decrease of the viscosity until a minimum point was observed. From this point, the polymerization reaction takes place and an increase of the complex viscosity is observed due to the formation of a three-dimensional net of crosslinked molecules. The rheological analysis of the epoxy system studied show that this resin analyzed at 2.5 $K\cdot min^{-1}$ presented a slower polymerization reaction than the samples treated at 5 and 10 $K\cdot min^{-1}$. Due to the slower formation of the epoxy system this slower polymerization reaction allows a better cure control of the system.

The gel temperature can be obtained drawing a tangent to the evolution of the complex viscosity curve, characterized by no further increase of the crosslinking density of the polymer. The smallest increase of the complex viscosity in the beginning of the analysis is characteristic of a slower ordering of the system. In this case, it was observed in Table I that the gel temperature value decreased with the increase of heating rate for epoxy prepreg system.

In spite of the evolution of the complex viscosity data in the gel region, it is more appropriate to use the crossing

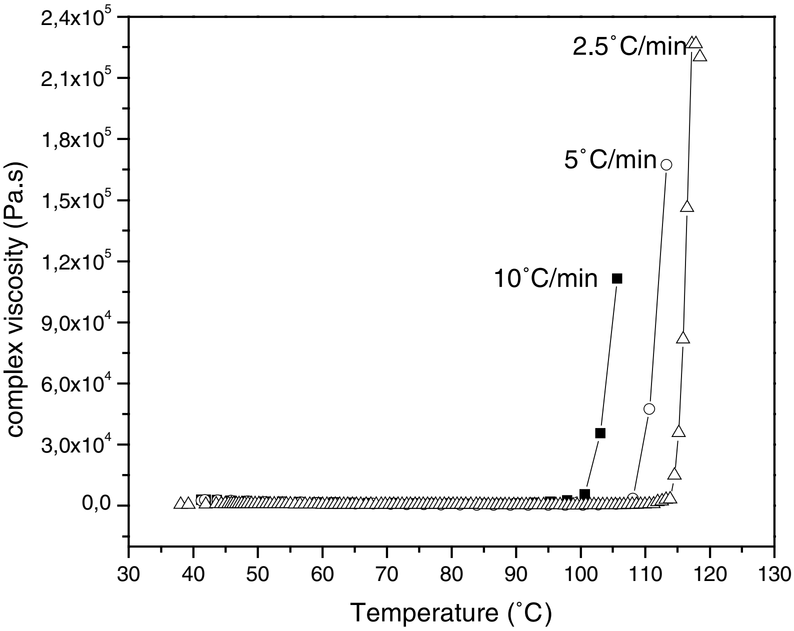

Figure 1 Variation of complex viscosity with the increase of temperature of *F161* prepreg.

of G' with G''. Table I presents also the rheological results for the prepreg material obtained with *F161* epoxy system. Similar to the complex viscosity analyses, it was observed that the gel temperature value, obtained by the crossing of G' and G'', showed that the temperature decreases with the increase of the heating rate. Therefore, the gel temperature obtained by complex viscosity was lower compared to the one obtained by the crossing of loss and storage moduli.

However, it is very important to apply the pressure in the autoclave curing cycle below of the gel temperature, in order to allow a good wetability of fibers. The appropriate temperature can be determined by the study of isothermal rheological curves.

Fig. 3 illustrates the isothermal rheological curves of *F161* epoxy system obtained at 100°C. The gel time values were obtained in the same way that the gel temperature (by the crossing of G' and G'' in Fig. 2 and by the increase of the complex viscosity in Fig. 3).

The gel time of the *F161* epoxy system at 110 and 120°C are 85 and 40 seconds, respectively. The rheological results show an increase of the complex viscosity due to the increase of the density of crosslinked bonds of the resin system (Fig. 3). Therefore, the gel time value of epoxy system analyzed at 100°C was longer than the values found of 110 and 120°C, being 135 s. The rheological analysis of the *F161* epoxy system shows that this resin treated at 110°C and 120°C presented a faster polymerization reaction than the sample treated at 100°C, increasing the crosslinked bonds in a shorter time. Consequently, at 110 and 120°C, the voids and/or porosity probably increases more due to the trapping of the larger quantity of volatiles in the polymerized material.

One more important observation is that using a heating rate of 2.5 K· min^{-1} the adequate temperature to apply pressure in the autoclave curing cycle is around 100°C. In this point the resin system reach the gel time in a shorter time, that in its turn it can permit to a good wetability of fibers and the appropriate polymerization kinetics as it has been supported by DSC results.

3.2. DSC analyses

To calculate the total heat of reaction belonging to the full conversion, ΔH_0, the DSC dynamic scans at different heating rates were performed. Repeated experiments were done for each heating rates. The overall heat evolved in the reaction has been determined as the average value of reaction heats calculated from each thermogram. The corresponding value for the *F161* system was

TABLE I Complex viscosity parameters of *F161* epoxy prepreg

	Complex viscosity parameters			Modulus parameters	
Heating rate (K· min^{-1})	η_{minima} (Pa.s)	$T_{\eta\ \text{minima}}$ (°C)	T_{gel} (°C)	$G' = G''$(Pa)	T_{gel} (°C)
2.5	58	58	114	63972	116
5.0	241	60	107	53650	111
10	319	70	99	45467	103

$\Delta H_0 = 49.4\ \mathrm{J}\cdot\mathrm{g}^{-1}$. This value was smaller than which was obtained for neat resin system [2]. The glass transition, *Tg*, for the completely cured material was 116.5°C.

Isothermal DSC curves are shown in Fig. 4. Because of the small sample masses and the relatively low reaction rates, with regard to the course of the reaction the effect of the sample temperature variation was not taken into account. Fig. 4 shows the DSC curves of a typical isothermal epoxy/amine curing which highlights the rapid increase in the rate of reaction, followed by an exponential increase of the reaction rate and the eventual cessation of reaction. The peak area of the exothermic regions at different times were used to determine the fractional conversion of the epoxy resin assuming that the evolved heat during curing is directly related to the disappearance of epoxide groups.

The value of the extent of curing, α, is usually obtained by dividing the heat ΔH_t evolved at time t by total the heat ΔH_0 generated during the whole reaction (see Equation 1):

$$\alpha = \frac{\Delta H_t}{\Delta H_0}. \tag{1}$$

In graphical terms, ΔH_0 is proportional to the peak area above the dynamic DSC curve. Analytical representation

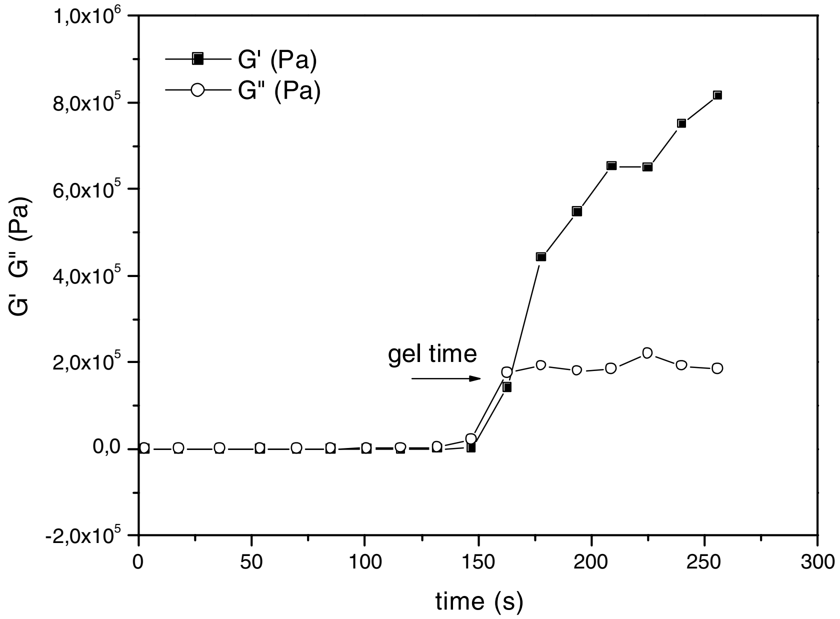

Figure 2 Isothermal rheogram of a *F161* epoxy system 100°C.

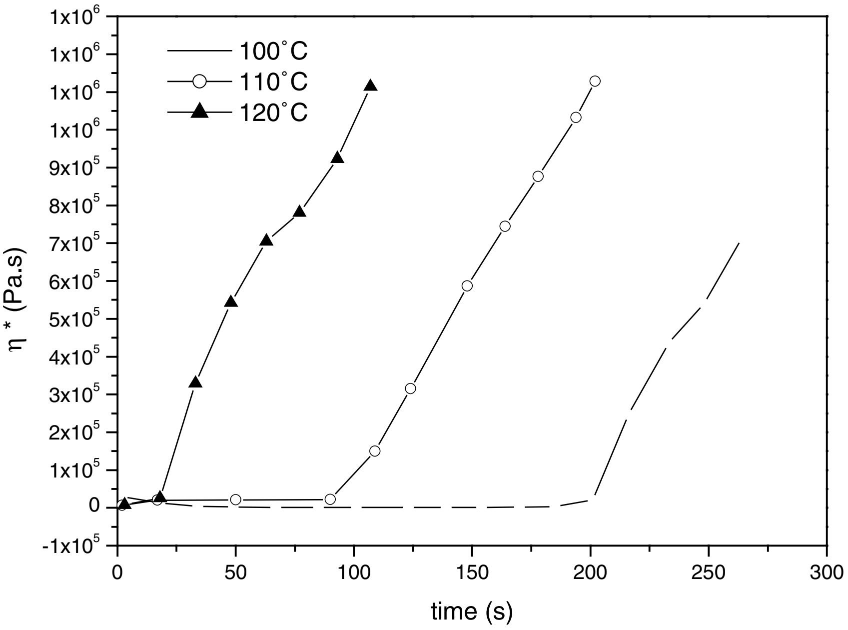

Figure 3 Increase of viscosity in isothermal conditions of *F161* epoxy system.

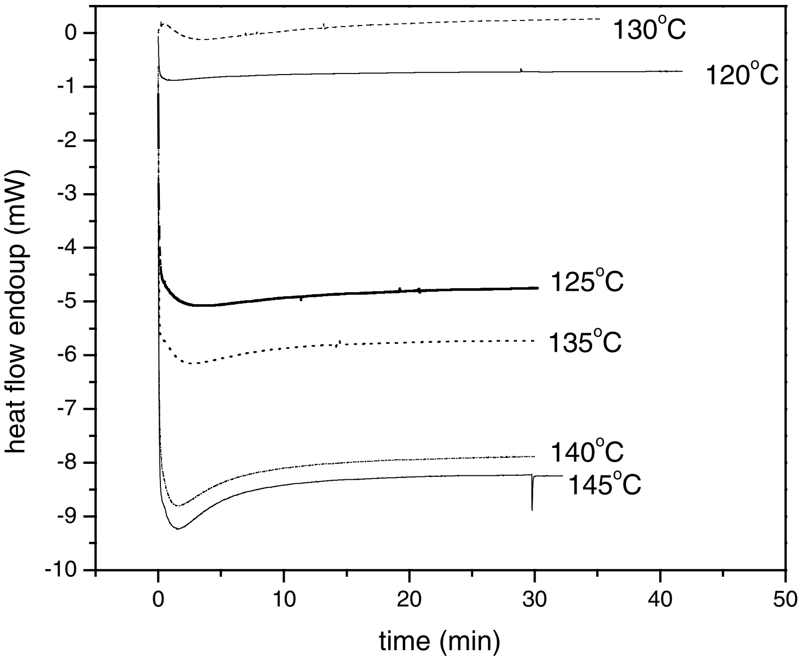

Figure 4 Heat flow measured by DSC during cure at different isothermals for *F161* system.

of such a curing process is often studied through existing models such as *n*th order and *autocatalytic* models. These are:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n, \quad \text{for } n\text{th order} \tag{2a}$$

$$\frac{d\alpha}{dt} = k(1-\alpha)^m \alpha^n, \quad \text{for } \textit{autocatalytic} \text{ reaction} \tag{2b}$$

where: α is the degree of chemical conversion, n and m are the orders of the reaction, k is the reaction rate and $d\alpha/dt$ is the derivative α with respect to time. Since the autocatalytic model is more flexible to fit various kinetic data, it is used to describe the cure kinetics of *F161* system prepreg used for this study.

The $d\alpha/dt$ parameters are obtained from the dH/dT ratio (reaction heat), at a time t, from the total enthalpy, ΔH (Equation 3).

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H}, \tag{3}$$

where ΔH is the experimental enthalpy corresponding to the total area of the peak representative to the reaction or from the theoretical enthalpy found in the literature.

The temperature dependent reaction rate k is commonly described by the Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right), \tag{4}$$

where R is universal gas constant, T is temperature, E is activation energy and A is pre-exponential factor.

Kinetics parameters in the kinetic analysis were obtained following conventional methodology, i.e., m, n and k were calculated at different temperatures (120–145°C) by means of multilinear regression of the kinetic Equation 5. Equation 4 was used to determine the activation energy (E) and the pre-exponential factor (A). The kinetics parameters concerned to the curing of carbon fabric/epoxy *F161* prepreg were shown in the Table II.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k + n\ln(1-\alpha) + m\ln\alpha, \tag{5}$$

The enthalpy and the sum of the reaction order increase with the increase the temperature of the isotherms. The enthalpy and the order of reaction are in relationship with the curve area obtained by DSC, which in turn it is directly involved with disappeared of epoxy groups during the cure.

The sum of exponent factors ($m + n$) is constant between 1.2–1.9, slightly higher than the order found by *n*th order model and dynamic method, which was in the range of 1.1–1.5. The heats of a dynamic reaction, ΔH, varies in the range of 45.6–52.7 J· g^{-1} with a mean value of 49.4 J· g^{-1} of the carbon/epoxy *F161* prepreg. The values of the heats of reaction using the autocatalytic model and isothermal method vary between 44.9–46.6 J· g^{-1}. The average of activation energy, E_a, of *F161* system was 96.2 kJ· mol^{-1}.

The values obtained for the pre-exponential constant (~ 9 s^{-1}) and for the activation energy are inside the ones described in the literature for the reactions between the epoxy groups and aromatic amines (50–100 kJ· mol^{-1}) [1–6, 21].

The majority of the final properties of a composite are obtained during the cure of the matrix material of the composite. During the curing cycle, chemical reactions

TABLE II Kinetics parameters obtained by isothermal method of carbon/epoxy resin (*F161)* prepreg

Isotherms (°C)	n^*	m^*	$-\Delta H$ (J· g^{-1})	ln A (s^{-1})	E (kJ· mol^{-1})	Tg (°C)
120	0.87	0.30	46.1	8.4 ± 0.1	96.5	115.4
125	0.67	0.68	45.4	8.6 ± 0.1	96.4	115.8
130	0.62	0.75	45.1	8.4 ± 0.1	96.3	115.9
135	0.78	0.98	44.9	8.7 ± 0.1	96.0	116.1
140	0.98	0.74	45.7	8.6 ± 0.1	96.5	116.2
145	1.3	0.57	46.6	10.1 ± 0.1	95.8	116.4

**n* and *m* are the orders of the reaction.

occur, which cause a polimerization of the matrix material (resin) to obtain the desired properties of the material. The curing of the resin can be considered the most important phase of the process of manufacturing. Before curing, a considerable investigation has been made into a composite component. If the matrix is not properly cured, the outcome of the curing is irreversible and that portion is usually scrapped. No amount of work before cure can ensure that an incorrectly cured part will be usable. It seems that the most critical step to obtain good composites is the cure cycle.

To monitor curing, mathematical models are used to predict the current state of resin system. The resin state prediction is related to the resin degree of cure α_c of the resin and can be modeled before, during, and after the curing process. The degree of curing of the resin indicates the progress of the reaction of the resin at a given temperature and time conditions. The success of any model-based composite cure control system depends on the accuracy of prediction of the degree of curing at any time.

Cure modeling involves the study of cure reaction kinetics, physical property correlation, and cure variable analysis. Several rate equations have been used to describe the extent of reaction, reation rate and reaction order for various thermoset systems [1–6, 21–25]. Teorical expressions and ghraphical possibilities are available to predict the behavior of the epoxy matrix as a function of the curing temperature, time or degree of curing and they will be discussed in the followings.

Four steps process for curing cycle is suggested by the prepreg supplier. Firstly, the temperature is raised from 30 to 116°C at 2.5 K· min^{-1}; holding at 116°C for 60 min (second step). In the third step the temperature will be raised up to 177°C using the same heating rate and holding at this temperature for at least 120 min (fourth step). Based on this information, a mathematical simulation of the degree of conversion of the *F161*-epoxy resin was carried out and represented in Fig. 5. This simulation is based on the rearrangement of the Equations 2a and 4, as follow:

$$\ln\frac{\partial\alpha}{\partial t} = \ln A - E_a/RT + n\ln(1-\alpha) \qquad (6)$$

$$\int \frac{1}{(1-\alpha)^n}\partial\alpha = \int A\cdot e^{-E_a/RT}\partial t \qquad (7)$$

If $\alpha = 0$, $t = 0$ and the integration constant is 0.

If $\alpha \neq 0$ so.

$$-\frac{(1-\alpha)^{(1-n)}}{(1-n)} + C_1 = A\cdot e^{-E_a/RT}\cdot t + C_2 \qquad (8)$$

or

$$-\frac{(1-\alpha)^{(1-n)}}{(1-n)} + C_3 = A\cdot e^{-E_a/RT}\cdot t \qquad (9)$$

where C_1 and C_2 are integration constants, and C_3 is the solution of C_1 and C_2

$$t(\alpha) = (A\cdot e^{-E_a/RT})\left[-\frac{(1-\alpha)^{(1-n)}}{(1-n)} + C_3\right] \qquad (10)$$

Considering $\alpha = 0$ and $t = 0$:

$$C_3 = \frac{1}{(1-n)} \qquad (11)$$

Rearranging Equations 10 and 11, are obtained the Equation 12 and 13:

$$t = \frac{1-(1-\alpha)^{(1-n)}}{A(1-n)\exp(-E_a/RT)} \qquad (12)$$

$$\alpha = 1-\left[1-(1-n)A\cdot t\exp(-E_a/RT)\right]^{(1/(1-n))}. \qquad (13)$$

Equation 13 was used in the predetermined time and temperature range [24 , 25] to obtain the Fig. 5 which presents the two simulation of the prepreg system conversion degree as function of temperature. First, for a time interval of 238.4 min; because it is the time necessary to elevate the temperature from 30 to 177°C, using 2.5 K· min^{-1} the heating rate as suggested by supplier. The second curve was represented by the time interval of 238.8 min that is the time necessary to increase the temperature from 30°C to 177°C, using a new temperature, 100°C, during the cycle of cure. The temperature of 100°C was chosen based on the rheological curves. In this temperature the gel time is more controlled than another temperatures studied in the present work (110 and 120°C).

Fig. 5 shows the degree of conversion of the carbon/*F161*-epoxy prepreg as a function of temperature during a simulation of the curing process carried out in the autoclave. Fig. 5 resumes all steps described previous,

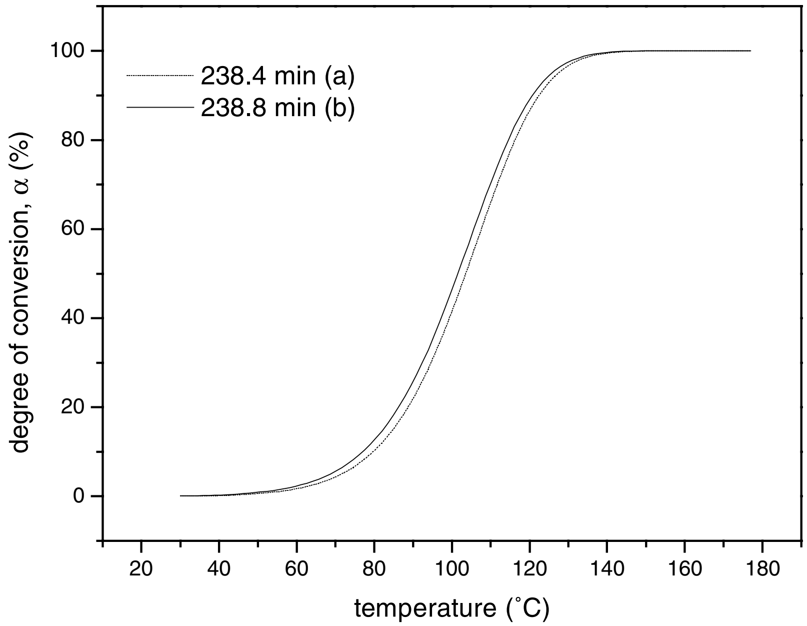

Figure 5 Total degree of conversion for the carbon/epoxy *F161* prepreg as function of autoclave cure temperature: 2 (a) suggested of supplier, (b) 100°C as step.

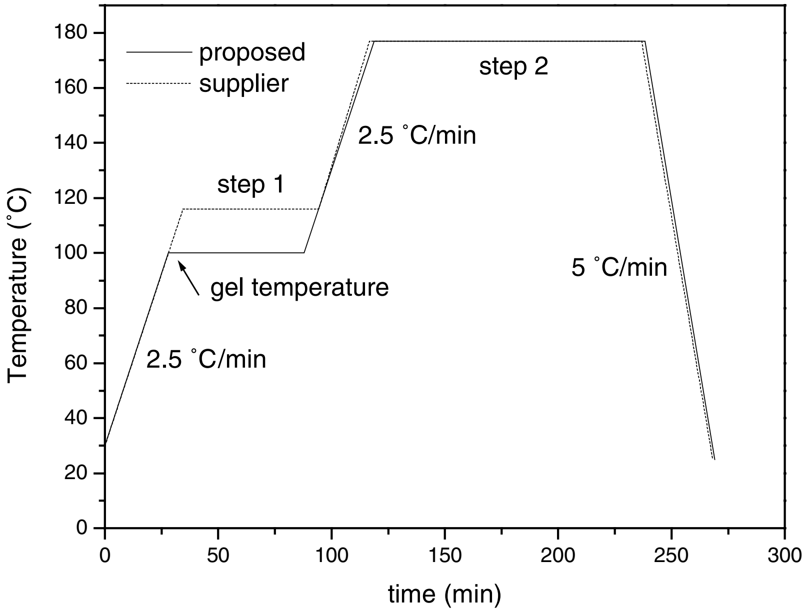

Figure 6 Cycle of cure of *F161* epoxy system.

showing the evolution of polimerization reaction in all curing cycle employed in the autoclave polymeric composites processing. In both cycle of curing a high degree of conversion, about 100% was observed. Each element of the theoretical model-resin degree of curing relates to the processing to one or all these goals to produce a good laminate.

The cure modeling environment appears to be capable of fully utilizing the power of the computer to accurately trace and monitor raw materials, from entry into the processing facility through cure, and to use this resin condition data to predict the cure requirements interactively during the curing cycle.

3.3. Curing cycle

Considering that the autoclave processing involves several steps, such as reinforcement and resin choice, vacuum/pressure cycles, etc the heating system must consider the gel temperature, heating rate and the initial and final temperature of polymerization. The carbon fiber/epoxy composite processing steps can be executed with safety and reliability. Using the DSC and rheological information together, is it possible to establish the appropriate cure cycle of carbon fiber/epoxy *F161* resin system in order to produce a composite material with an appropriate quality to be used as airplane structural part. Fig. 6 present two cure cycles: one obtained to the results of this work and the other suggested by the prepregs supplier.

The benefit of this study directly related to the aerospace area where the cure cycle can be detrimental to prejudice the use of this material in airplane applications.

4. Conclusion

In this work it was shown that differential scanning calorimetry (DSC) and rheology analysis are important tools to follow and delineate the curing behavior of the carbon fiber/*F161* epoxy resin system and to establish the curing cycle optimization in order to produce composite material with the requested quality to use in structural components. In this case the appropriate parameters were: 2.5 $\text{K} \cdot \text{min}^{-1}$ heating rate; the adequate temperature to apply the pressure in the autoclave curing cycle is around 100°C (for 1 h); and the final polymerization temperature is 177°C (for 2 h).

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