HEATING RATE LIMITS IN FAST CURE PROCESSING OF THICK CARBON FIBRE LAMINATES

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Abstract
The demand for fast processing of advanced composite aero-structures is driven by their potential high-volume application. The work presented here focuses on the effects of accelerating the autoclave cure processing of highly toughened epoxy matrix prepreg thick laminates based on a thermo-chemical simulation. This necessitates development of cure kinetics models adapted to characterise the resin behaviour under faster processing conditions. The effects of cure acceleration on possible temperature overshoot and feasibility of enthalpy reduction are assessed through the application of a 1-D energy balance equation, incorporating heat conduction and heat generation due to the exothermic reaction. The model allows to design thermal profiles which guarantee homogeneity of the cure and uniformity of temperature distribution limiting any risk of exotherm. This simulation becomes the main tool for addressing the intensification of the process, which is carried out in two different ways: (i) through cure profile optimisation in which cure duration is minimised subject to an overshoot constraint; and (ii) through reformulation of the matrix resin to allow distributed heat generation and more effective heat dissipation to minimise overshoot.

1. Introduction

The challenge to produce critical structural components in carbon reinforced epoxy materials, which comply with tight performance requirements and production costs reduction, is a lively debate in the aeronautical industry. Typically led by low volume production rate, this industry is extremely conservative and historically bound to autoclave manufacturing process to produce composite parts.
The projected increase in volume production of next generation single aisle aircraft (which represents the largest profit in todays' aircraft market [1 - 3]) triggers a development of technological solutions to accommodate the market demand of a higher production speed. Innovative manufacturing processes competitive to autoclave technology such as the Heat Transfer Fluid [4 - 6] or the Cage System [7] comply with rapid processing conditions but porosity and compaction issues still need to be addressed. In addition, the management of the enthalpy involved in the reaction is still one major concern to avoid exothermic risk in fast cure cycles and achieve both high conversion degree and high glass

transition temperature [8]. This justifies the use of autoclave processing which ensures higher uniformity of temperature and compaction. However, autoclave process intensification is associated to an increase of temperature rate and/or cure temperature and/or dwell time reduction with a potential risk of exotherm and inhomogeneity of conversion [9 - 12].
This paper evaluates the cure of carbon reinforced epoxy thick composite components and the impact of accelerating the autoclave curing process. The development of a simulation approach facilitates the design of optimised thermal profiles to guarantee aeronautical grade quality of thick composite laminates.

2. Methodology

The autoclave heat transfer mechanism to cure composite prepreg laminates is a quite complex physical-chemical problem which involves heat conduction, heat convection and heat generation due to the exothermic reaction [13]. This paper focuses on the thermo-chemical analysis of the autoclave processing. The internal heat convection is usually not included due to the low resin flow rate and a Fourier anisotropic heat conduction approach can be implemented to study the problem. The 1-D heat transfer can be described as follows:

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left[K \frac{\partial T}{\partial z}\right] + \left(1 - v_f\right)\rho_r H_{tot} \frac{d\alpha}{dt} \tag{1}$$

where z represents the thickness direction coordinate and t the time; $\frac{d\alpha}{dt}$ is the reaction rate, α is the resin conversion degree and T the temperature; ρ is the laminate density, c_p is the specific heat capacity, K is the thermal conductivity coefficient; ρ_r is the resin density, v_f is the fibre volume fraction and H_{tot} is the total reaction enthalpy.
Boundary conditions include prescribed temperature on the tool side (set equal to the autoclave air temperature) and a global convective heat transfer on the bag side (which accounts for breathers, bleeders and part/air resistance). Adiabatic conditions are applied all around the laminate edges. The experimental characterisation of the heat transfer coefficient is still an open topic in the scientific community which is strongly dependent on autoclave geometry, pressure and temperature profiles and cell loads [14 - 16].
The laminate temperature distribution can be determined by solving Eq. (1) numerically via application of the weighted residual approach. This equation was implemented in a Microsoft Excel spreadsheet making use of standard functions taking into account laminate thickness, model parameters, cure cycle profile, thermal and chemical properties and boundary conditions to demonstrate that cure simulation can be carried out with accessible and easy to use tools. The laminate thickness was discretised into 100 elements and the time step was set to 60 seconds. The output of this analysis is the temperature and degree of cure distribution and their evolution with time. This is then used to compute a maximum temperature overshoot and cure cycle time. The cure time is defined as the time required for the minimum degree of cure in all plies to reach a pre-specified arbitrary limit. Minimum degree of conversion is set to 80 % as reached in a simulated Manufacturing Recommended Cure Cycle (MRCC) profile and the maximum allowed temperature overshoot is 15 °C.
The flexibility of the model and versatility of its application to design and optimise composites manufacturing processing is demonstrated on a HexPly® 8552/AS4 unidirectional epoxy prepreg laminate. The MRCC for this material suggests to apply an initial ramp of 2 °C/min up to 110 °C for 1 hour dwell, followed by a second ramp at 2 °C/min up to 180 °C for 2 hours dwell [17]. The relevant physical properties of the material are listed in Table 1. Thicknesses of interest for this material range between 2 and 50 mm, including both typical fuselage/wing skins dimensions and local features.

Table 1. HexPly® 8552/AS4 main physical properties [17 - 19].

Prepreg property	Value
Fibre density (kg/m^3)	1790
Resin density (kg/m^3)	1300
Specific heat capacity (J/kg K)	1289
Longitudinal fibre thermal conductivity (W/m K)	10.5
Transversal fibre thermal conductivity (W/m K)	3.1
Resin thermal conductivity (W/m K)	0.26
Transversal prepreg thermal conductivity (W/m K)	1.17
Fibre volume fraction (%)	57.3
Fibre Areal Weight (FAW) (g/m^2)	134
Cured Ply Thickness (CPT) (mm)	0.130
Glass transition temperature in the fully cured state (dry) (°C)	200

The following cure kinetics model [18] is applied to simulate the reaction kinetics behaviour of the HexPly® 8552 epoxy matrix system. This model considers both the autocatalytic and diffusion phases of the reaction as expressed by:

$$\frac{d\alpha}{dt} = \frac{A \cdot e^{-\frac{E}{RT}} \cdot \alpha^m \cdot (1-\alpha)^n}{1 + e^{C[\alpha - (\alpha_{C0} + \alpha_{CT} T)]}} \quad (2)$$

Here A is the pre-exponential factor, E the activation energy, m and n reaction orders, C a parameter controlling the breath of the transition of the reaction from chemical to diffusion control, α_{C0} and α_{CT} the intercept and slope of the critical degree of cure dependence on absolute temperature. The values of these parameters are reported in Table 2.

Table 2. Cure kinetics parameters for HexPly® 8552 epoxy matrix system [18].

Parameter	Value
A (1/s)	152800
E (J/mol)	66500
m	0.81
n	2.74
C	43.1
α_{C0}	-1.68
α_{CT} (1/K)	$5.47 \cdot 10^{-3}$

In addition to significant processing time reduction, the thermal cure profile must also guarantee cure homogeneity with no thermal spikes, which could degrade the material performance and potentially cause uncontrolled exothermic reaction. Adjusting the heating rate and dwell temperature is a potential way to address these objectives. The dependence of temperature overshoot and cure time on these parameters for a single dwell and a two dwell cure profile is investigated in this work.

3. Results and discussion

3.1 Single dwell cure profile

To identify cure cycles faster than the MRCC, first dwell at 110 °C can be removed, heating up directly to the final cure temperature. In this investigation heat up ramp rate was varied from 1 to 10 °C/min with a heat up rate increment of 1 °C/min, while cure temperature was varied between 180 and 200 °C with a temperature increment of 2 °C. Resulting cure times and temperature overshoots were assessed for shortest cure cycles with allowable temperature spikes.
Overshoot appears to be minor (less than 0.5 ºC) in a 2 mm thick laminate. This allows a reduction in cure time of about 75 % achieved at the highest ramp rate of 10 °C/min and at the highest temperature of 200 °C. These conditions also result in a uniform conversion degree for this thickness. Overshoots are significant (up to 80 °C) in a 50 mm thick laminate under all conditions. Therefore, a 50 mm thick laminate cannot be cured using a single dwell profile. A complete cure can be achieved in a 5 mm thick laminate within 48 minutes with minimal conversion variation through the thickness. In the 15 - 20 mm thick range some selected conditions prevent the excessive exotherm risk. A 42 % time reduction versus MRCC in the 15 mm thick laminate drops down to 10 % in the 20 mm thick one. Up to 15 mm thickness, unacceptable overshoot is avoided at both 180 and 182 °C whichever the considered heat up ramp rates. Acceptable overshoot is achieved for the whole temperature range 180 – 200 °C when limiting the heat up rate to 1 and 2 °C/min. In the 20 mm thickness, only the 1 °C/min heating up rate gives acceptable overshoot (although longer times are required) on the whole range of the considered temperatures. Table 3 reports the minimum cure times and associated acceptable overshoots for the investigated cases compared to those resulting from a simulated MRCC for the same thicknesses. The results highlight that a single dwell can be applied up to 20 mm without overcoming the overshoot limit, while it is not applicable to the 50 mm case as the overshoot reaches 80 °C. It should be noted that the MRCC also fails to meet the constraint at this thickness.

Table 3. Minimum cure time and corresponding overshoot in a single dwell curing process compared to a simulated MRCC at same thicknesses.

Thickness (mm)	**2**	**5**	**15**	**20**	**50**
Heat up ramp (°C/min)	10	10	10	1	10
Cure temperature (°C)	200	200	182	200	200
Cure time (min)	48	48	85	183	51
Temperature overshoot (°C)	0.5	3.1	15.0	8.3	80.1
Simulated MRCC cure time (min)	204	204	204	204	204
Simulated MRCC temperature overshoot (°C)	0.2	1.2	9.9	17.1	61.8

3.2 Two dwell cure profile

Particularly for thick sections, it is potentially beneficial to introduce a first dwell at a lower temperature. This allows to reduce thermal lag within the laminate, to increase temperature uniformity and makes curing start at a slower rate to avoid excessive overshoots. This justifies the manufacturer's recommendation for a two dwell cure profile [17]. The impact of first dwell temperature (T_1) and curing temperature (T_2) variations are assessed to achieve a cure time reduction. T_1 varies between 110 and 130 °C, while T_2 varies between 180 and 200 °C. A temperature increment of 2 °C is considered for both dwell phases.

Overshoots are negligible in a 2 mm thick laminate. The value of T_1 has a weaker effect than T_2 on cure time. The maximum cure time reduction versus MRCC is about 18 %. This general pattern can be also observed with thicker laminates up to 20 mm. Overshoots increase with thickness for all tested conditions but remain within the 15 °C allowable limit. For the 20 mm thick laminate there are combinations which exceed the limit but this can be mitigated by increasing T_1. The application of the MRCC on a 20 mm thick laminate results in exceeding the overshoot limit by about 2 °C. In terms of cure time, increasing T_2 has a higher impact than T_1 with a maximum reduction around 18 %. The minimum cure time was 165 min, which represents an 18 % reduction compared to the MRCC. In the 50 mm thick laminate altering the temperature does not result in reducing the overshoot value below 15 °C. The overshoot ranges between 36 and 62 °C which is comparable to the MRCC overshoot that is around 62 °C. Even a further increase of T_1 to 140 °C does not have any beneficial effect, which opens the way to a three dwell cure profile. Table 4 reports the minimum cure time and corresponding acceptable overshoots for all investigated cases compared to the MRCC results.

Table 4. Minimum cure time and corresponding overshoot in a two dwell curing process compared to a simulated MRCC at same thicknesses.

Thickness (mm)	**2**	**5**	**15**	**20**	**50**
First dwell temperature (°C)	130	130	130	130	130
Cure temperature (°C)	200	200	200	200	200
Cure time (min)	165	165	165	165	165
Temperature overshoot (°C)	0.1	0.7	4.7	7.6	36.5
Simulated MRCC cure time (min)	204	204	204	204	203
Simulated MRCC temperature overshoot (°C)	0.2	1.2	9.9	17.1	61.8

A potential way to reduce overshoot in ultra-thick laminates is to increase the first dwell time to a value sufficient to allow consumption of resin reactivity before the higher temperature dwell. Figure 1 illustrates the dependence of overshoot on the duration of the first dwell for a 50 mm thick laminate. The overshoot decreases with increasing first dwell duration. This impact is more significant at higher T_1. For T_1 = 130 °C, T_2 = 200 °C and a ramp rate of 2 °C/min, it is possible to achieve acceptable overshoot in the cure of the ultra-thick laminate for a first dwell duration of around 115 minutes. In this case the total cure time is 215 minutes. At higher first dwell temperatures, overshoot levelling is achieved earlier.

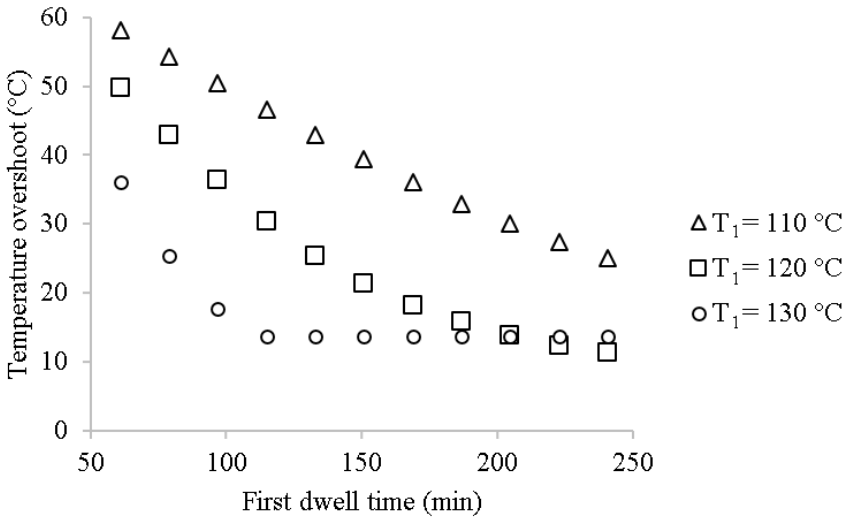

Figure 1. Influence of first dwell time/temperature on overshoot for a 50 mm thick laminate.

3.3 Matrix reformulation

A potential way of overcoming overshoot problems in ultra-thick laminates is through modifying the chemical formulation of the system. A hypothetical modification of the chemistry is investigated here assuming it is possible to vary the values of reaction enthalpy H which has an impact on heat generated during the reaction and the activation energy E which influences the kinetics of the reaction. It has been assumed that a reduction of 30 % on the current values is possible.

A few conditions of limited overshoot were observed for a single dwell profile with a ramp of 2 °C/min up to a cure temperature of 180 °C applied to a 50 mm thick laminate. Limited overshoots can be achieved moving between maximum 30 % reduction of enthalpy coupled to a 21 % reduction of the activation energy and minimum 9 % reduction of enthalpy coupled to a maximum 30 % reduction of activation energy. It is interesting to note that a 60 % time reduction is achievable with a single dwell profile compared to the MRCC. This evaluation has been carried out assuming an 80 % final degree of conversion which is reached after nearly 2 hours and 15 minutes. However, the fictitious matrix system achieves a maximum degree of conversion of nearly 90 % with a curing time of around 4 hours whilst maintaining a nearly uniform conversion distribution along the thickness. Figure 2 shows the conversion distribution at the time the whole laminate has reached 80 % degree of cure and at the end of the cure when the conversion degree is over 92 %. Dropping both activation energy and reaction enthalpy could have a combined effect on an earlier start of the reaction and a better control of heat distribution. This permits a relatively longer duration of the chemically controlled phase which allows the achievement of a higher conversion degree.

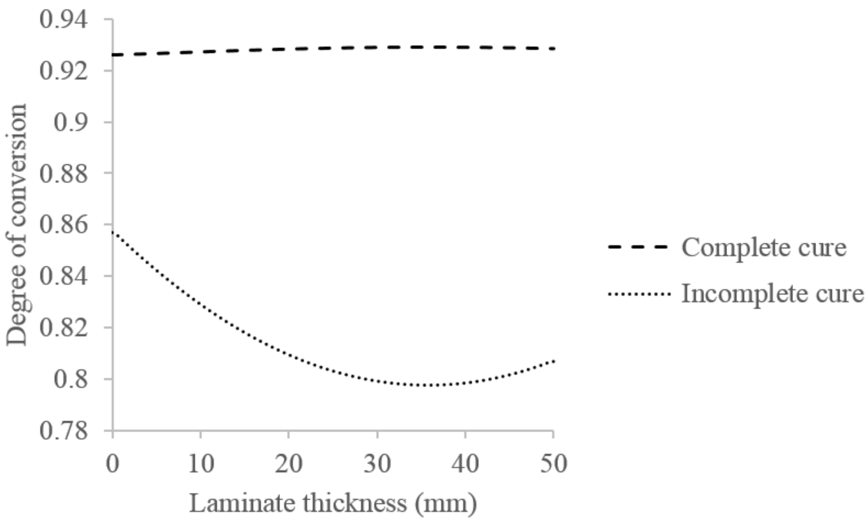

Figure 2. Comparison of degree of conversion distributions along a 50 mm thick laminate at different reaction progress levels.

4. Conclusions

The effect of variation of heating rates and dwell temperatures to comply with a rapid autoclave curing process of a HexPly® 8552/AS4 epoxy prepreg thick laminate has been assessed using a Microsoft Excel based simulation tool. The investigation focused on cure times and temperature overshoots. Compared to the MRCC the increase of heating rate certainly improves time reduction limiting at the same time the exotherm risk. This is more evident in a single dwell cure profile up to a 20 mm thickness. In a two dwell cure profile, the increase of the first dwell temperature mitigates a temperature runway later during the final dwell. For ultra-thick laminates either single or two dwell profiles do not meet the requirement of fast curing avoiding high overshoots (unless sufficiently increase of the first dwell temperature). A possible solution is the formulation of matrix systems characterised by lower enthalpy and activation energy levels. Increasing the heating up rate to satisfy the requirement of rapid processing conditions in aerospace is certainly viable on 15 mm thick laminates by applying very fast ramps of 10 °C/min with cure time around 85 minutes. Rapid curing of a 20 mm thick laminate in shorter times (around 180 minutes at a curing temperature of 200 °C) is possible only by increasing the cure temperature since heating ramps over 1 °C/min result in unacceptable overshoots. To safely cure a 50 mm thick laminate only multiple dwells or matrix reformulation can be taken in consideration. Constraint on time length of dwell application limits flexibility in cure profile optimisation.

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