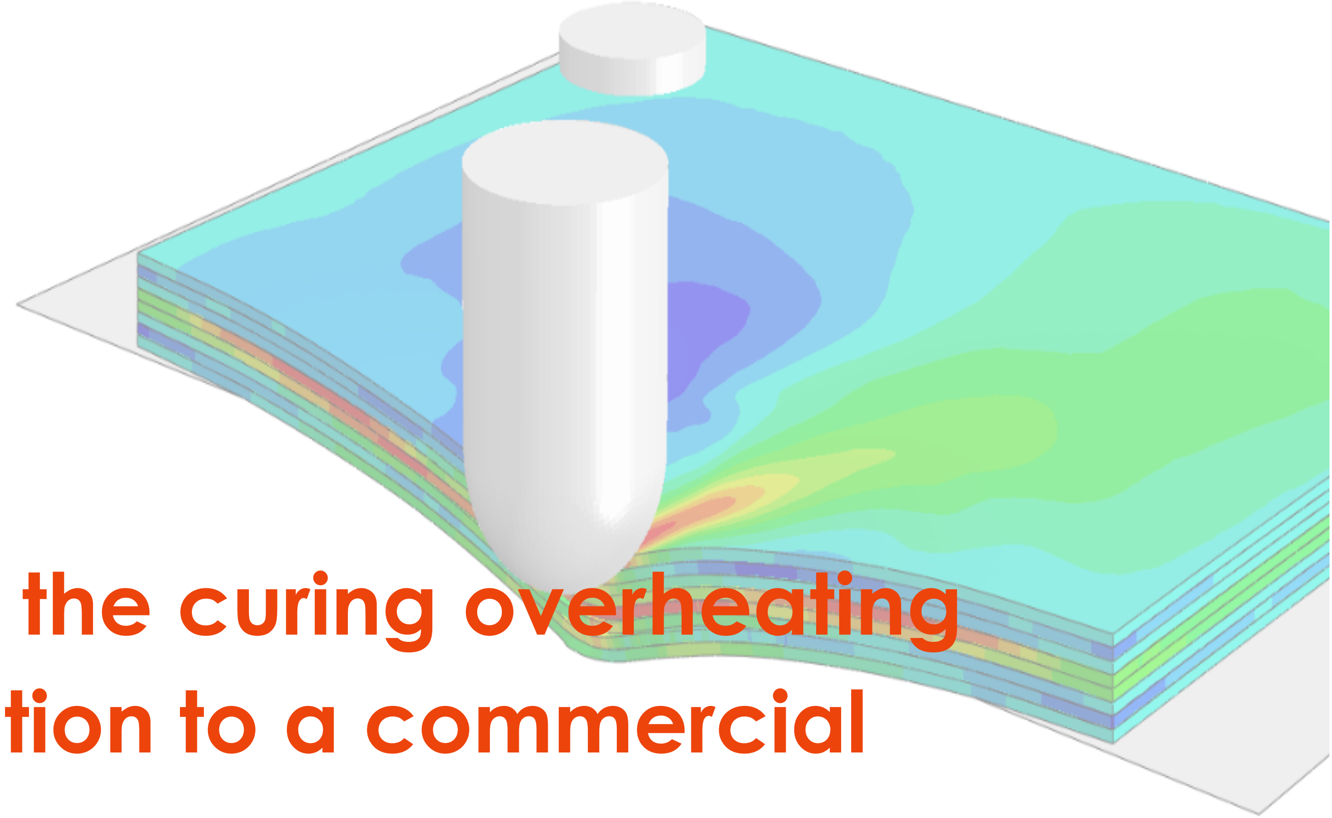

Analytical prediction of the curing overheating and overshoot. Application to a commercial prepreg.

Cârstea Didina Ramona Casandra

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Contents

1. Introduction

Why is it important to have occurrence in thermal runaway?

1. Overheating may result in delamination

local overheating → caused → inhomogeneous curing process → can lead → surface waviness, matrix degradation, and delamination.

2. Heat balance

when heat dissipation → cannot → compensate for heat generation → then → thermal runaway occurs.

3. Overheating is critical when dealing with thick laminates

the recommended curing cicle → doesn't take into account the sample geometry → so → it is not valid for thick sections → causing → undesirable effects such as overheating or thermal runaway

Many people have implemented a numerical model, but that is complex and computationally expensive to run.

An analytical model would simplify and speeds up the design of cure cycles.

2. The Numerical Model

Heat propagation:

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \rho q \frac{\partial \alpha}{\partial t}, \quad (1)$$

Reaction:

$$\frac{\partial \alpha}{\partial t} = A e^{\frac{-E_a}{RT}} (1 - \alpha), \quad (2)$$

Boundary conditions:

$$T(w) = T_m, \quad k \frac{\partial T}{\partial x}\Big|_{x=0} = h(T(0) - T_m), \quad (3)$$

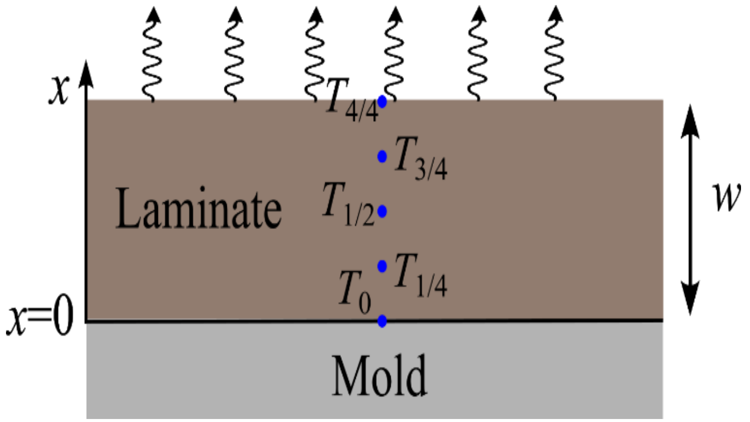


Figure 1. Schematic representation of the geometry of the model.

Table 1. Measured physical parameters used in the numerical simulations and analytical calculations.

Property	
Thermal conductivity out-of-plane at 40°C, k (W/m K)	
Specific heat capacity at 60°C, c (J/kg K)	
Apparent convective coefficient, h, (W/m^2 K)	
Density, ρ (kg/m^3)	
Specific heat of reaction, q (J/kg)	
Activation energy, E_a (J/mol)	
Pre-exponential constant, A (s^{-1})	
Overheating, ΔT_{Max}	
Thickness, *w*	
Mould temperature, T_m	

3. Dimensionless model

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\chi^2} + \theta_T\,\frac{\partial\alpha}{\partial\tau}, \qquad \frac{\partial\alpha}{\partial\tau} = \frac{1}{\theta_T}\, e^{\frac{\theta}{1+\varepsilon\theta}}(1-\alpha),$$

$$\theta\left(\sqrt{\delta}\right) = 0, \qquad \frac{\partial\theta}{\partial\chi}\Big|_{\chi=0} = \theta(0)\,\frac{Bi}{\sqrt{\delta}}, \qquad (4)$$

Five parameters:

$$\varepsilon \equiv \frac{RT_m}{E_a},\ \theta_T \equiv \frac{q}{c}\frac{E_a}{RT_m^2}, \delta \equiv \rho\,\frac{q}{k}\frac{E_a}{RT_m^2}\,w^2 A e^{-\frac{E_a}{RT_m}}, Bi \equiv h\,\frac{w}{k}, \theta_{Max} = \frac{\Delta T_{Max}}{\varepsilon T_m}.\ (5)$$

4. The Analytical Model

4.1 Critical thickness related to a given overheat, w_c.

The model for determining the thickness related to overheating involves determining the dependence of the critical FK parameter, δ_c, as a function of ε, θ_T, Bi and $\theta_{Max} = \frac{\Delta T_{Max}}{\varepsilon T_m}$.

we will first consider infinite Todes parameter and perfect upper insulation ($Bi = 0$).

then

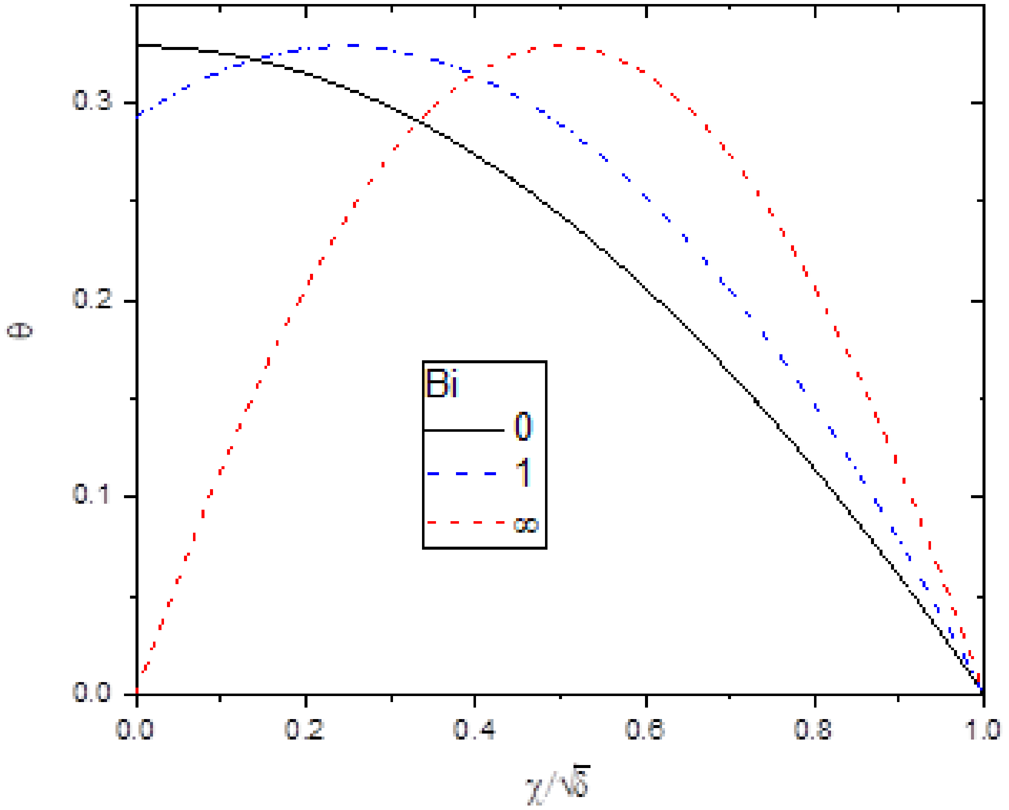
we will develop a second model that considers finite Todes values

finally

we will develop a general model that also takes into account convective heat losses.

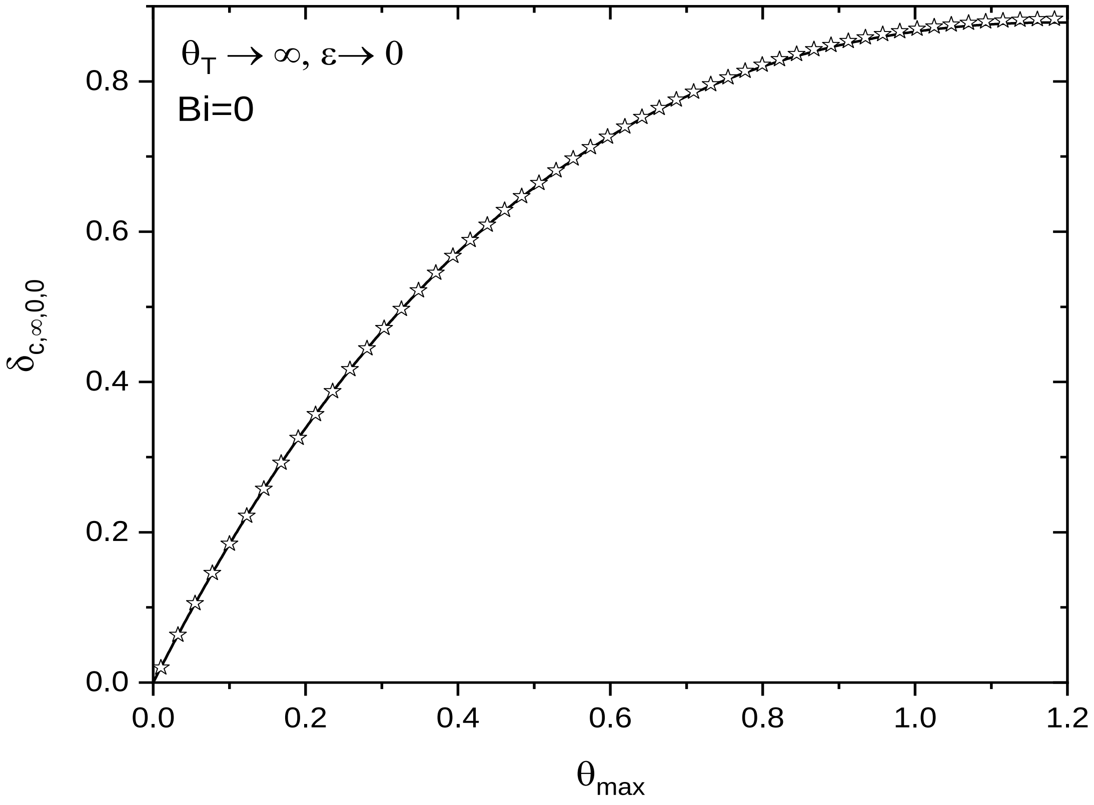
Case a) Highly exotermic reaction: $\theta_T \to \infty$, $\varepsilon\theta \ll 1$ and $Bi = 0$

The temperature profile for $\theta_{Max} = 0.329$ shows a steady increase in temperature from the thermal contact side to the insulated side.



$$\theta = 2ln\left[e^{\theta_{Max}/2}\, sech\left(\frac{e^{\theta_{Max}/2}}{\sqrt{2}}\chi\right)\right], \quad (6)$$

Figure 2. Stationary temperature profiles, Eq. (6), for different values of Biot parameter, $\theta_{Max} = 0.329$ and $\delta_{c,0} = 0.5$.



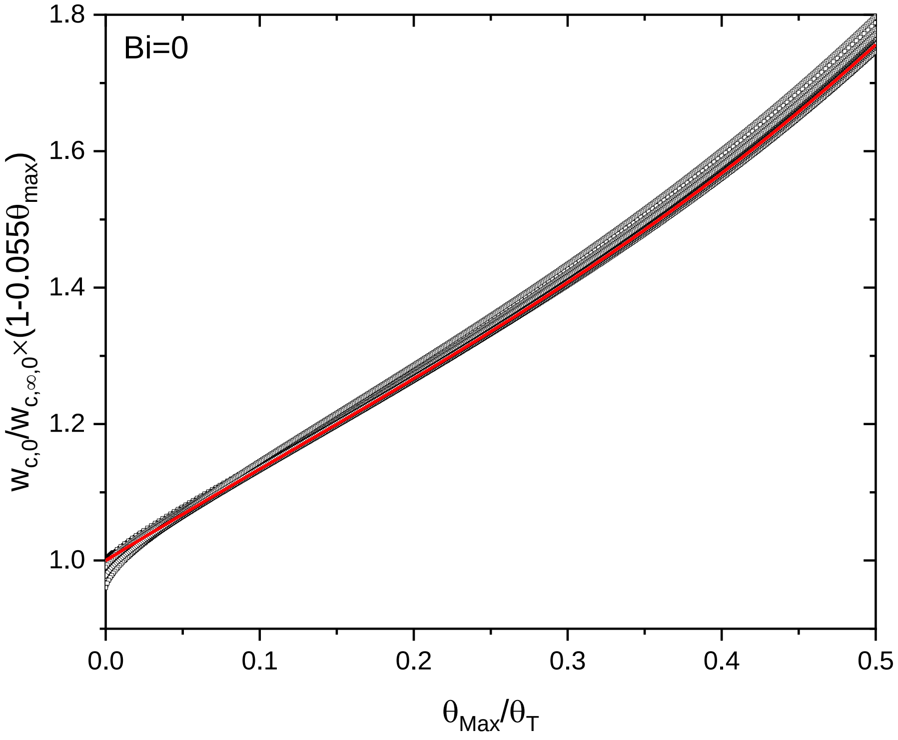
$$\delta_{c,\infty,0} = 2e^{-\theta_{Max}}\, arcosh^2\left(e^{\theta_{Max}/2}\right), (7)$$

Thus for a given overheating, θ_{Max}, we can determine from Eq. 7 the critical value $\delta_{c,\infty,0}$ and, finally, the critical thickness is determined from the definition of the FK parameter,

$$w_{c,\infty,0} = \sqrt{\delta_{c,\infty,0}\frac{k}{\rho q}\frac{RT_m^2}{A\,E_a}e^{\frac{E_a}{RT_m}}}, (8)$$

Figure 3. Critical value of the FK parameter as a function of the dimensionless overheating. Solid line theoretical prediction for $\theta_T \to \infty$ and $Bi = 0$, Eq. (7). Stars, numerical analysis for $\theta_T = 10^6$, $\varepsilon = 0.004$ and $Bi = 0$.

Case b) Moderate exothermal. *Finite values of* θ_T

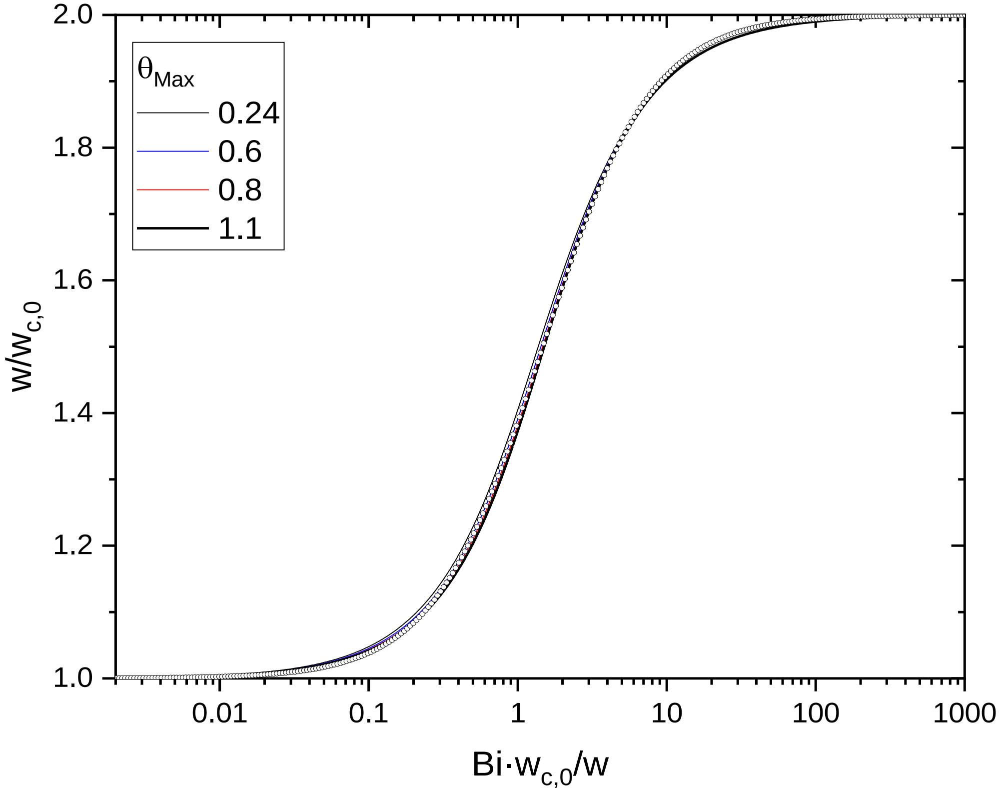


We have observed that the dispersion of the data is highly reduced. We have fitted the numerical data to a third-order polynomial, so the approximate dependence of the critical thickness on the system parameters for $Bi = 0$ is:

$$w_{c,0} = \frac{w_{c,\infty,0}}{1-0.055\theta_{Max}}\left[1 + 1.38\frac{\theta_{Max}}{\theta_T} - 0.57\left(\frac{\theta_{Max}}{\theta_T}\right)^2 + 1.67\left(\frac{\theta_{Max}}{\theta_T}\right)^3\right], (9)$$

Figure 4. Symbols: critical thickness determined from numerical simulations for different values of θ_T, θ_{Max} and ε: $0.02 \le \theta_T \le 10^6$, $0.01 \le \theta_{Max} \le 1.1$ and $0.01 \le \varepsilon \le 0.1$. Red line: non-linear fit, Eq. (9).

Case c) Final solution, $Bi \neq 0$



$$w_c = w_{c,0}\left[2 - \left(1 + 0.63\ \left[h\frac{w_{c,0}}{k}\right]^{1.2}\right)^{-1}\right], (10)$$

Figure 5. Lines: theoretical critical thickness as a function of the Bi number for different values of the temperature overheat, θ_{Max}. Symbols: fitted solution, Eq. (10).

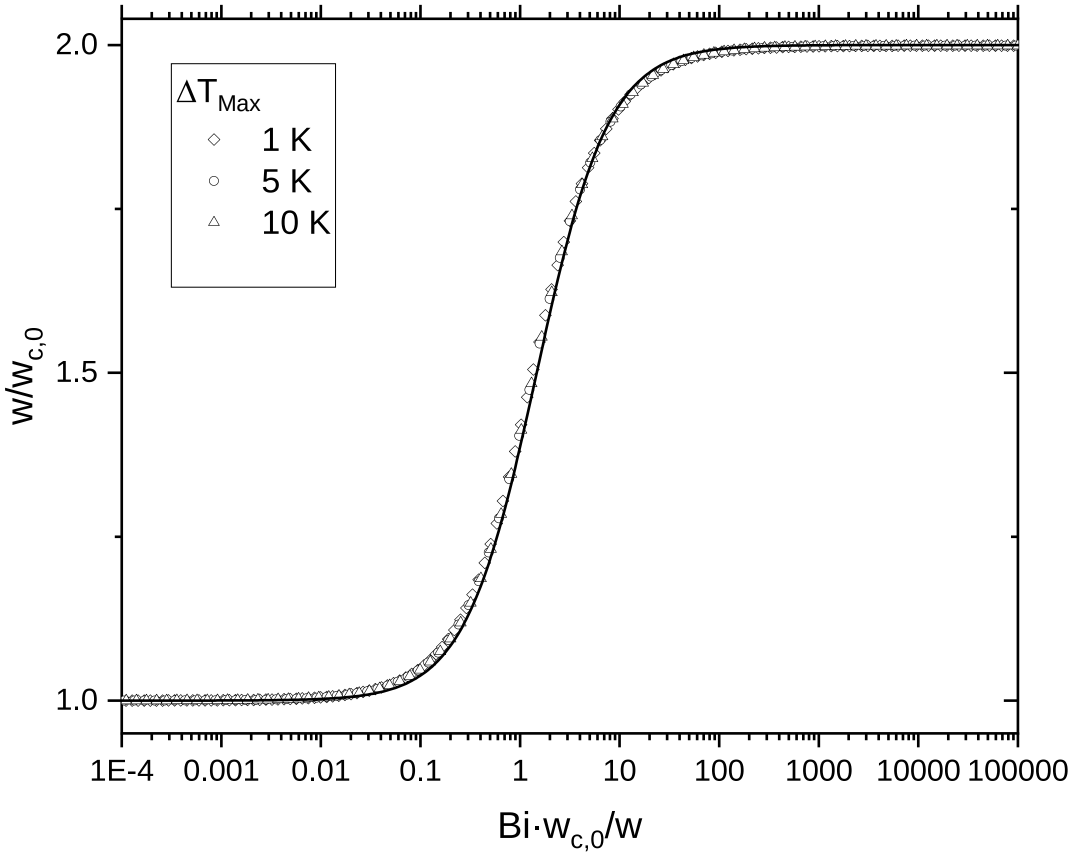


Figure 6. Symbols: critical thickness determined from numerical simulations and for three different temperature overheats. Line: analytical solution Eq. (10).

Measured physical parameters used in the numerical simulations and analytical calculations.

The thermal conductivity of the prepreg was measured with a homemade Poensgen apparatus.

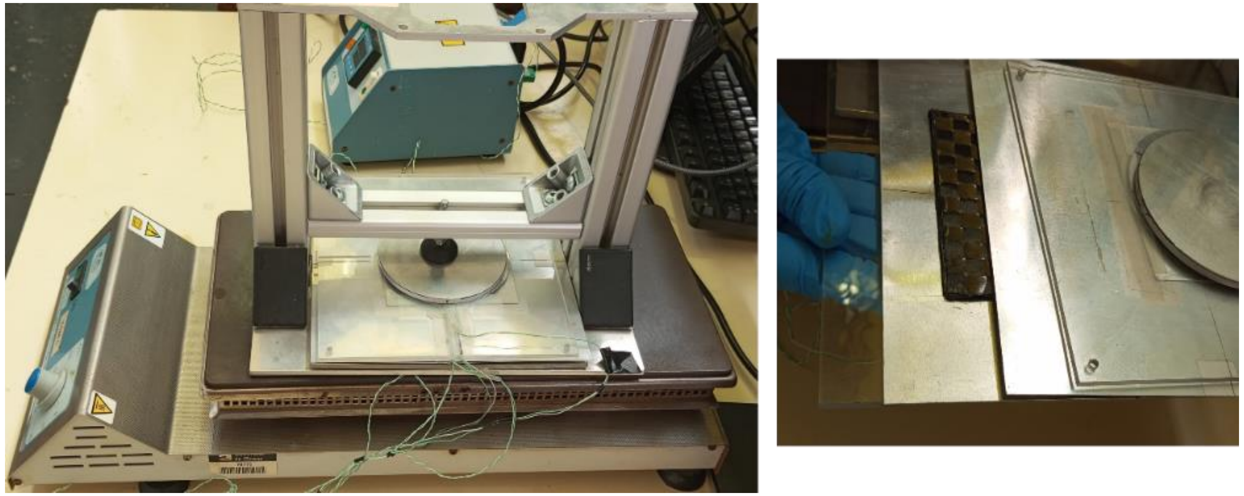


Figure 7. (a) Homemade Poensgen apparatus, the system is placed on top of a hot plate. (b) Sequence of plates placed on top of the lower aluminium plate from bottom to top: polymethyl methacrylate (PMMA) reference plate, aluminium plate, CFRP laminate, aluminium plate, PMMA reference plate and aluminium round plate.

$$k = 0.23\, W/m\, K$$

Determination of the specific heat of reaction and kinetic parameters

To determine the **specific heat of reaction** and **kinetic parameters**, five DSC measurements were performed at heating rates, $\beta \equiv \frac{dT}{dt}$, of 0.6, 1.25, 2.5, 5 and 10 K/min. From the integration of the DSC signal we determined the specific heat of reaction; the average value was:

Property	**Value**
Thermal conductivity out-of-plane at 40ºC, k (W/m K)	0.23
Specific heat capacity at 60ºC, c (J/kg K)	
Apparent convective coefficient, h, (W/m^2 K)	
Density, ρ (kg/m^3)	
Specific heat of reaction, q (J/kg)	1.60×10^5
Activation energy, E_a (J/mol)	
Pre-exponential constant, A (s^{-1})	
Overheating, ΔT_{Max}	
Thickness, w	
Mould temperature, T_m	

q= $\mathbf{1.60 \pm 0.05x10^5}$ **J/kg**

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The heat capacity experiments were carried out on a Mettler Toledo DSC822e.

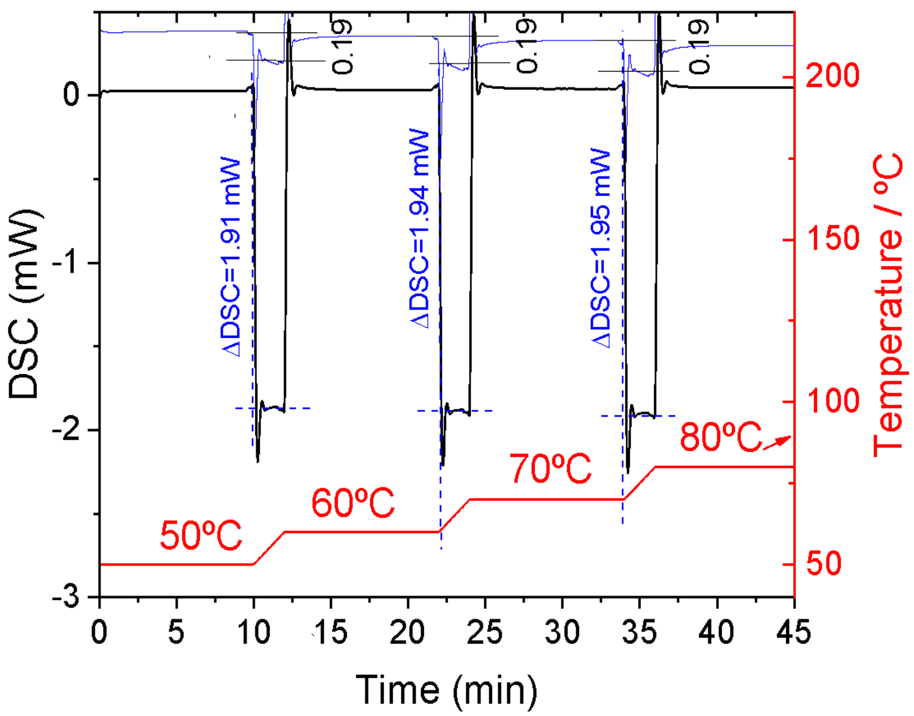


Figure 8. Temperature program and DSC measurement of the sapphire crystal used to determine the calibration of the heat capacity measurement.

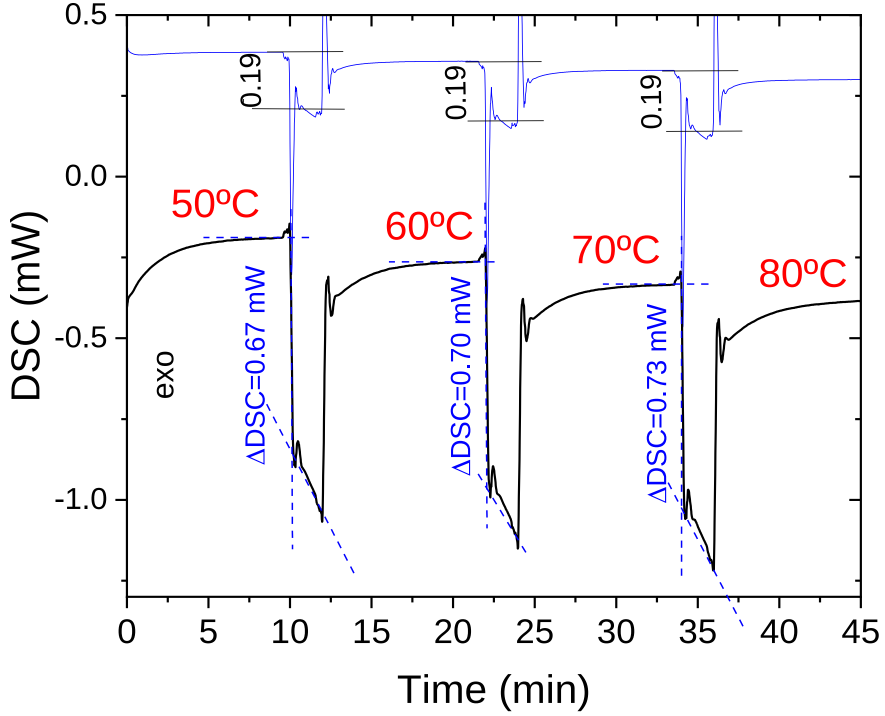


Figure 9. Temperature program and DSC measurement of a VTC401 prepreg of mass 3.177 mg used to determine its heat capacity.

Determination of the specific heat of reaction and kinetic parameters

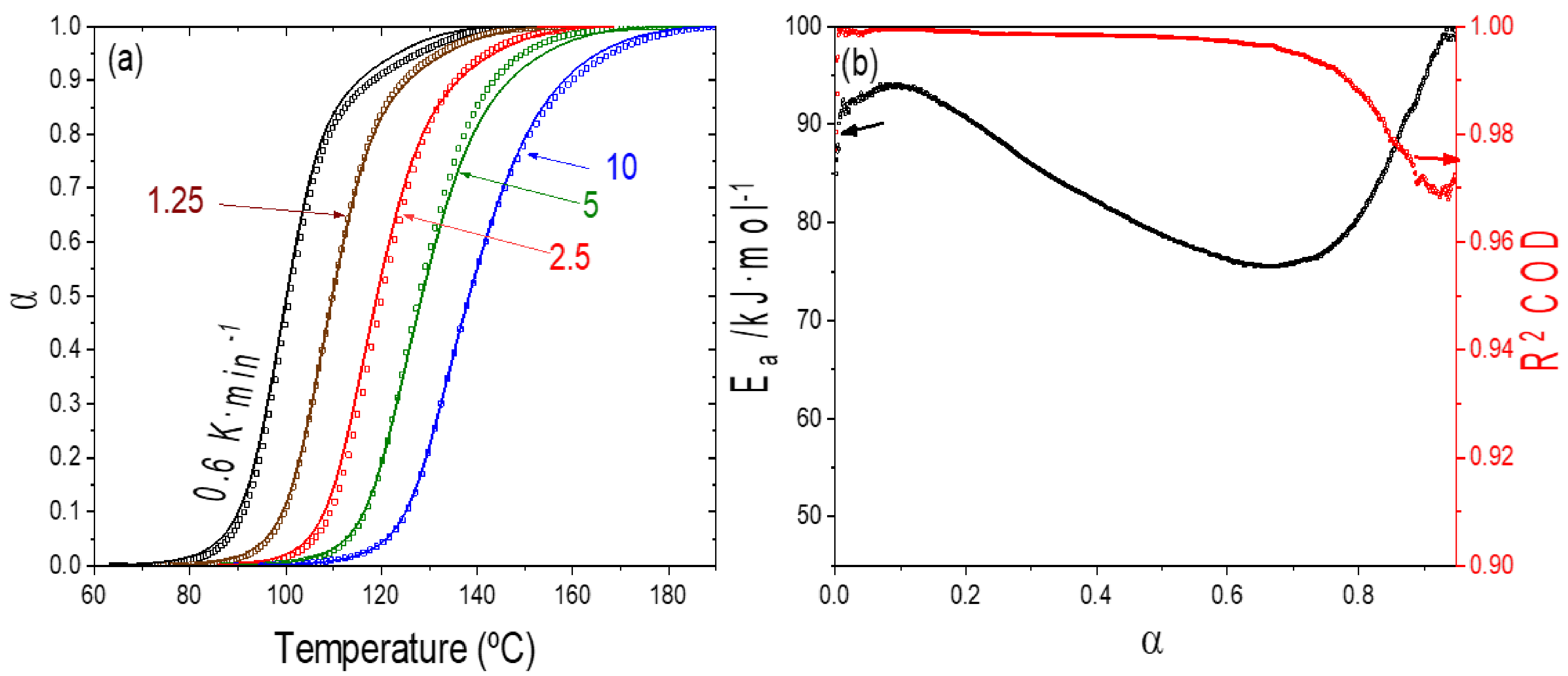


Figure 10. (a) Curing degree evolution obtained from DSC experiments (squares) and predicted evolution (solid lines). (b) Activation energy determined using Friedman isoconversional analysis and R^2 coefficient of determination of the Friedman linear fitting. We assumed a constant activation energy of 90 kJ/mol and a pre-exponential term of $2.2\times10^{9}\ s^{-1}$

Property	Value
Thermal conductivity out-of-plane at 40ºC, k (W/m K)	0.23
Specific heat capacity at 60ºC, c (J/kg K)	1250
Apparent convective coefficient, h, (W/m^2 K)	40
Density, ρ (kg/m^3)	1210
Specific heat of reaction, q (J/kg)	1.60×10^5
Activation energy, E_a (J/mol)	9.0×10^4
Pre-exponential constant, A (s^{-1})	2.2×10^9
Overheating, ΔT_{Max}	
Thickness, w	
Mould temperature, T_m	

5. Materials and methods

5.1 Composite’s curing

The materials used in the experiments are CFRP laminates made of carbon epoxy prepreg VTC401 of 193 g/m^2 areal weight, carbon fiber sheet T700 and 42% resin weight content from SHD Composite Materials Ltd (reference VTC401-C193-PW-T700-12K-42%RW-1270).

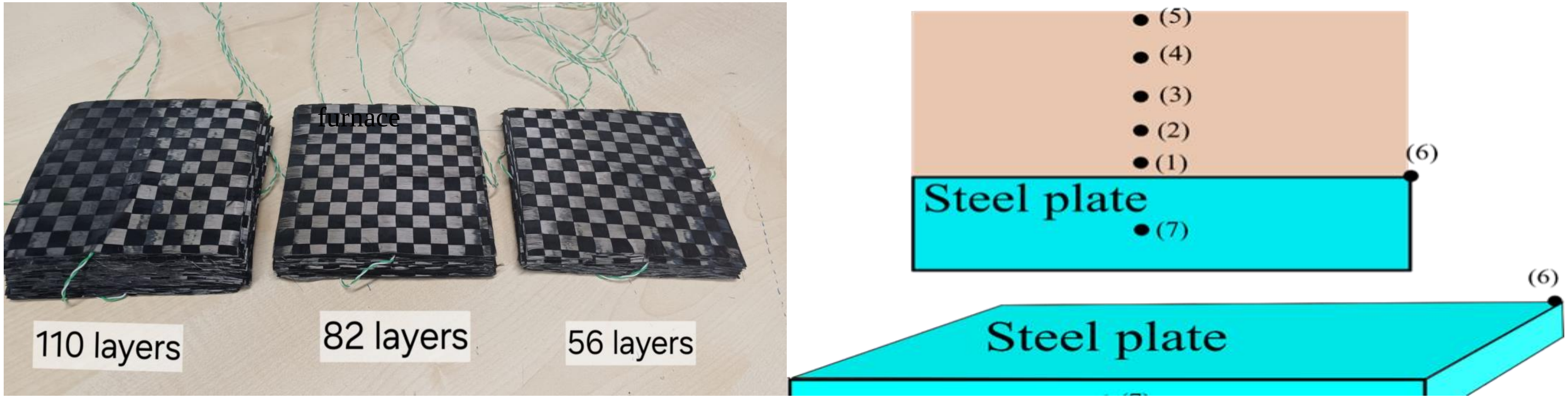


Figure 11. Manufactured CFRP panels of dimensions 200×200×*w* mm^3, where *w* is 14.6, 21.4, or 26.5 mm, corresponding to 56, 82, and 110 layers with five embedded thermocouples. Diagram of the cross-section of the laminate placed on a steel plate and diagram of the positions of the two thermocouples placed on the steel plate.

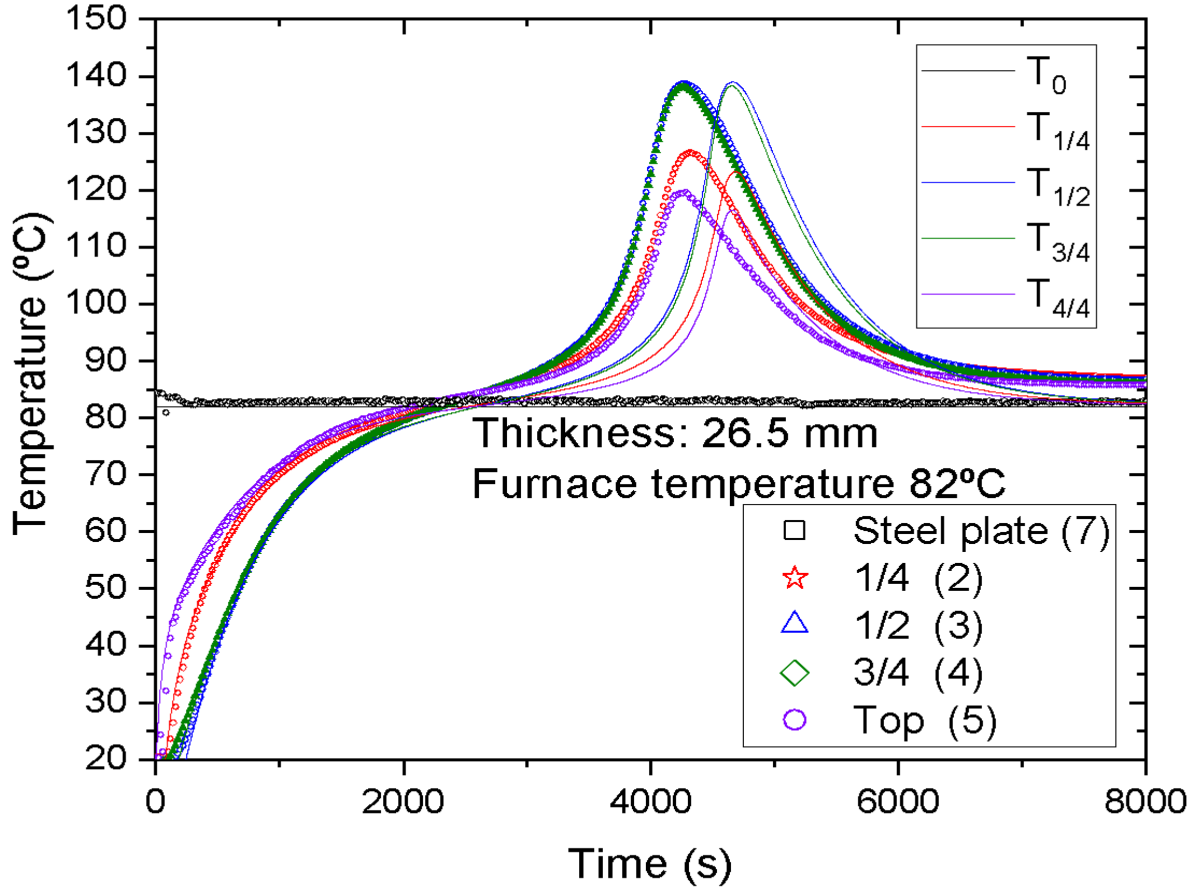


Figure 12. Solid lines: numerical evolution of the temperature at the locations indicated in the legend according to the positions identified in Figure 1.

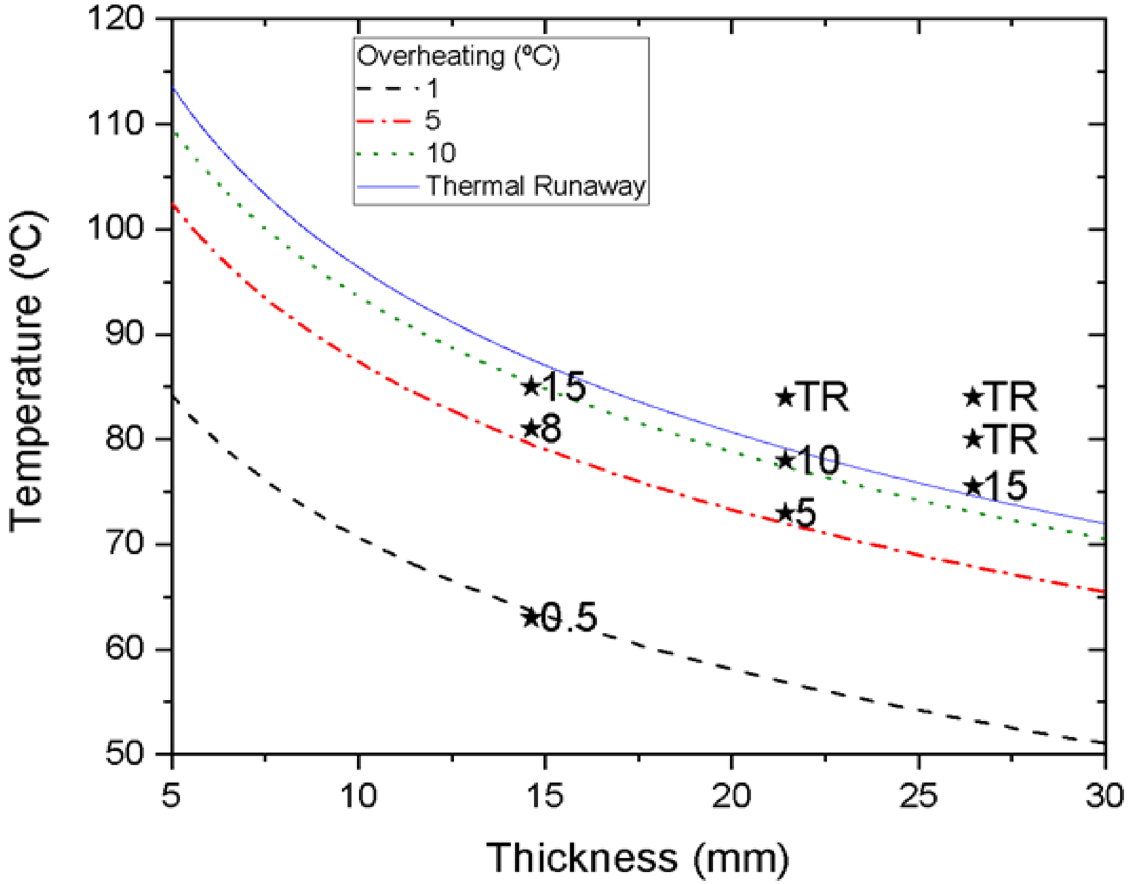
Symbols: evolution of the temperature measured during the curing process of a 26.5 mm thick laminate when the oven temperature is 82°C

Table 2. Maximum overheating measured in the laminate curing experiments together with the maximum overheat calculated by the numerical simulations.

Thickness mm	Temperature ºC	Measured Overheating / ºC	Calculated Overheating / ºC
14.6	63	0.5	0.97
14.6	81	8	7.65
14.6	85	15	13.4
21.4	72	6	6.26
21.4	77	10	12.6
21.4	84	35	37.6
26.5	73	16	18.4
26.5	80	41	45.4
26.5	82	57	57.5

UdG

6. Experimental validation



The analytical solution is used to create a transformation map relating the curing temperature to the critical thickness for overheating and thermal runaway. The physical parameters of laminates used in nine experiments show perfect agreement between predicted and measured overheating, as you can see in Fig. 14.

Figure 13. Lines: analytical prediction of the curing temperatures to reach a given overheating. Stars: curing temperature and thickness for the experiments.

7. Conclusions

- We have developed a simple 1D model to determine the **formation of thermal gradients** within a planar geometry sample during the **isothermal curing process of a resin**. The model considers the heat generated by the curing process, the heat dissipated through the sample and different boundary conditions: perfect conduction on one side and convective losses on the other.

- **The model can't predict curing reactions, but it can predict overheating**. An analytical model predicts critical thickness for overheating or thermal runaway based on curing temperature, thermal conductivity, and other parameters.

- The model was tested against nine laminate samples, showing good agreement between experimental data, numerical analysis, and the analytical model.

Thank you for your attention!

carstea.casandra@gmail.com

http://amade.udg.edu

testlab.amade@udg.edu

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