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Optimization of curing process of carbon/epoxy prepreg for large Solid Rocket Motor casings

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Abstract

This paper deals a study for the optimization of the curing process of large Solid Rocket Motor (SRM) casings, by means of experimental analyses and also by using a Finite Element Method (FEM) model simulating the curing cycle of a large composite casing. The various phenomena occurring during polymerization and their interaction were taken into account and implemented in the model. As a result, the temperature profile and the degree of conversion depending on the curing cycle progress were obtained, thus giving a prediction of the glass transition temperature and the mechanical properties as a function of temperature on different positions of the casing, evolving with time. The simulation will be performed on solid rocket motor casing for the future VEGA.
The temperature profile and the degree of cure depend on the curing cycle process, therefore the simulation is important to predict the real behaviour of the large SRM casings. The simulation parameters used were found in a previous work by chemical-physical analysis that led to know the reaction kinetics of the carbon /epoxy prepreg developed by Avio S.p.A.

1. Introduction

The cure process is the most critical phase during the manufacture of polymer-matrix composite component, especially for large components, in fact during cure some defects may arise, such as resin degradation and residual stress. These conditions happen especially in thick laminates, where the high thickness causes a series of phenomena that could bring to low degree of cure and so low mechanical properties of the component. This aspect shows how the curing process is very important to guarantee high final properties of the composite. This is critical for small-scale composites and it is even more crucial for large-scale structures with considerable thickness like SRM casing. When the composite stratified is completed, the SRM is ready to cure into the autoclave. During the cure process, heat and pressure are simultaneously applied to the laminate which starts an exothermic reaction and squeezes the air and excess resin out of the laminate. The proper selection of the applied heat and pressure is critical in order to produce a high quality composite part; the aim of the processing procedures is to ensure that the resin is evenly distributed, forms a void-free continuous phase saturating the fibers in the desired ratio, and is completely cured [1]. The exothermical reaction that occurs into the thermosetting resin influences the temperature distribution of the curing part. Therefore the distribution not only depends on the amount of heating power supplied to the case support but also on the amount of heat generated by exothermic reaction of the resin. The exothermic reaction of the resin might lead to excessively high localized temperatures in the part. This results is a non-uniform state of cure and an increase in the residual thermal stresses leading to degradation of the matrix [1-3]. In general for the SRM casings, it is common practice to increase the curing time in order to cope with the uncertainty related to conversion evolution, but this is not always a feasible way from an industrial point of view and does not prevent from an incorrect setup of intermediate temperature steps. In this cases, a numerical simulation is essential to analyze the evolution of thermal properties in relation with rheological ones.
Different consolidation and cure models, based on physical laws, have been proposed to simulate the autoclave curing process of laminates. Lindt [4] presented a consolidation model, based on lubrication theory, to determine the squeezing flow variables due to the compaction of the laminates. Lee and Springer [5] developed a thermochemical flow model and provided a one-dimensional solution of the cure and temperature distribution for flat-plate

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composites. Instead Gutowski [6] and Dave et al. [7] proposed a three-dimensional flow model with vertical and horizontal directions and one-dimensional consolidation of the composite material. Like Loos and Springer [5] also Gutowski [6] and Dave et al. [7] considered a deformable unidirectional fiber reinforcement system where the load is sheared by the network fiber and the resin. Based on the studies included herein, it is evident the importance of a numerical approach to simulating the composite curing cycle. Kim et al. [8] used a direction finite-difference method to trace the cure front of the continuously laid prepreg composite in one-dimension. Loos and MacRae [9] developed a special two-dimensional finite element software to simulate the resin film infusion process includes curing. Young [10] developed an finite element code to model non-isothermal mold filling in RTM process in which used the finite-difference technique, and solved the heat transfer in the mold and the non-isothermal flow in the cavity as separate problems using the output from one as boundary conditions for the other.
In this paper we used a software to perform simulation of the curing cycle of SRM casing given its geometry and boundary conditions. The simulated results obtained will be compared with experimental results obtained in large scale on SRM casing by means of a data logger instrument as will be explained later.

1.2 Modelling of cure process

The FEM software in general allows to simulate three physical phenomena like flow resin inside porous medium, heat transfer inside reinforcement and mold and chemical reaction of the resin; this three phenomena are strictly coupled. To analyse the phenomena, the entire model is generally divided into four sub-models; thermomechanical, flow, void and stress. However, only the thermomechanical model allows to define the temperature and degree of cure trend in the whole system. The thermomechanical trend is generated by some thermal fluxes that are driven from the outside or that are generated inside by the polymerization reaction. So, in order to simulate the cure process of SRM casing it must be taken into account the energy balance on the system, that can be written as:

$$\rho C_p \frac{\partial T}{\partial t} = \vec{\nabla}\{k_c \, \nabla T\} + \rho_r V_r \dot{Q} \tag{1}$$

Where ρ represents material density, T is the temperature, Cp is the specific heat, t is the time, k is the thermal conductivity coefficient of the composite material, ∇ is the Laplace operator, $\dot{Q}$ is the heat generation rate by chemical reaction and V_r is the volumetric percetage. The subscripts c and r refer to the properties of the composite and matrix, respectively. From left to right we have in sequence the dispersion term, transportation term, diffusion term and source term. The curing equation of the resin is modeled as a weighted summation of sub-reactions:

$$\frac{d\alpha}{dt} = \sum_i w_i(t) \frac{d\alpha_i}{dt} = \sum_i w_i(t) \, f_i(T, \alpha) \tag{2}$$

where the weight factors can be function of time. In most general cases, only one sub-reaction is used, and the function f(T,α) is Kamal-Sourour [11]. The reaction kinetics and the related parameters were obtained by differential scanning calorimeter (DSC) experiment. Experimental data obtained from DSC have been fitted into a semi-empirical model representing the rate of cure as a function of temperature and the degree of cure. The Kamal-Sorour's reaction kinetics used for our study can be written with the following equation:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \tag{3}$$

where K_1 and K_2 are kinetic constants; K_1 is a constant for the catalytic reaction, while K_2 is a constant for the autocatalytic reaction, where the partial reaction order are n and m respectively. Both K_1 and K_2 follow the Arrhenius law. It is possible to explicit K_1 and K_2 equation as follows:

$$K_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)$$
$$K_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \tag{4}$$

where A_1 and A_2 are the pre-exponential factors, E_1 and E_2 are the activation energies of the two reaction involved into the resin during the polymerization.

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There is an extension of this Kamal-Sourour model [12] which takes into account a diffusive factor that occurs at high degree of cure values because strictly linked to the macromolecules free volume. In this case the equation (3) can be rewritten as:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \left[\frac{2}{1 + \exp\left[(\alpha - \alpha_f)/b\right]} - 1\right] \quad (5)$$

where α_f is the maximum conversion degree and b is the diffusion coefficient. In this study we adopted the basic kinetic model without the diffusive contribution. An analysis with diffusive terms will be performed in the future.
Based on the experimental results obtained from fitting, it was possible to know all the parameters of the (3); in particular K_1 and K_2 from which it is possible to obtain A_1 and A_2 and E_1 and E_2, n and m. In the software use the equation (3) is written as follows:

$$f(T,\alpha) = \left[A_1 \exp\left(-\frac{E_1}{T}\right) + A_2 \exp\left(-\frac{E_2}{T}\right)\alpha^m\right](1 - \alpha)^n \quad (6)$$

The SRM case is constituted of different components with different materials; Two different simulations were performed; the first one was performed on a model with only the case support material without other components and with a specific curing cycle. Furthermore it was performed an experimental analyses on the naked case support instrumented with different thermocouples and submitted to the same curing cycle. The curing cycle set in reality was used for case support validation and simulation for setting the convection coefficients H_c. Thanks to a data logger it was possible to monitor the temperature trend during the set cycle. Scope of the first simulation was to confirmed different air convection coefficients into the autoclave, obtained by an iterative process, and calibrate the kinetic model according to the parameters studied of the composite material. The kinetics parameters used for these simulations were obtained through some chemical-physical tests presented in paper [13].
Once the convective coefficients and the validity of the kinetic model are confirmed, a second simulation can be used to consider the SRM model in its entirety, taking into account all relevant components and materials; the cure process adopted is the same of the first simulation. This simulation allows to analyse the degree of cure in different points of the casing, in particular close the zones where the convection coefficients are variable, and the temperature distribution and relative delays.
The materials adopted during the simulation were defined within the software by inserting some necessary chemical-physical parameters such as density, specific heat, conductivity and so on; four materials have been defined, metal for cylinder and skirt support, thermal protection, and prepreg.
In order to reduce the computation time, some consideration can be done about the model. First of all, thanks to axialsymmetric geometry of the casing, only a portion of the model has been modelled; this simplification has been handled with appropriate boundary conditions. To make this portion of the model representative of the whole geometry, a null heat flux condition has been adopted on the lateral surfaces for each material. Another boundary condition is related the inside of the case support, in fact this area is a confined space so it is necessary to impose an adiabacity state with null heat flux. Another boundary condition applied was convection heat; three different convection coefficients were used for simulation, called A, B and C respectively high, medium and low value; therefore three different regions were created with their coefficients. This coefficients are obtained by iterative process.
On the cylinder where the air flow is higher inside the autoclave has been used the A value; on the FWD dome has been used B value that simulates a lower air flow with respect to the cylinder part due to the fact that it is positioned near the autoclave door and the case support has two series of holes at different diameters; and at the end on the AFT dome the lowest flux with a C value has been used due to the fact that this part is positioned on the back of autoclave and the case support has only one series of hole that induces a stagnation of the air flow.

1.2 Experimental and FEM results of case support

The first part of this study is related to an experimental test conducted only on the base case support subjected to the curing cycle with multiple ramp. During the test the case support has been instrumented with thermocouples positioned at various points and connected to a data logger that was placed close to the FWD dome; the related thermocouples were positioned as follows:
- two TC (#2, and 15) were positioned horizontally on fwd and aft domes;
- two TC (#3 and 14) were positioned on fwd and aft base skirt support;
- two TC (#8 and 9) were positioned on the cylindrical part of the case support, in the upper parts.

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- two TC were positioned embedded in the composite/TP panel (Figure 1). The configuration of this panel aimed to replicate the material thicknesses of SRM casing near FWD skirt.

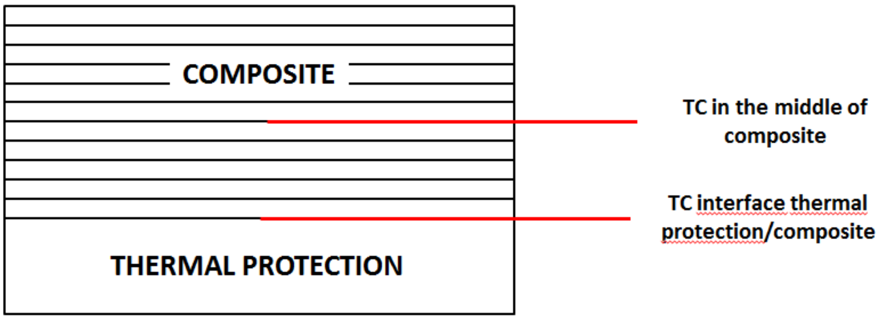

Figure 1 Scheme of TC positioning on composite/TP panel

The experimental results obtained from this test has been compared with the simulation results, with the aim to set up convection coefficients and to analyze the temperature trends and relative delays; the convection coefficients have been obtained at the end of an iterative process.

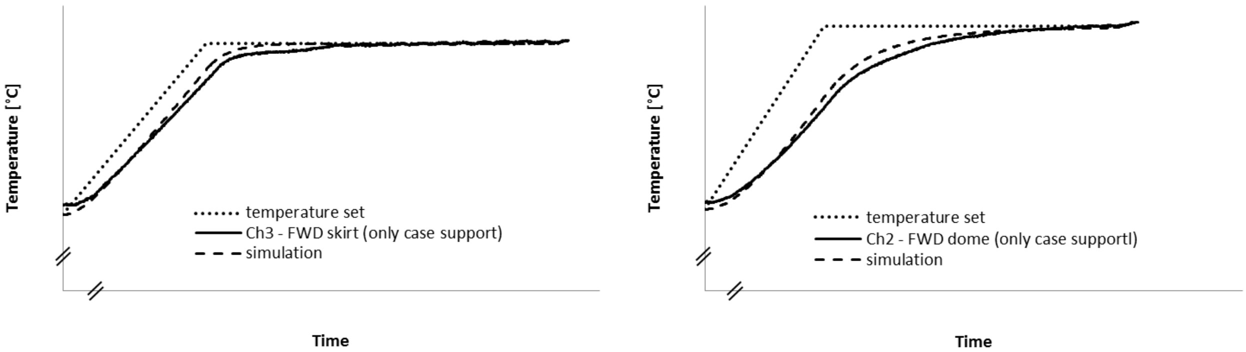

Figure 2 Temperature trend on FWD skirt and on FWD dome (only case support)

The following parts of the model have been considered; channel 3 on the FWD skirt, channel 2 on FWD dome, channel 14 on AFT skirt and channel 15 on AFT dome. Furthermore, the channel into the composite structure has been considered, in particular channels 4 and 5 near FWD skirt. Figure **2** shows the comparison of temperature distribution between simulated and experimental data in different point of the case support in particular on the FWD skirt (channel 3) and on FWD dome (channel 2). This comparison shows a good overlapping between experimental and simulated data, while it can be seen a small delay compared to the temperature set for all multiple ramp. This delay is more pronounced on the FWD dome due to the different convection coefficient than to the FWD skirt.

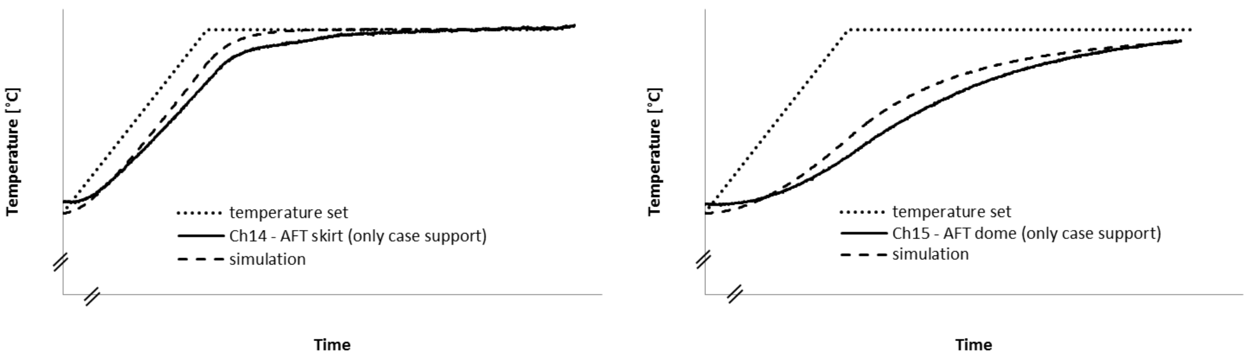

Figure 3 Temperature trend on AFT skirt and on AFT dome (only case support)

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Figure 3 shows the same temperature trends as the previous figure in the symmetric part of the model close to the rear of the SRM casing; comparing the temperature set with the experimental one it can be noticed a delay close the AFT dome. This results is robust because in the AFT dome zone there is a lower convection coefficient compared with the cylindrical and FWD dome zones. It is possible to see also in Figure 3 a very good overlapping between experimental results and simulation results. From these results we can conclude that the convection coefficients found experimentally allows to simulate the real temperature distribution in the autoclave.
The same considerations can be done on the temperature distribution inside composite material. In this regards it can be seen in Figure 4 the experimental and simulated temperature distribution inside composite material. In particular channel 4 was taken to the mid-thickness of composite material in FWD zone; channel 5 was taken to the composite/thermal protection interface in FWD zone. Experimental and simulation trends are perfectly overlapping, also on exothermic peak. It is possible to observe the exothermic peak due to the presence of thermal protection, which keep heat dissipation within the composite, increasing the temperature of the same.

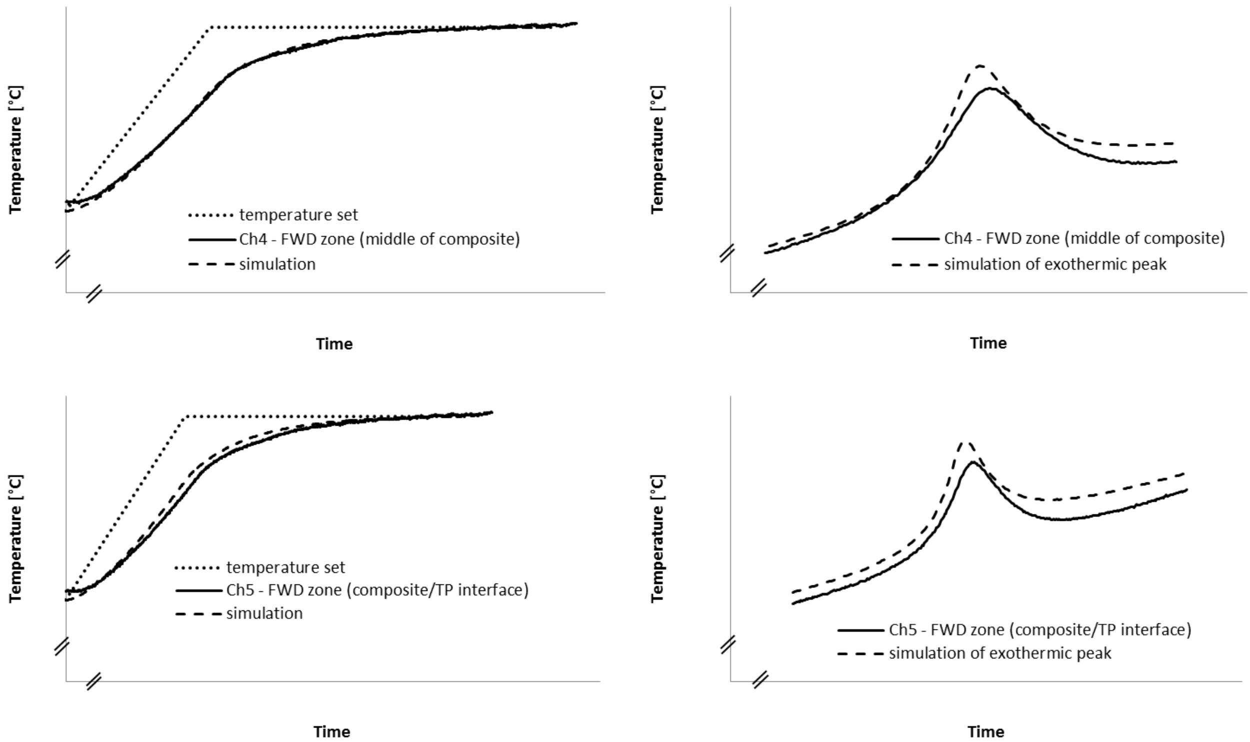

Figure 4 Temperature trends on FWD zone in composite material

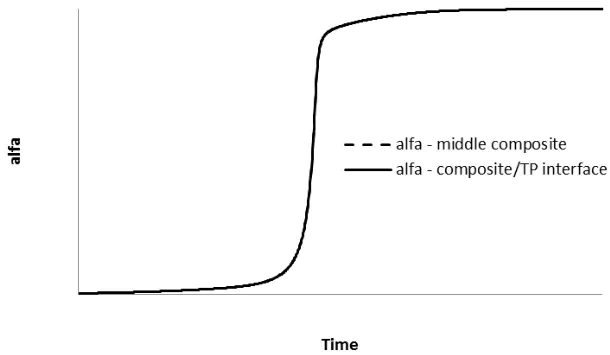

Figure 5 Degree of cure of the composite material panel

This result provides an important indication of reaction kinetic. The experimental kinetic parameters found simulate very well the experimental results. Another important result obtain from these simulation is the degree of cure. For FWD zone the cure process is complete as show in Figure 5; as can be noticed there are no differences between the

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middle of composite and composite/thermal protection interface, in fact in both results the same trend of degree of cure is obtained.

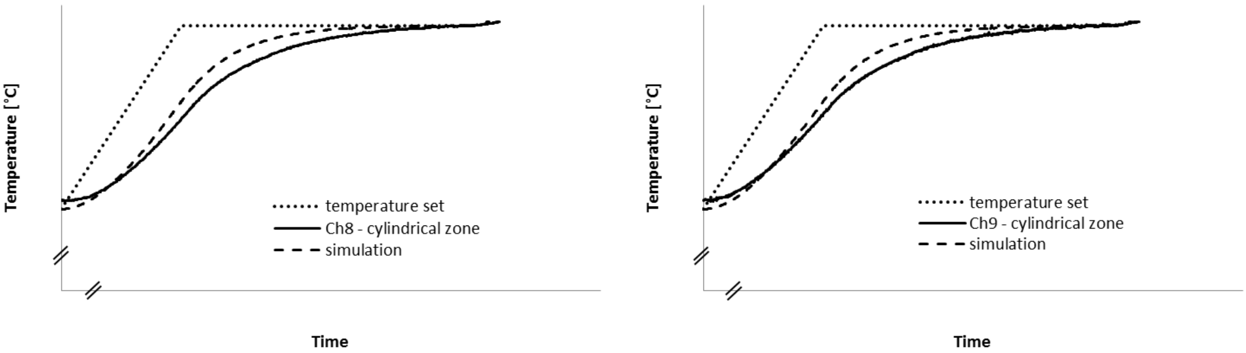

Figure 6 Temperature trends on cylindrical zone

In Figure 6 are shows the temperature trends close to the cylindrical zone. Also in this trends it is possible to notice the perfect overlapping between experimental and simulation results; it can be observed a delay compared to the temperature set for the multiple ramp. It can be concluded that:

- the three different convection coefficients have been confirmed;
- calibration of the kinetic model is good.

From the second simulation will be possible evaluate both the temperature distribution than conversion the degree in different zones of the SRM casing and for the different materials.

1.3 Solid Rocket Model FEM results

From the first simulation it was possible to calibrate the model based on the convective coefficients obtained and the kinetic parameters. After that it can be performed a second simulation in which the Solid Rocket Motor casing is updated with all the main components and related materials. The same boundary conditions of the first simulation are adopted, null lateral heat flux and convection. On this model the same cure cycle with multiple ramp has been applied in order to check the temperature distribution and degree of cure on the composite case during curing cycle. The temperature evolution, and the degree of cure of the composite, have been verified in the following position:

- FWD and AFT dome on the composite surface;
- FWD and AFT dome in the middle of composite;
- FWD and AFT dome in the composite/thermal protection interface;
- FWD and AFT skirt on the composite surface;
- FWD and AFT skirt in the middle of composite;
- FWD and AFT skirt in the composite/thermal protection interface;
- Cylindrical zone on the composite surface;
- Cylindrical zone in the middle of composite;
- Cylindrical zone in the composite/thermal protection interface;
- Cylindrical zone in the middle of the case support;

Figure 7 shows the temperature distribution between FWD dome (on the left) and AFT dome (on the right) in different points of the composite: composite surface, middle of composite and on the thermal protection/composite interface. These temperature distribution are compared to the temperature set for the curing cycle. It can be seen the temperature distribution of the AFT dome presented a delay compared to FWD dome; this is quite understandable since there is a lower convection coefficient in the back. It can been also noticed an increase of the exothermic peak in the thermal protection/composite interface for both FWD and AFT dome.

This is due to the fact that near the interface the presence of thermal protection prevents thermal dissipation due to exothermicity of the composite by generating an increase of the same peak. The conversion degree close to AFT dome zone is shifted to higher times because here there is a convection coefficient lower than the FWD dome zone. This shift effect can be seen in Figure 8. For both FWD dome and AFT dome the conversion degree between composite surface and thermal protection/composite interface has a different slope; on the composite surface the conversion degree increases more slowly than the TP/composite interface, because in this zone there is not heat

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dissipation effect due the thermal protection. To the TP/composite interface the presence of the thermal protection implies a sudden temperature increase in the composite, therefore the conversion degree increases rapidly.

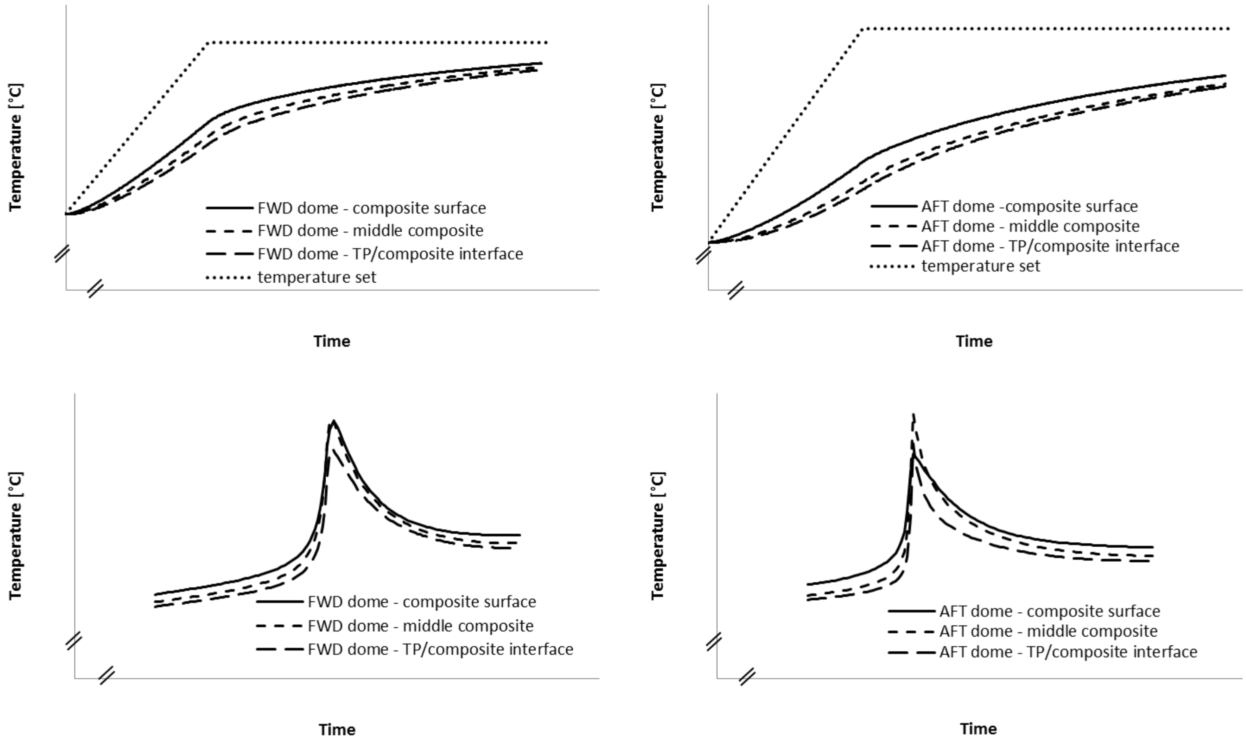


Figure 7 Temperature distribution for FWD and AFT dome in the composite material

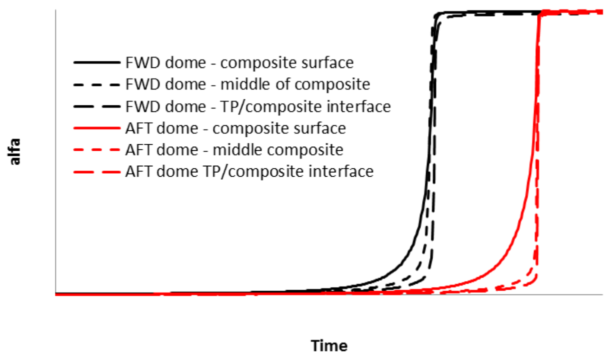
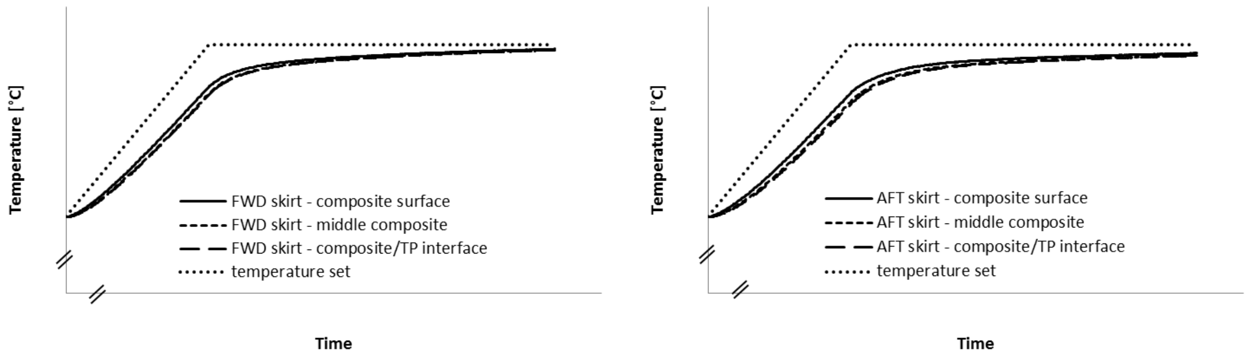


Figure 8 Conversion degree for FWD and AFT dome in the composite material



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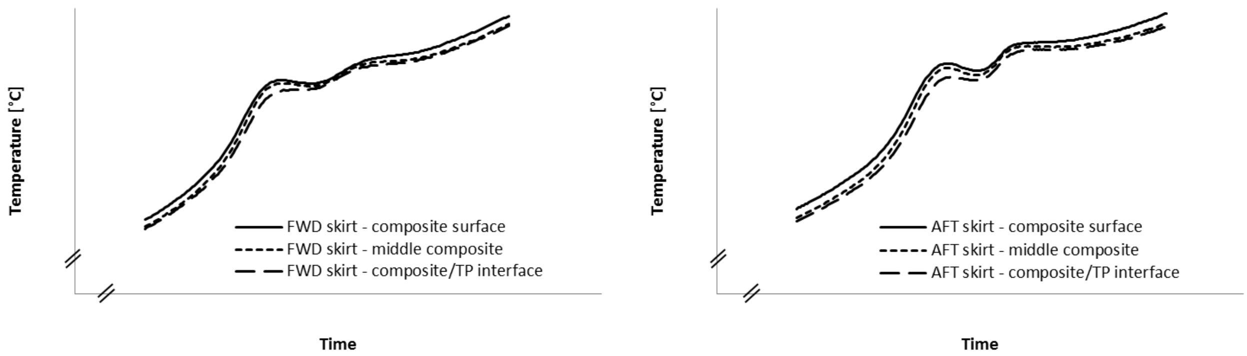

Figure 9 Temperature distribution for FWD and AFT skirt in the composite material

Figure 9 shows the temperature distribution between FWD skirt zone and AFT skirt zone in different points of the composite: composite surface, middle of composite and on the thermal protection/composite interface.
As can be noticed that there are no difference between forward and after zone of the skirt; this is understandable because both FWD and AFT skirts are subjected to the same H_C. It can be also to noticed the small exothermic peak, because in this parts there is no thermal protection so there is heat dissipation.
The conversion degree of the FWD and AFT skirt zones are shown in Figure 10; it is visible a small difference between the zones in particular there is a slightly shift to the right for the degree of cure in the AFT zone. No slope difference is observed between the external composite surface and the internal part in contact to the skirt support, unlike what was observed in the dome zones, because here there is no thermal protection presence.

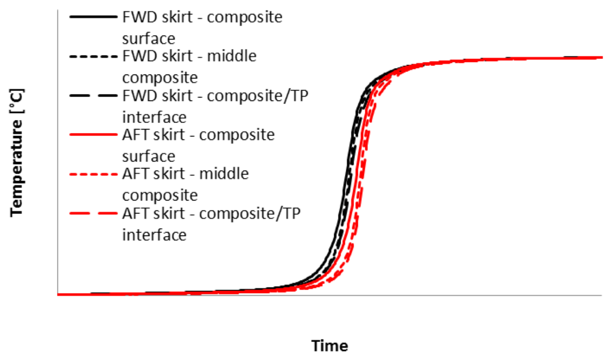

Figure 10 Degree of cure for FWD and AFT skirt in the composite material

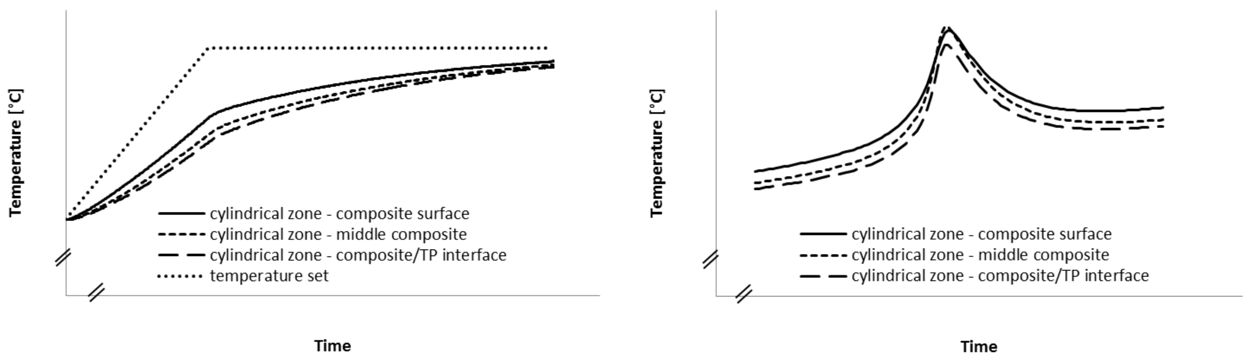

Figure 11 Temperature distribution of the composite material in the cylindrical zone

Figure 11 shows the temperature distribution for the cylindrical zone of the SRM casing; the exothermic peak of the composite is also well visible in the cylindrical part as unlike the skirt zones here there is a presence of thermal protection which greatly influences the exothermicity of the composite. In coherence to the physical phenomena the

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temperature distribution decreases from the outside to the inside of the composite material; which is intuitive because the heat is given from the outside zone. This aspect can also be seen for the exothermic peak.
The conversion degree (Figure 12) in this zone shows a similar trend with what was observed close to FWD and AFT dome zone, that is a slope difference between external and internal zone of the composite material; on the surface of the composite the conversion degree increases slowly than the TP/composite interface. On the other hand in the middle and in composite/thermal protection interface the thermal protection presence induces an even higher reactivity than the surface of the composite.

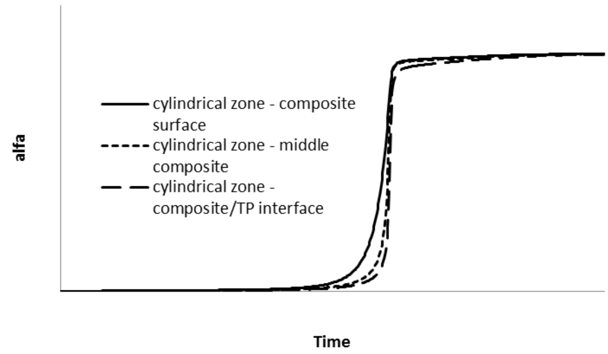

Figure 12 Conversion degree of the composite material in the cylindrical zone

Finally Figure 13 shows temperature distributions on the composite surface in different zones of SRM casing (FWD dome, AFT dome, FWD skirt, AFT skirt, cylindrical zone). Analysing the temperature trends it can be seen that moving from forward to after zone there is a delay in temperature distribution; it is reliable as the convection coefficients vary considerably from FWD to AFT zones. This can be well seen in conversion degree (Figure 14) trend also, in fact in the AFT dome it is necessary more time to conclude the polymerization reaction, so the related degree of cure is shifted to greater times.

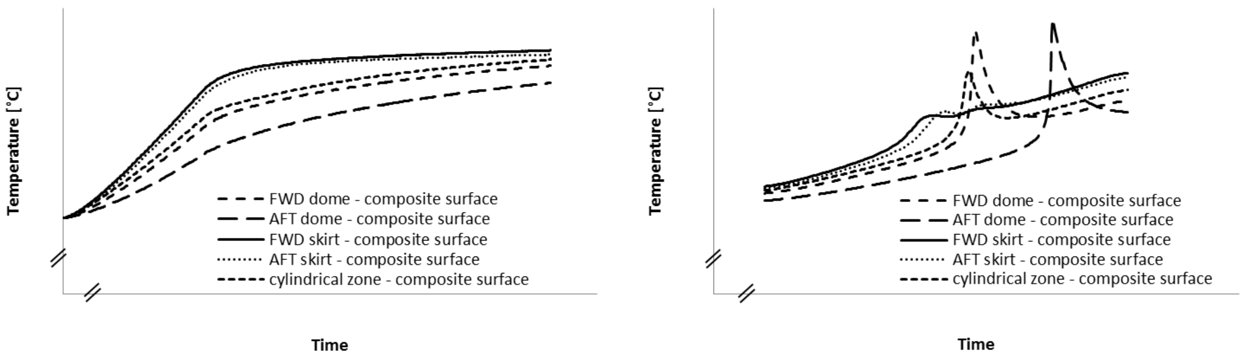

Figure 13 Temperature distribution of the composite material on the surface of SRM casing

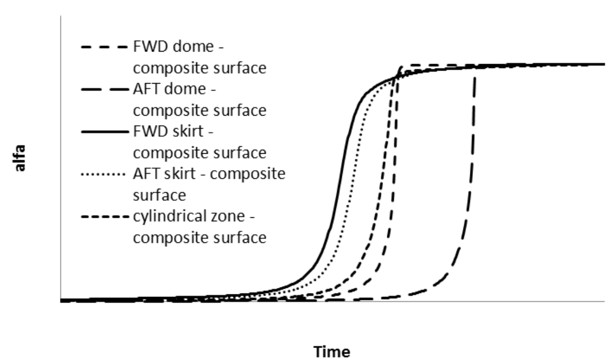

Figure 14 Conversion degree of the composite material on the surface of SRM casing

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2. Conclusion

The study presented here allowed to evaluate the temperature distribution inside the autoclave and then on the SRM casing and to simulate the SRM cure cycle by setting the reaction kinetics found experimentally. The results obtained show that the value of convection coefficients and the kinetics model of the prepreg material are correct, therefore they were adopted during the simulation.
The following studies are going to be performed as further development:

1. Use an extension of Kamal - Sourour model which contains the diffusive factor;
2. A large-scale test will be carried out in which an SRM will be instrumented with appropriate thermocouples prior to polymerization. The experimental data obtained from this test will be compared to those obtained by simulation; the simulation will be performed first with kinetic model without diffusion factor and then with complete model of that terms.

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