

## NUMERICAL OPTIMIZATION OF THERMOCHEMICAL CURING PROCESS OF EPOXY MATRIX COMPOSITES

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### ABSTRACT

*Composite materials are increasingly used in aerospace applications due to their high specific strength and specific stiffness compared to conventional metal alloys. In contrast to metallic parts, mechanical properties of composite parts are heavily dependent on the manufacturing processes. Curing process has of greatest importance in manufacturing of composite parts. During the curing process, degree of cure distribution throughout the composite is determined by the temperature distribution in the sample. The differences in the degree of cure influence the mechanical properties and performance of the composite material by resulting in residual stresses and permanent deformation on the part. Therefore, process variables must be carefully chosen in order to achieve the desired mechanical performance. In this study, numerical model of the thermochemical curing process is built in both MATLAB and ABAQUS. After verification of the numerical models, the curing process of a cylindrical composite part is optimized to minimize the differences in the degree of cure distribution during the curing process.*

### INTRODUCTION

Fiber reinforced composite materials have been used increasingly in aerospace, automotive and energy industries over the past few years due to their high strength to weight and stiffness to weight ratios [Ozaslan et.al., 2018]. These properties are especially needed for aerospace applications where the weight is a crucial design constraint. In fact, the high technology of the composites has evolved in the aerospace industry. But, the high technology of the composites has driven the applications outside the aerospace industry. Sporting goods such as tennis rackets and golf shafts are major outlet for composite materials [Tsai, 2008]. Other applications of composites materials include bodies of racing cars and yachts, and some other equipment where weight, stiffness and strength are important.

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In aerospace industry, important components produced from these materials include fuselage of space vehicles and motor casing of rockets. These high performance aerospace structures require tailored design and manufacture. There are numerous manufacturing methods to produce components from composite materials such as pulforming, pultrusion, and infusion. But among them filament winding distinguishes itself when it comes to produce bodies of revolution such as cylinders and spheres in an efficient way.

Filament winding is a process in which resin-impregnated continuous fibers are wrapped around a rotating mandrel that has the internal shape of the desired product by moving the carriage (Figure 1) [Faria, 2013]. Hollow axisymmetric components (usually circular in cross section) as well as some irregular shapes are produced.

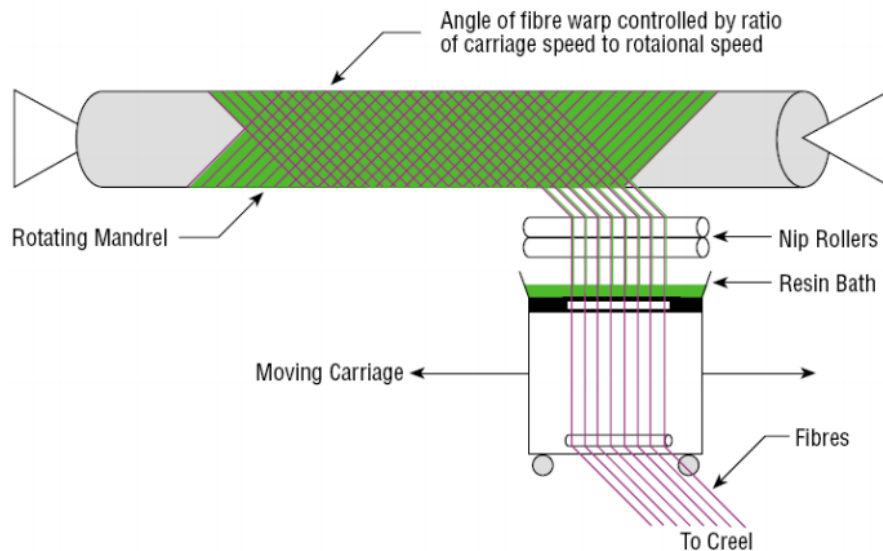


Figure 1: Filament winding process [Faria, 2013]

Many design and manufacturing parameters affect the mechanical performance of composite parts produced via filament winding process such as winding angle, fiber volume ratio, mandrel rotating speed, carriage velocity and curing kinetics. Among them curing has a special importance; since during the curing process degree of cure distribution through the composite may result in non-uniform fiber volume distribution, residual stresses and permanent deformation on the part. This leads to degradation in mechanical properties and performance of the composite part. Thus, the manufacturing process needs to be optimized in order to achieve the required mechanical properties.

In this study, numerical model of the thermochemical curing process is built in both MATLAB and a commercial finite element solver, i.e. ABAQUS. Then, the numerical models are verified by comparing the results with those obtained from the literature. After verification of the numerical models, the curing process of a cylindrical composite part is optimized to minimize the differences in the degree of cure through the thickness of the composite during the curing process.

## METHOD

### Modeling of Curing Process

Curing of the resin is accomplished by increasing the temperature of the part gradually to a pre-set value, keeping the part at that elevated temperature for a predetermined length of time, and then gradually decreasing the temperature of the part to room temperature. During the curing process exothermic polymerization reactions take place and heat is released as the degree of cure increases from 0 to 1. The magnitudes and duration of the temperatures applied during the curing process is designated as the cure cycle and it significantly affects the performance of the finished part [Loos and Springer, 1983]. In principle, the degree of cure should be the same at every point on the part during the cure cycle. However, this is

hardly achievable especially for thick-sectioned parts with thickness greater than 5mm. That is because; the low thermal conductivity of the resin hinders the dissipation of the released heat during the curing cycle. Hence, as the cure progresses, temperature distribution and thereby the degree of cure through the thickness of the part will be non-uniform at each time over the entire curing cycle.

Many researchers have studied modeling the filament winding process including the curing process such as [Lee and Springer, 1990] and [Zhao, 2011] in order to simulate the effects of manufacturing variables on the mechanical performance of the composite part. Researchers use almost the same equations to model the thermochemical curing process which yields temporal and spatial variation of the temperature, degree of cure, and viscosity of the resin.

Temperature distribution inside the composite part during curing cycle can be determined solving the energy conservation equation that considers the cure kinetics. For axisymmetric one-dimensional cylindrical geometries, the energy equation is written as

$$\rho c_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) + \rho_r v_r H_u \frac{d\alpha}{dt} \quad (1)$$

where  $\rho$  and  $c_p$  are the density and specific heat of the composite,  $k$  is the thermal conductivity in the radial direction,  $\alpha$  is the degree of cure,  $H_u$  is the total heat of reaction of the resin,  $\rho_r$  and  $v_r$  are density and volume fraction of the fiber. The second term on the right hand side is the rate of heat released due to exothermic polymerization reactions. There exist several models to estimate the evolution of the rate of cure for different resin types in the literature. A widely used and generic model is expressed as [Dusi et.al., 1987]

$$\frac{d\alpha}{dt} = \frac{H_T}{H_u} (K_1 + K_2 \psi^a) (B - \psi)^b (1.0 - \psi^d)^c \quad (2)$$

where  $H_T$  is the isothermal heat of the reaction of the resin,  $B$  is a constant,  $a$ ,  $b$ ,  $c$  and  $d$  are the orders of cure reaction,  $K_1$  and  $K_2$  are the rate constants, and  $\psi$  is a function of degree of cure. Expressions for  $\psi$  and  $K_{1,2}$  are given in Eq. (3) and Eq. (4), respectively.

$$\psi = \frac{H_u}{H_T} \int_0^t \frac{d\alpha}{dt} dt \quad (3)$$

$$K_{1,2} = A_{1,2} \exp(-E_{1,2}/RT) \quad (4)$$

where  $A_i$  are the pre-exponential constants,  $E_i$  are the activation energies, and  $R$  is the universal gas constant.

In general, viscosity of the resin is a function of temperature and degree of cure and changes dramatically during the curing process. A mathematical model has been developed by [Lee et.al, 1982] and is expressed as

$$\mu = \mu_\infty \exp\left(\frac{U}{RT} + \kappa\alpha\right) \quad (5)$$

where  $\kappa$  and  $\mu_\infty$  are constants, and  $U$  is the activation energy for viscosity.

### Numerical Models

For an axisymmetric composite-mandrel system, the energy equation has been discretized using finite volume method in MATLAB. Heat generation term is omitted for the mandrel which is generally made of aluminum or steel. The resulting system of differential equations is solved via MATLAB's inherent ode15s stiff differential equation solver. Once the evolution of the temperature and degree of cure with time is obtained for every point in the composite, the viscosity of the resin is evaluated using Eq. (5). In addition to MATLAB, the curing process has been modeled using a commercial finite element solver, i.e. ABAQUS by implementing the source term in the energy equation via FORTRAN subroutines. In FORTRAN subroutines the degree of cure is calculated from the cure rate expression using

explicit Euler method. Whereas both models are able to handle cases where material properties are function of temperature and degree of cure, the finite element model is utilized for complex geometries.

### Verification of the Numerical Models

The numerical models developed in MATLAB and ABAQUS are verified by comparing the models' results to those taken from the literature. Two composite-mandrel geometries used in verification studies are shown in Figure 2.

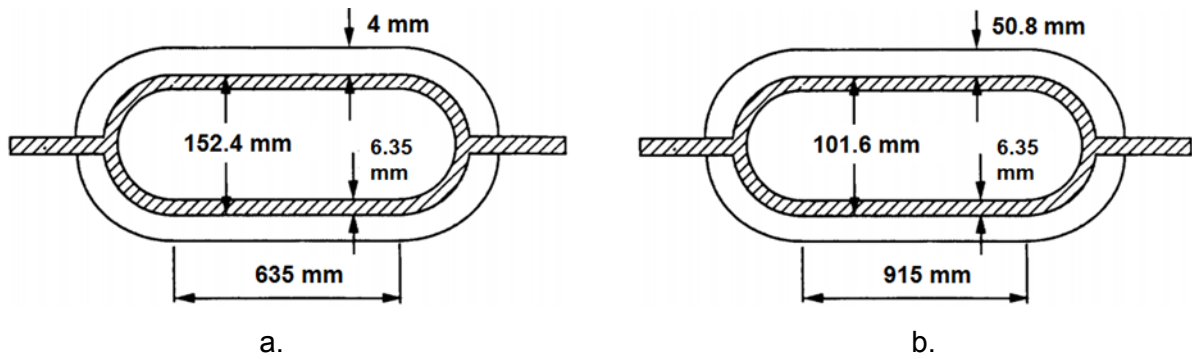


Figure 2: Sample geometries a) thin composite, b) thick composite [Lee and Springer, 1990]

In both samples the composite is made of Fiberite 976 resin and Thornel T-300 fiber, and the mandrel is made of Aluminum 6061-T6. Material properties of the composite and mandrel are given in [Lee and Springer, 1990], and is not restated here for conciseness. The cure cycles for the thin and thick composite geometries are shown in Figure 3. The cure cycle temperature is applied as Dirichlet boundary condition to the inner surface of the mandrel and outer surface of the composite.

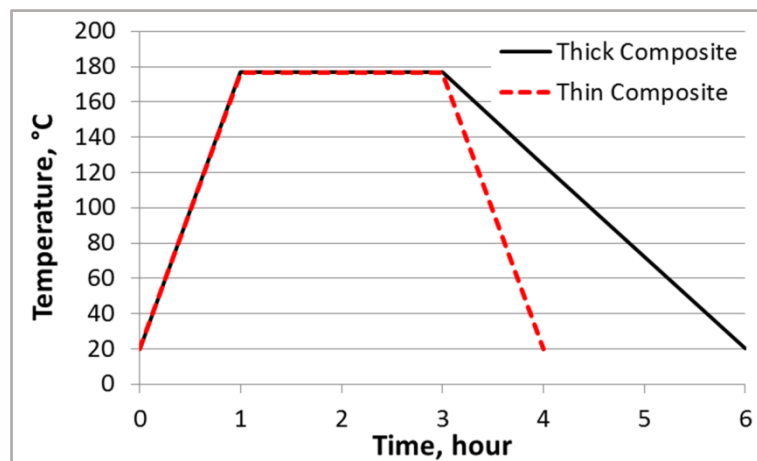


Figure 3: Cure cycles for the thin and thick composite geometries

Temperature and degree of cure variations at the midpoint of the composites are chosen as comparison variables. Comparison results are shown in Figure 4 and Figure 5 for the thin and thick composite geometries, respectively. It is clearly seen that for the thin composite geometry results of the numerical models are in an excellent agreement with the reference values. Temperature at the midpoint of the composite follows the cure cycle temperature very closely. However, for the thick composite geometry, there exists a temperature overshoot inside the composite. It stems from the fact that thick composite is not able to dissipate the heat caused by the exothermic reactions as fast as the thin composite. It is noticeable that developed numerical models give very close results; but they overestimate the temperature peak compared to the reference result. It may be related to the fact that reference results had been obtained by a code that takes into account the shrinkage of the

resin during curing cycle. This phenomenon has not been included in the developed code, yet. Since the numerical models yield almost exact results, and give satisfactory results compared to the reference values, it is deduced that the governing equations have been implemented properly.

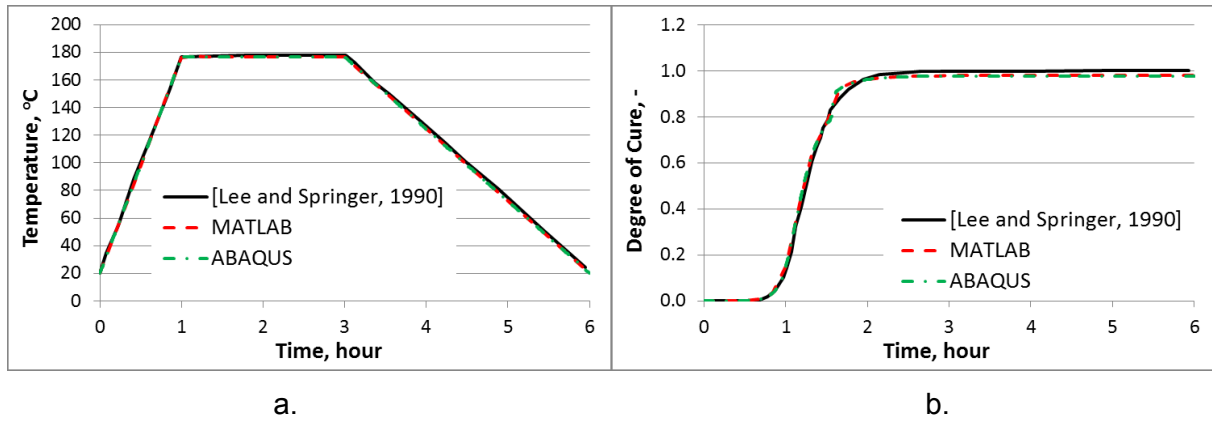


Figure 4: Comparison results for thin composite: a) temperature variation, b) degree of cure variation at the midpoint of the composite

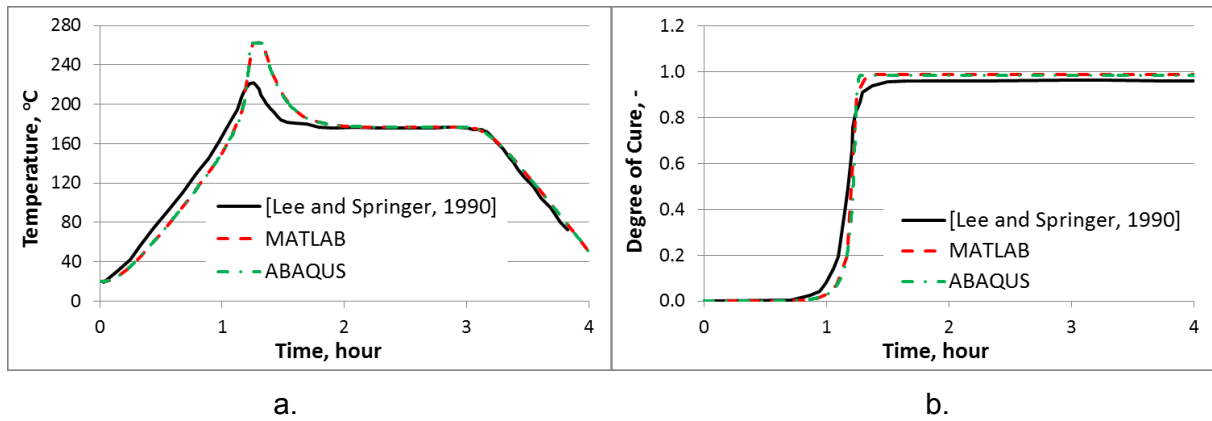


Figure 5: Comparison results for thick composite: a) temperature variation, b) degree of cure variation at the midpoint of the composite

### Optimization

In general, for each specific resin Manufacturer's Recommended Cure Cycle (MRCC) is employed as the temperature cycle. However, using MRCC for thick composites results in non-uniform temperature and degree of cure distributions through thickness. This then leads to residual stresses and distortions on the part. In order to assure that temperature gradients are kept below acceptable limits and degree of cure is fairly uniform through the thickness of the thick composite an optimized process is necessary [Parthasarathy et.al., 2004], in other words, the MRCC must be modified.

The main objective of the optimization is keeping the temperature and degree of cure through the thickness as uniform as possible during the cure cycle without increasing the cycle time considerably. Thus, the objective function of the optimization,  $\Phi$ , is defined as

$$\Phi = j_1 + wj_2 \quad (6)$$

where  $j_1$  is the maximum temperature difference between the midpoint temperature and the surface temperature of the composite and  $j_2$  is the total cure cycle time, and  $w$  is the weighting factor for scaling the time to the temperature difference.

The composite part studied in this work is made of AS4 carbon fiber and 3501-6 epoxy resin with fiber volume fraction of 56%. Thickness of the composite part is 45 mm, and its internal diameter is 480 mm. The mandrel is 10 mm thick and made of Al 6061-T6. The MRCC for the resin is given in Figure 6.

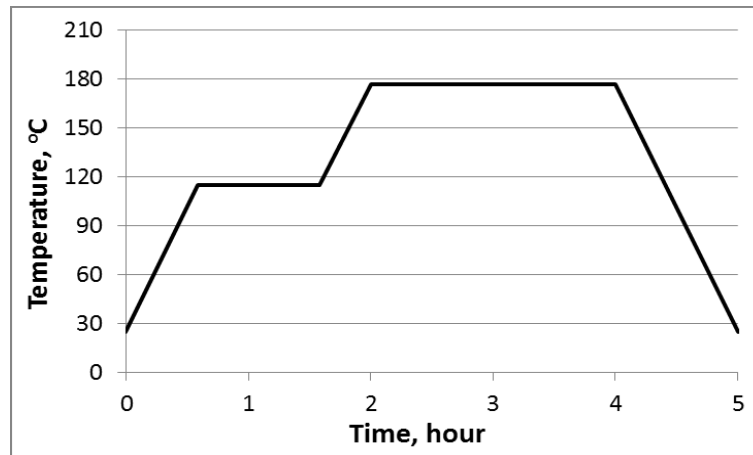


Figure 6: MRCC for 3501-6 epoxy resin

The curing rate expressions for the 3501-6 epoxy resin is expressed as follows [Li et.al., 2017]

$$\begin{aligned} \frac{d\alpha}{dt} &= \frac{H_T}{H_u} (K_1 + K_2\psi)(0.47 - \psi)(1.0 - \psi) & \alpha \leq 0.3 \\ \frac{d\alpha}{dt} &= \frac{H_T}{H_u} K_3(1.0 - \psi) & \alpha > 0.3 \end{aligned} \quad (7)$$

The cure kinetic parameters for the 3501-6 epoxy resin are given in Table 1. Thermal properties of the resin and fiber are functions of temperature and degree of cure, and they are given in Table 2. The properties of the composite are evaluated using rule of mixture.

Table 1: Cure kinetic parameters for 3501-6 epoxy resin [Kim and White, 1997]

Parameter	Value	Parameter	Value
$A_1$ (s <sup>-1</sup> )	3.503e7	$E_1$ (kJ/mol)	80.7
$A_2$ (s <sup>-1</sup> )	-3.356e7	$E_2$ (kJ/mol)	77.8
$A_3$ (s <sup>-1</sup> )	3.266 e3	$E_3$ (kJ/mol)	56.6
$H_u$ (kJ/kg)	198.9	$H_T/H_u$	1.0

Table 2: Thermal properties of the resin and fiber [Li et.al., 2017]

Parameter	Value
Density (kg/m <sup>3</sup> )	3501-6 epoxy resin: 1272 AS4 carbon fiber: 1790
Specific Heat (J/kg/K)	3501-6 epoxy resin: 4184(0.468+5.975e-4T-0.141α) AS4 carbon fiber: 1390+4.5T
Thermal Conductivity (W/m/K)	3501-6 epoxy resin: 0.04184(3.85+(0.035T-0.141)α) AS4 carbon fiber: 0.742+9.02e-4T

## Results

During the optimization process, form of the MRCC, i.e. two-step cure cycle, is kept unchanged. Heating and cooling rates, dwell times and the corresponding temperatures are allowed to be changed by the optimization algorithm in order to minimize the objective function. Additionally, it is assured that the degree of cure is greater than 0.95 at every point through the thickness at the end of the curing process.

Figure 7 compares the MRCC to the optimized cure cycle. In order to reduce the temperature gradient through the thickness, the optimization algorithm decreases the heating and cooling rates considerably. Substantial increase in overall cycle time is then alleviated by reducing the dwell times. Optimized cure cycle is approximately 16% longer than the MRCC.

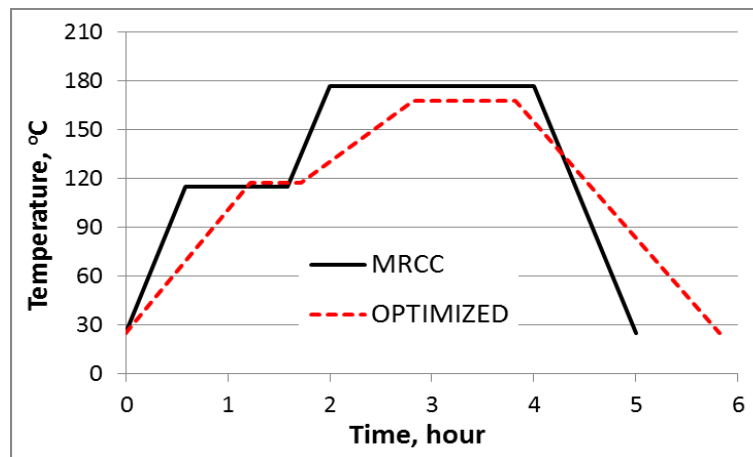


Figure 7: MRCC and optimized cure cycle

Figure 8 compares the temperature and degree of cure distribution through the thickness of the composite at the time point where the degree of cure difference between the midpoint and surface is maximum. It is clearly seen that the optimized cure cycle yields more uniform temperature and degree of cure distribution than those obtained using the MRCC through the thickness of the composite. Maximum degree of cure difference through the thickness is reduced by approximately 50%.

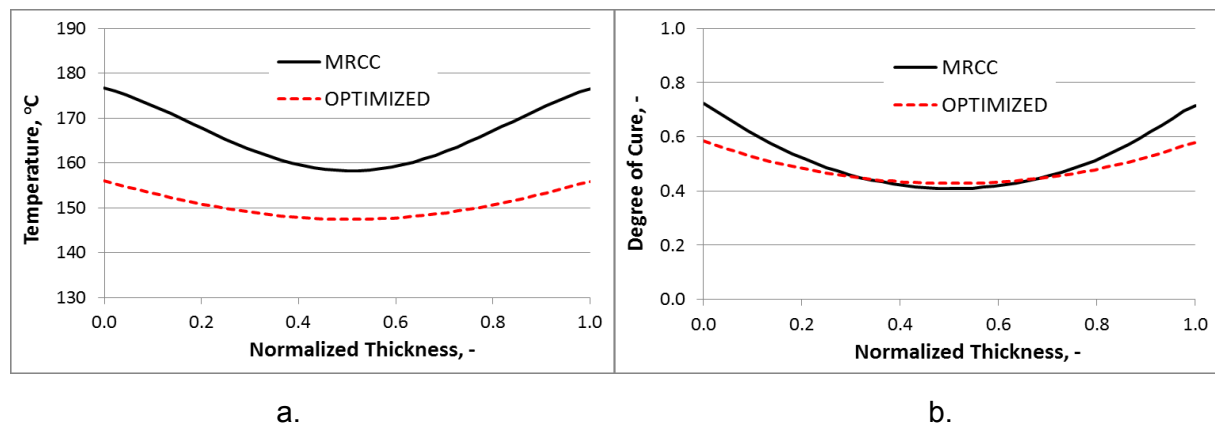


Figure 8: Comparison results: a) temperature distribution, b) degree of cure distribution through the thickness of the composite

## CONCLUSION AND FUTURE WORK

The curing of the filament wound composites has been studied using a thermo-chemical model. The recommended cure cycle for a given resin has been optimized using the developed numerical framework so as to minimize the degree of cure distribution through the thickness of the composite during curing process. The optimized cure cycle reduces the maximum degree of cure difference between the midpoint and surface of the composite by 50%.

Temperature changes during the process result in shrinkage in the resin, and thermal expansion and contraction of the composite and mandrel. Moreover, viscosity of the resin alters and fibers move inside the resin during the process. These phenomena in conjunction with cure kinetics affect the residual stress evolution on the part, and consequently influence the mechanical performance of the composite. Thus, as a further development these physics are going to be added to the numerical model.

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