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Optimization of thermal curing cycle for a large epoxy model

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ABSTRACT

Heat generation in an exothermic reaction during the curing process and low thermal conductivity of the epoxy resin produces high peak temperature and temperature gradients which result in internal and residual stresses, especially in large epoxy samples. In this paper, an optimization algorithm was developed and applied to predict the thermal cure cycle to minimize the temperature peak and thermal gradients within the material of an industrial epoxy model during the curing process. An inverse analysis was used to obtain the new coefficients of Kamal's equations for the model. To validate and verify the developed model, temperature profiles for several points of the material in the model were obtained by numerical simulation and compared with the previously experimentally measured data. With validated curing simulation, the mentioned inverse analysis and optimization algorithm were utilized to find the thermal curing cycle with several isothermal holds and temperature ramps. The new objective reference was proposed for the first time and used to optimize the cure cycle, which subsequently produced the same temperature profiles for all points. The results showed that the obtained optimized thermal curing cycle was most effective to decrease the peak temperature as well as temperature gradients of the material.

1. Introduction

In the manufacturing of the large epoxy samples, appropriate prediction of thermal cure cycle has a great effect on the quality and costs. Epoxy resins have frequently been used and attracted both academic and industrial interests in the past decades. The main reasons for the use of these materials are to keep an outstanding balance among adhesion and mechanical properties, humidity and heat resistance, and electrical insulation properties [1-4]. These properties are significantly affected by the manufacturing processes to minimize the voids, shrinkage, and cracks [5-9]. The first concern is generated temperature overshoot because of an exponential increase in casting temperature caused by the epoxy exothermic cross-linking reaction. The second concern is development of complex and high gradients of the cure degree and temperature during the curing process. An enhancement in the overall quality and in-service performance of a completed epoxy material can be developed by uniform curing, which can also prevent incomplete curing, entrapped bubbles, and air or voids in the materials [10].

The curing process of most thermosets like epoxy resin generates a lot of heat, and the extent of this heat is a function of time, location, conduction, and heat exchange with the environments. Low thermal conductivity of the casting causes to vary temperature and rate of reaction significantly through the casting and generate high peak temperature in the middle of the part, especially it is true for large epoxy samples. Internal and residual stresses, and consequently cracking or crazing will be developed by large temperature differences within a casting during cure. Uniform cure, temperature, and properties inside an element can be achieved by controlling the mold temperature profile [11]. Correspondingly, variation of local thermal histories and accordingly different curing process thorough an epoxy sample enhance a discrepancy of the local mechanical properties. Adjusting the cure time and temperature can control this variation. Obtaining a proper model to allow the curing process being controllable completely, needs to consider both the thermal process and polymerization together [11].

For a large epoxy sample, both the material properties and the geometry of the part are most effective to optimize the cure process, especially the part thickness which considerably influences the cure performance [12]. Also, only for thin epoxy sample and a small quantity of material, the cure cycle is usually provided by manufacturers [13]. Because of the low-temperature gradient through a thin element, the different thermal curing cycles are easy to apply. Nevertheless, the geometry of large epoxy samples causes a considerable temperature gradient during cure [12]. The manufacturer's recommendations did not report the thermal cure cycle for a large epoxy, and to obtain an appropriated thermal cure cycle usually it consumes a lot of time, and can leftover considerable amounts of material, particularly for large epoxy parts. However, determination a suitable and even optimized thermal cure cycle for large epoxy samples is most important [14]. Simulation of the curing process of thermosetting materials such as epoxy resin is an important tool, and it can provide valuable information to predict some defects before gelation and curing process [15]. In the work of Kasza et al. [16], the inverse approach was developed to determine the coefficients of the curing kinetics model, and their presented results showed that the inverse analysis was an appropriate approach to estimate the unknown material kinetics parameters. They reported that the size of the employed samples was the excellent advantage of the

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inverse analysis of the curing kinetics model in comparison with conventional procedures based on Differential Scanning Calorimetry (DSC) and other device measurements which requires small and homogeneous samples. Preparation of such samples is difficult, especially for the complex structure composites. In contrast, there is no limitation for the size of the object in the experiments for inverse analysis, and it can be accomplished for large-scale samples.

There are many numerical models on the curing of thick epoxy composites, but, on the cure simulation of large epoxy casting, particularly for optimization of their thermal cure cycle, a few works were performed [17]. Therefore, the main aim of the present work is to control the peak heat generation rate from the exothermic cross-linking, to minimize temperature gradients of the material. For simulation, a thermal cure cycle was developed and optimized by the inverse analysis and the optimization algorithm, and it is applied to a specific material system. In this work, for the first time, a temperature profile as an objective reference was selected. The inverse analysis was applied to determine an optimum boundary condition that it could enforce the profiles of all points to close the objective profile. The numerical simulation was conducted to predict temperature-rise during cure. The mentioned cure simulation proposes an optimal thermal cure cycle for large epoxy constructions.

2. Analyzing and modeling

2.1. Numerical simulation

The governing equations of resin flow and curing process are continuity, momentum, and energy equations [18]. The flow is laminar, the medium is considered homogeneous, and the properties such as density, viscosity and specific heat capacity vary with temperature based on the data of the work of Matysiak [18]. To model the curing process of epoxy material, the exothermic reaction effect was considered by source term $\dot{q}$, Eq. (1) in the energy equation:

$$\dot{q} = \rho\dot{\alpha}H_{\sum} \quad (1)$$

where ρ is the material density, and H∑ stands the total heat of reaction. $\dot{\alpha}$ is rate of the degree of cure (degree of cure $\alpha = H_t/H_{\sum}$ where H_t is the amount of heat generated from the beginning of the reaction until time t). In the present work, the following form of a single-stage curing kinetics model for the source term was selected [18]:

$$\dot{\alpha} = A_1 exp(-\frac{E_1}{RT})\alpha^m(1-\alpha)^n \quad (2)$$

where T and R denote the temperature and gas global constant, respectively. m, n, A1, and E1 are the parameters of the curing kinetics model which should be determined including the total heat of reaction by the inverse analysis. It is noticeable that these parameters are dependent on the materials type and composition.

Additional unsteady scalar conservation equation for α is used to capture the changes of the degree of curing value based on the following equation:

$$\frac{\partial(\rho\alpha)}{\partial t} + \nabla\cdot(\rho\vec{V}\alpha) = \rho\dot{\alpha} \quad (3)$$

where $\vec{V}$ defines the velocity of casting.

In this study, an unsteady and 2D- axisymmetric double precision model using CFD code based on finite volume method was utilized numerically to solve the system of equations. Coupling between continuity and momentum through pressure was solved by the PISO algorithm. Body forced weighed scheme with a second-order upwind scheme for the convective terms were used to discretize the equations. The no-slip condition was used for the walls. For each sample a particular temperature profile was utilized as boundary condition. The geometry and all points choosing for investigation of temperature profile and for the inverse analysis application were selected based on [18], and it was used to simulate this axisymmetric casting sample as shown in Fig. 1.

To confirm grid-independency of the results, several tests were performed, and finally, a uniform structured grid included 3519 cells was found to be enough and accurate. Also, for finding the optimum computational time, several tests with different time-step values were carried out. Eventually, time-step equal to 60 s was proper and applied for all simulations. It is noticeable that the time step of the present study was 60 times more than the one of [18]. It significantly reduced the computational time without decreasing accuracy, particularly considering the number of simulations needed in each iteration of the inverse analysis.

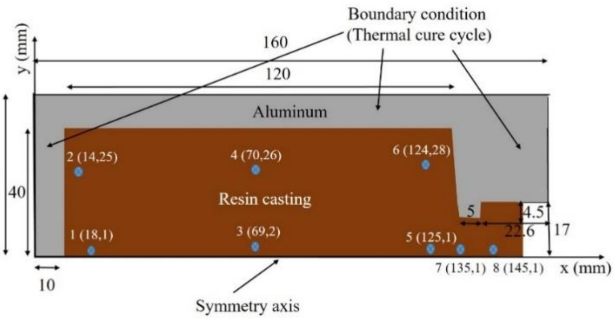

Figure 1. Schematic of the geometry, selected points and boundary condition of the epoxy sample [18]

2.2. Proposed optimization algorithm

In the inverse approach, the curing kinetics parameters are initially guessed, and then the temperature profile of the selected points are predicted by numerical simulation. The obtained temperature variations are compared with the measured data based on the defined objective function. If the value of the object function becomes more than the pre-defined specific criterion, the temperature distribution must be recalculated using new parameters. This process performs iteratively to minimize the objective function as follows.

$$OF = \sum_{i=1}^{I}\sum_{j=1}^{J}(T_{i.j}^{m} - T_{i.j}^{e})^2 \quad (4)$$

In this relation $T_{i.j}^{m}$ and $T_{i.j}^{e}$ are measured and estimated temperatures that they represent temperature at i-th location and j-th time step, respectively.

As previously mentioned, Eq. (4) requires recalculation based on the reproduced parameters of the curing kinetics model. In searching literature, it has been concluded that the Levenberg-Marquardt algorithm has more sufficiency for estimating latter parameters comparing with heuristic algorithms such as particle swarm optimization [18]. As a result, to determine the curing kinetics and its related parameters, Levenberg-Marquardt algorithm was used in the inverse calculations. According to [19], the well-known Levenberg-Marquardt algorithm optimizes an arbitrary function as the following:

$$P^{k+1} = P^k + [(J^k)^{transpose}J^k + \mu^k Q^k]^{-1}(J^k)^{transpose}[T^m - T^e(P^k)] \quad (5)$$

where P is vector of unknown parameters of the curing kinetics model. The sensitivity or Jacobian matrix J ($\frac{\partial T^e}{\partial P}$) is denote as the first derivative of the estimated temperature at each time with respect to the unknown parameter P. μ is a positive scalar named damping parameter, and Q is a diagonal matrix..

3. Result and discussion

3.1. Validation and verification of numerical method

To validate and verify the reliability of the proposed optimization algorithm and the inverse approach, a comparison was made between the results of the present model and measurement of Matysiak [18]. By simulation, profiles of all points of Fig.1 were determined using the parameters of the measured and initial guess given by Matysiak [18]. Results of the proposed method and those of [18] are tabulated in Table 1. The transient comparison of temperature history for some locations is shown in Fig.2. The results show that the temperature profiles of the proposed method and measured data of Matysiak [18] have an excellent agreement.

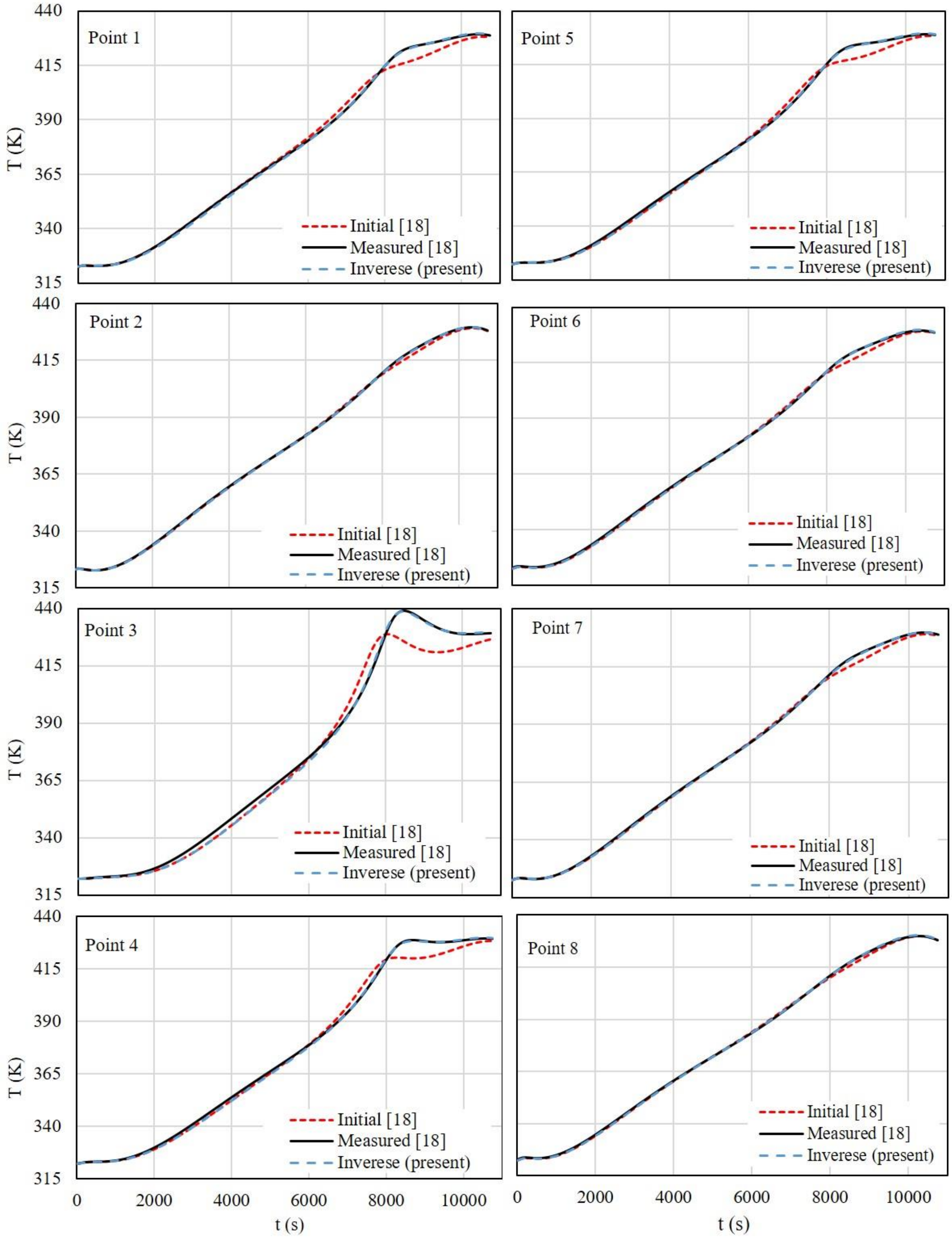

Figure 2. Comparison of the temperature profiles obtained using the measured and initial guess of work [18], and inverse parameters of present calculation

Table 1. Measured, initial and inverse curing kinetics parameters

Parameter	Measured [18]	Initial guess [18]	Proposed method
A_1	478400	406640.0	386214.6
E_1	8104.34	7942.25	8024.3
m	0.5016	0.4264	0.436
n	1.0363	0.8809	1.1115
H_Σ	112600.0	95710.0	115415.8

The inverse algorithm minimized the objective function to pre-defined specific criterion after 20 iterations. The complete simulation of the curing process was performed at least six times in each iteration. The points close to the boundary followed more the boundary condition, and their peak temperatures are lower than ones in the middle part. These differences are due to high generated heat in the exothermic reaction and low conductivity of the casting system. Using the proper thermal cure cycle can control and decrease the rate of exothermic reaction, which will be shown in the next section.

3.2. Optimization of cure cycle as an inverse

Utilizing a proper thermal cure cycle can control the exothermic reactions, and subsequently, the peak and gradient of temperature in the casting. In this section, for such consideration, an optimization of the thermal cure cycle using inverse analysis was performed. Initially, considering the constant temperature cure cycle, the temperature profiles were obtained. Temperature variation with respect to curing time is illustrated in Fig.3.

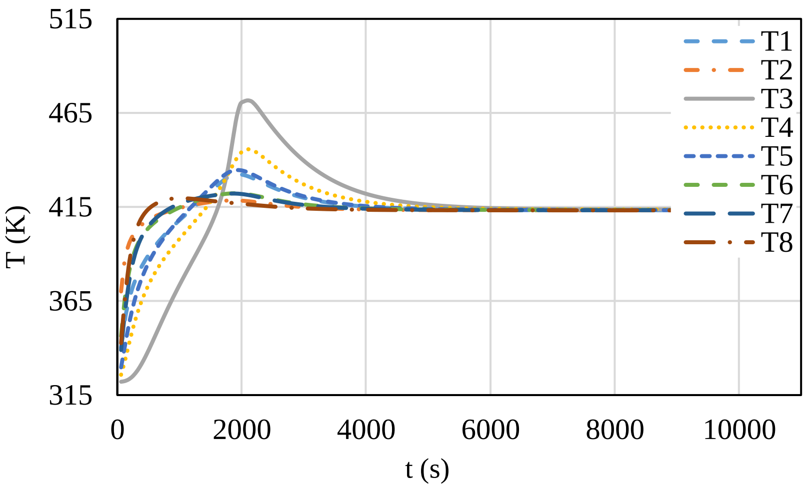

Figure 3. The temperature profiles of points in the epoxy sample for the constant temperature cure cycle (T=413.15 K)

This figure shows that there is a high peak temperature difference of about 60 ^{0}C between the maximum and minimum peak. In general, to have a better and more complete polymerization, the temperature of all points should reach 413.15 K even for a small moment. When the constant temperature cure cycle was applied, although the temperature of all points reached to 413.15 K, it generated more significant temperature gradients which are not desirable. As one observe in Fig. 3, before activation of an exothermic reaction, all domain is affected significantly by boundary condition, hence, the points close to the boundary followed more the temperature of the boundary, and those of the middle part due to low resin conductivity has lower temperature. After activation of the exothermic reaction, although the heat generates thoroughly in the casting, the maximum temperatures of casting margin are low. In fact, the heat transfers outside trough aluminum having the high conductivity contrary is high, to the middle part. Generally, these differences are due to high generated heat in the exothermic reaction and low thermal conductivity of the casting material. Using a proper thermal cure cycle can control and decrease the rate of the exothermic reaction.

Therefore, a cure cycle with seven unknown parameters was selected as illustrated in Fig. 4. Also, a pre-defined temperature profile as an objective profile was proposed to point 3, as shown in Fig. 5. Finally, the inverse analysis utilized to estimate the thermal cure cycle, which had an ability to close the temperature profile of point 3 to the pre-defined profile as shown in Fig. 5. Performing the optimization algorithm, solution converged after 27 iterations, and optimum thermal cure cycle was obtained, as depicted in Figs. 5, 6, and 7. The reducing trend of the maximum peak temperature to reach about 413.15 K during the iterations is depicted in Fig, 5. Obviously, there is good harmony and closeness between the temperature of point 3 and pre-defined profile. As it can be seen in Fig. 6, the peak temperature difference reduced from 60 to 12 ^{0}C, and also the temperature of all points reached the 413.15 K limit. Clearly, a more uniformly cure process was occurred by an 80 percent reduction in the peak temperature difference, which is excellent for any epoxy manufacturing. Fig. 7 illustrates the thermal cure cycles for several iterations. Numerical results of the initial and final parameters values of the first and 27th iterations are given in Table 2.

As illustrated in Fig. 7, the obtained thermal cure cycles from initial to final ones reached the maximum temperature at higher time as well as the peak temperature as shown in Fig. 5. The results displayed that temperature gradients and peak temperature of a large casting are strongly dependent on using processing history. On the other hand, chemical reactions propagate with respect to time from the beginning of the process. When the required time interval for the maximum temperature of the cure cycle increases, the fraction of chemical reactions at the maximum temperature of the cure cycle decreases, consequently the peak temperature becomes lower.

Table 2. Initial and inverse curing kinetics parameters

Parameter	$P_1\ (s)$	$P_2\ (s)$	$P_3\ (s)$	$P_4\ (s)$	$P_5\ (s)$	$P_6\ (K)$	$P_7\ (K)$
Initial	900	2700	1800	1800	3600	363.15	363.15
Final	1852.8	3036.9	2248.6	524.3	2558	377.55	338.55

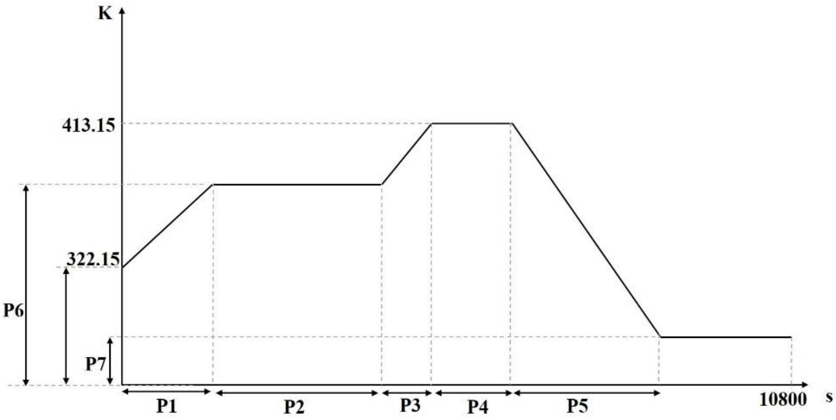

Figure 4 A cure cycle with seven unknown parameters

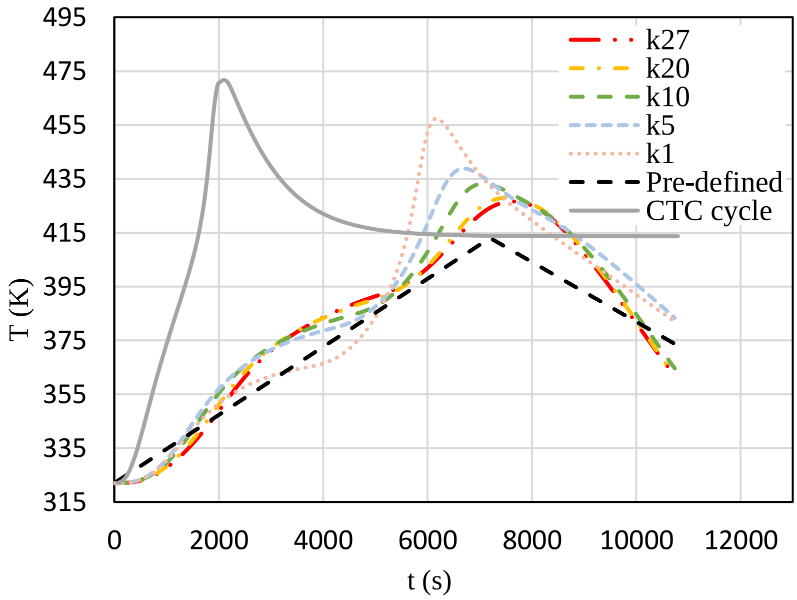

Figure 5 Temperature profiles of point 3 for pre-defined, constant temperature cure cycle (CTC) (T=413.15 K) and iterations 1, 5, 10, 20 and 27

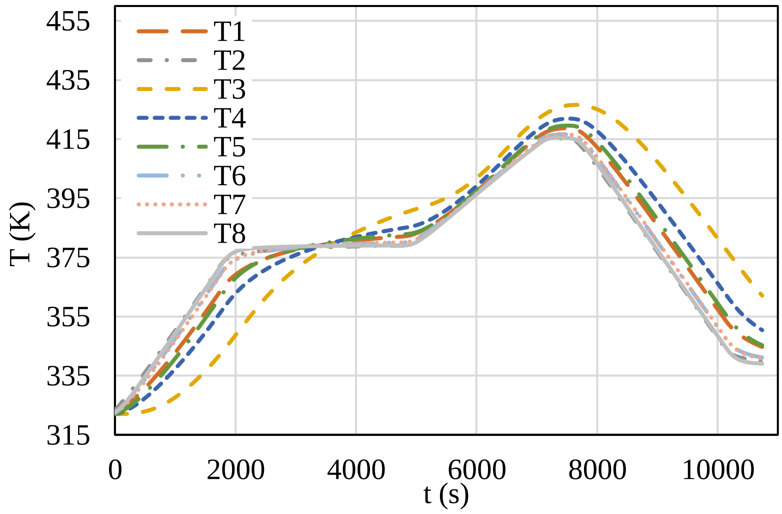

Figure 6 Temperature profiles of all points of the sample epoxy for optimum thermal cure cycle

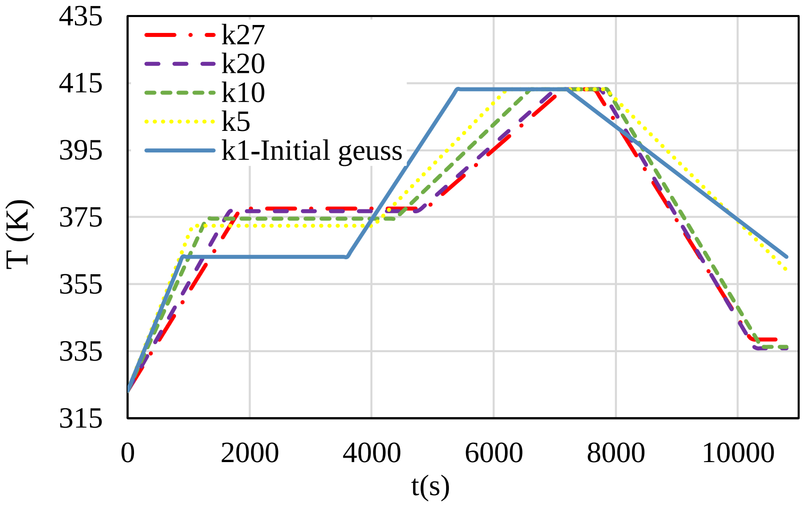

Figure 7. The cure cycles for iterations 1, 5, 10, 20 and 27

4. Conclusion

High peak temperature and temperature gradients, and subsequently internal and residual stresses are developed in large casting parts due to exothermic reaction during the curing process and low thermal conductivity of epoxy resin. In the present work, a thermal cure cycle was obtained using an optimization algorithm to minimize the exothermic peak and temperature gradients of the material during the curing process. The result indicated that:

1. The applied inverse analysis and optimization algorithm were suitable to find the optimum thermal cure cycle.
2. This obtained cure cycle was most effective to minimize temperature gradients in the processing of large epoxy samples.
3. Considering the constant temperature cure cycle, the peak temperature difference was 60 0C between the maximum and minimum peak in the casting system. Utilizing the optimum cure cycle, the peak temperature difference was reduced to 12 0C.
4. The 80 percent reduction in the peak temperature difference shows more uniformly cure process.

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