Effect of cure cycle on temperature/degree of cure field and hardness for epoxy resin

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Abstract: A 3-dimensional finite element model is developed to simulate and analyze the temperature and degree of cure field of epoxy casting part during cure process. The present model based on general finite element software ABAQUS is verified by literature example and experimental data. The numerical results show good agreement with literature example and measured data, and are even more accurate than the simulation of literature. After modeling successfully, the influences of heat convection coefficients and temperature cure cycle ramps have on the temperature and degree of cure gradient are investigated. Moreover, the effect of non-uniform temperature and degree of cure field within epoxy casting part on mechanical properties is demonstrated. The present model provides an accurate and novel method that allows further insight into the process of cure for epoxy resin.

Keywords: Epoxy resin, Temperature field, Degree of cure field, Mechanical properties, Finite element method

Introduction

From their discovery by Pierre Castan in 1938 to now, epoxy resins has been attracting the interests of the industry and academia community. This is because they maintain an excellent balance between various properties such as adhesion properties, electrical insulation properties, humidity resistance, heat resistance, and mechanical properties. Otherwise, epoxy resins can be combined and cured with various curing agents with a view to producing cured and uncured blends with tuned properties [1-5].

Determination of cure cycle is one of the important factors for successful fabrication of thick epoxy product with dependable quality and at low cost. The first concern is a non-linear increase in internal temperature induced by the exothermic chemical reaction of epoxy, which results in temperature overshoot. The second concern relates to the complex temperature and degree of cure gradients that develop during the curing process. Non-uniform curing can lead to incomplete cure or resin degradation and entrapped volatiles or voids, which may ultimately cause a reduction in the overall quality and in service performance of the finished component. Therefore, numerical simulation was attempted to predict temperature rise during cure and the cure simulation was applied to suggest an optimal cure cycle for specific epoxy structures. Although little work focused on the cure simulation of epoxy, there have been many numerical models for the curing of thick thermoset matrix composites, which can be applied to epoxy.
Loos and Springer [6] developed a one-dimensional model to simulate the curing process of a flat-plate by solving the governing equation using finite difference method. Lee et al. [7-9] studied modeling for cure simulation of thick composite cylinders. They established one-dimensional cure model using the finite difference method. Bogetti and Gillespie [10] also used finite difference method to develop a two-dimensional cure simulation analysis of thick thermoset composites. They compared their simulation result with measured data and predicted the temperature and degree of cure distributions within an arbitrary cross-sectional geometry. White and Hahn [11] proposed an optimal temperature cycle that can reduce residual stress during cure of composite structures. Ciriscioli et al. [12, 13] developed an algorithm that can minimize void and residual stress inside the composite structure. They measured the temperature, ionic conductivity and compaction in thick graphite/epoxy laminates, and the data were compared to the results calculated by the Loos-Springer CURE model. Twardowski et al. [14] compared the experimental temperature profiles of a thick part to the results calculated by a one-dimensional simulation, from which the effect of initial degree of cure was investigated. Hojjati and Hoa [15] established model based on dimensionless parameters for cure of thermoset composites and predicted the temperature and degree of cure fields of a thick composite. White and Kim [16] proposed the stage cure technique for fabricating thick composites and investigated the effect of stage cure on the mode I interlaminar fracture toughness and shear strength. Yi et al. [17] conducted the finite element simulation by assuming thermal properties as a function of temperature and degree of cure. Kim and Lee [18] developed an autoclave cure cycle with cooling and reheating steps for thick thermoset composite laminates using finite difference analysis. They indicated that the developed cure cycle was effective for reducing temperature overshoot. Blest et al. [19] developed a model including resin flow, heat transfer, and the cure of multiplayer thermoset composite laminates during an autoclave processing, which was validated by comparing the numerical results with the experimental data. Park and Lee [20] developed a two-dimensional cure simulation by finite element method. They calculated through-the-thickness temperature distributions of arbitrary shape composite structures including the mandrel. Oh and Lee [21] studied the cure cycle for glass/epoxy composite laminate by 3-dimensional finite element model based on commercial finite element software ANSYS. An optimized cure cycle with the cooling and reheating steps was developed by minimizing the objective function to reduce the temperature overshoot in the composite. Park et al. [22] introduced a three-dimensional finite element model can be used for cure simulation of composite structures with arbitrary geometry under non-uniform autoclave temperature distribution. Guo et al. [23] developed a cure model for thermoset matrix laminates also based on ANSYS, and proved the conventional cure cycles recommended by prepreg manufacturers for thin laminates should be modified to reduce out-of-plane temperature gradient. Yan [24] developed a two-dimensional finite element model to simulate and analyze the mechanisms pertaining to resin flow, heat transfer, and consolidation of laminates during autoclave processing. Numerical examples, including a comparison of the numerical results with one-dimensional and two-dimensional analytical solutions, were given to validate the finite element formulation. Yan [25] conducted two-dimensional cure simulation of thick thermosetting composites by using a weighed residual method. Numerical examples proved that heat transfer anisotropy has an important effect on the temperature field.
In most of the previous researches, the temperature and degree of cure fields were simulated using one or two dimensional finite difference analysis. Only a few literatures studied the temperature and degree of cure fields by finite element analysis. Although several special-purpose numerical software’s have been developed to study the curing process, little literature analyze this issue by means of general-purpose numerical software [21,23]. General-purpose finite element software has well developed pre- and post-processors, especially for finite element analytic software ABAQUS which has original advantage in dealing with non-linear coupled problem. The objective of this study is to gain a fundamental understanding of the cure process unique to thick epoxy casting product. Three-dimensional transient heat transfer finite element model during cure cycle for a thick epoxy cylinder part is established by ABAQUS with its subroutines in FORTRAN. The simulation of the cure process accounts for thermal and chemical interactions during cure process. The effect of temperature cycle on the hardness of epoxy is also discussed.

Heat conduction analysis and FEM equations

Equations of heat conduction and curing kinetics

The heat conduction process of composite materials curing is a transient thermal transfer process with nonlinear internal heat generation source, which is from the exothermic enthalpy of resin matrix curing process. According to Fourier’s heat conduction equation and energy conservation law, the mathematical model was established as follows:

\[ \rho V_r H_r \frac{d\alpha}{dt} + k_{xx} \frac{\partial^2 T}{\partial x^2} + k_{yy} \frac{\partial^2 T}{\partial y^2} + k_{zz} \frac{\partial^2 T}{\partial z^2} = \rho C_p \frac{\partial T}{\partial t} \]

where \( k_{xx}, k_{yy}, k_{zz} \) are heat transfer coefficients of \( x, y, z \) directions, respectively; \( \rho \) and \( C_p \) are the density and the specific heat of composite material; \( \rho_t, V_r, \alpha, d\alpha/dt \) are the density, volume fraction, degree of cure, curing rate of resin; \( H_r \) is the exothermic enthalpy from resin curing process. The rate of cure could be expressed by the function of degree of cure and time, the formula of which is given through the study of resin curing kinetics:

\[ \frac{d\alpha}{dt} = f(\alpha, t) \]  \hspace{1cm} (1)

The convection boundary condition is:

\[ n_{xx} k_{xx} \frac{\partial T}{\partial x} + n_{yy} k_{yy} \frac{\partial T}{\partial y} + n_{zz} k_{zz} \frac{\partial T}{\partial z} = -h(T - T_\infty) \]  \hspace{1cm} (2)

where \( n_{xx}, n_{yy}, n_{zz} \) are the components of exterior normal on the boundary, regarding to \( x, y, z \) axis; \( h \) is the heat exchange coefficient between boundary and media nearby; \( T_\infty \) is the temperature of media nearby. In the case of \( h \to \infty \), the boundary condition could be converted to temperature boundary condition; when \( h \to 0 \), it could be converted to adiabatic boundary condition.

Then initial condition is

\[ T = T_0 \]
\[ \alpha = 0 \]  \hspace{1cm} (3)
where $T_0$ is the temperature of inner composite material at the initial time.

The heat outflow process of resin is defined by ABAQUS subroutine HETVAL; degree of cure is defined by ABAQUS subroutine USDFLD; the convection boundary condition is defined by ABAQUS subroutine FILM; temperature boundary condition is defined by ABAQUS subroutine DISP.

**Discrete FEM equations**

Using 3-D 8 nodes element DC3D8 in ABAQUS (shown in Figure 1), the degree of freedom of nodes are temperature and degree of cure. Applying the same shape function $N(X)$ to temperature $T$ and degree of cure $\alpha$, their approximation functions are:

$$T(X,t) \approx N(X,t)T(t)$$
$$\alpha(X,t) \approx N(X,t)\alpha(t)$$ \hspace{1cm} (4)

where, $X=(x, \ y, \ z)$ is the location vector. Substituting Eq. (5) into Eqs. (1)-(4), we have the discrete FEM equations of heat conduction and curing kinetics.

$$C_T\dot{T} - \rho H\ C_\alpha \dot{\alpha} + (K_T + K_h)T = F_h$$
$$C_\alpha \dot{\alpha} = F_\alpha$$ \hspace{1cm} (5)

where,

$$C_T = \int_v N^T \rho C_T NdV$$
$$C_\alpha = \int_v N^T NdV$$
$$K_T = \int_v B^T KBdV$$
$$K_h = \int_{S_h} N^T hNdS_h$$
$$F_h = \int_{S_h} N^T KT_\alpha dS_h$$
$$F_\alpha = \int_v \bar{f}(\alpha, T)dV$$

$$B = \begin{bmatrix}
\frac{\partial N_1}{\partial x} & \cdots & \frac{\partial N_m}{\partial x} \\
\frac{\partial N_1}{\partial y} & \cdots & \frac{\partial N_m}{\partial y} \\
\frac{\partial N_1}{\partial z} & \cdots & \frac{\partial N_m}{\partial z}
\end{bmatrix}$$ \hspace{1cm} (6)

$N_i$ is the shape function at the ith node; $N$ is the shape function matrix; $h$ is the heat exchange coefficient. The element stufiness matrix $K_h$ is only valid for the nodes on boundaries, and load vector $P_h$ only works for total load vector of the nodes on boundaries.

Since thermochemistry problem is the question of coupled fields, thus, Eq. (6) could be represented as matrix form:
\begin{equation}
\begin{pmatrix}
C_T & -\rho H_a C_a & \\
0 & C_a & \\
\end{pmatrix}
\begin{bmatrix}
\dot{T} \\
\end{bmatrix}
+
\begin{pmatrix}
K_T + K_h & 0 & \\
0 & 0 & \\
\end{pmatrix}
\begin{bmatrix}
T \\
\end{bmatrix}
=
\begin{bmatrix}
F_h \\
F_a \\
\end{bmatrix}
\end{equation}

which could also be simplified as:
\begin{equation}
C \dot{U} + KU = F
\end{equation}

The Eq. (9) is the final discrete FEM equations.

**Fig. 1.** DC3D8 element.

**Time integral**

A series of ordinary differential equations in time period are represented by Eq. (9), which is integrated in time field in order to solve the transient heat transfer process. Normally, it is not possible to get the analytical solution of these equations. Thus, they are approximately expressed by algebraic equations. \( \theta \) method is a common method used to solve the first order differential equations. Using \( \theta \) method, \( U(t) \) in Eq. (9) could be represented as:

\begin{equation}
U(t) \approx U(t - \Delta t) + \left[ (1 - \theta) \dot{U}(t - \Delta t) + \theta \dot{U}(t) \right] \Delta t
\end{equation}

When \( \theta = 0 \), it's a full explicit Euler method; When \( 0 < \theta \leq 1 \), it belongs to implicit differential. In the case of \( 0 < \theta < 1 \), it is first order accuracy, except when \( \theta = 1/2 \) it is first order accuracy. Besides, the results are conditional stable when \( 0 \leq \theta < 1/2 \). Regarding to \( 1/2 \leq \theta \leq 1 \), there is unconditional stable result. Therefore, we choose \( \theta = 1/2 \).

Assuming the specific heat and density of material is constant in the process of cure, we applied to \( \theta \) method Eq. (9) with the assumption of \( \theta = 1/2 \):

\begin{equation}
\left( \frac{C}{\Delta t} + \frac{1}{2} K^n \right) U^n = \left( \frac{C}{\Delta t} - \frac{1}{2} K^{n-1} \right) U^{n-1} + \frac{1}{2} P^n + \frac{1}{2} P^{n-1}
\end{equation}

where \( n \) and \( n-1 \) are the current and previous time step, respectively.
**Iteration of Newton-Raphson method**

In ABAQUS, Newton-Raphson method with quadratic convergence is employed to solve nonlinear problems.

\[ U^{n,k} \] represents the \( k \)th Newton-Raphson iteration result in the solving process for \( U^n \). Stagger vector is \( R^{n,k} \) defined as:

\[
R^n_k = \left( \frac{C}{\Delta t} + \frac{1}{2} K^n_k \right) U^n_k - \left( \frac{C}{\Delta t} - \frac{1}{2} K^{n-1}_k \right) U^{n-1}_k - \frac{1}{2} P^n_k - \frac{1}{2} P^{n-1}_k
\]  \( \text{(11)} \)

Eq. (11) is satisfied when \( R^{n,k} = 0 \).

The tangent stiffness matrix \( \frac{\partial R^{n,k}}{\partial U^n_k} / \partial K^{n,k} \) used in Newton-Raphson iteration could be solved by Eq. (12):

\[
\frac{\partial R^n_k}{\partial U^n_k} = \frac{C}{\Delta t} + \frac{1}{2} K^n_k + \frac{1}{2} \frac{\partial K^n_k}{\partial U^n_k} - \frac{1}{2} \frac{\partial P^n_k}{\partial U^n_k}
\]  \( \text{(12)} \)

Considering Eq. (13) in matrix form, the stagger vector (Eq. (14)) and tangent stiffness matrix (Eq. (15)) are given as:

\[
R^n_k = \begin{bmatrix}
\frac{1}{\Delta t} \left( C_T - \rho H_T C_a \right) + \frac{1}{2} \begin{bmatrix} K^n_{T_k} + K^n_{hk} & 0 \\
0 & 0 \\
0 & 0
\end{bmatrix}
\end{bmatrix} T^n_k
\]  \( \text{(13)} \)

\[
\frac{\partial R^n_k}{\partial U^n_k} = \begin{bmatrix}
\frac{1}{\Delta t} \left( C_T - \rho H_T C_a \right) + \frac{1}{2} \begin{bmatrix} K^n_{T_k} + K^n_{hk} & 0 \\
0 & 0 \\
0 & 0
\end{bmatrix}
\end{bmatrix} T^n_k
\]  \( \text{(14)} \)

During each step of Newton-Raphson iteration, Eq. (16) is used to solve \( \delta U^n_{k,k} \):

\[
\frac{\partial R^n_k}{\partial U^n_k} \delta U^n_k = -R^n_k
\]  \( \text{(15)} \)

Substituting Eqs. (14-15) into Eq. (16), the final form of increment for \( \delta U^n_{k,k} \) is:

\[
\begin{bmatrix}
K^n_{k11} & K^n_{k12} \\
K^n_{k21} & K^n_{k22}
\end{bmatrix}
\begin{bmatrix}
\delta T^n_k \\
\delta \alpha^n_k
\end{bmatrix}
= \begin{bmatrix}
-R^n_{T_k} \\
-R^n_{\alpha_k}
\end{bmatrix}
\]  \( \text{(16)} \)
where,
\[ K_{k11}^n = \frac{C_T}{\Delta t} + \frac{1}{2} \left( K_{Tk}^n + K_{hk}^n \right) + \frac{1}{2} \left( \frac{\partial K_{Tk}^n + K_{hk}^n}{\partial T^n} T_k^n - \frac{1}{2} \frac{\partial P_{hk}^n}{\partial T^n} \right) \]
\[ K_{k12}^n = -\frac{\rho H C_a}{\Delta t} + \frac{1}{2} \left( \frac{\partial (K_{Tk}^n + K_{hk}^n)}{\partial \alpha^n} - \frac{1}{2} \frac{\partial P_{hk}^n}{\partial \alpha^n} \right) \]
\[ K_{k22}^n = \frac{C_a}{\Delta t} + \frac{1}{2} \frac{\partial P_{hk}^n}{\partial \alpha^n} \]
\[ R_{nk}^n = \left[ \frac{C_T}{\Delta t} + \frac{1}{2} \left( K_{Tk}^n + aK_{hk}^n \right) \right] T_{k}^n - \frac{\rho H C_a}{\Delta t} C_{k}^n - \frac{1}{2} p_{hk}^n \]
\[ - \left[ \frac{C_T}{\Delta t} - \frac{1}{2} \left( K_{Tk}^{n-1} + K_{hk}^{n-1} \right) \right] T_{k}^{n-1} + \frac{\rho H C_a}{\Delta t} C_{k}^{n-1} - \frac{1}{2} p_{hk}^{n-1} \]
\[ R_{\alpha k}^n = \frac{C_a}{\Delta t} \alpha_{k}^n - \frac{1}{2} p_{\alpha k}^n - \frac{C_a}{\Delta t} \alpha_{k}^{n-1} - \frac{1}{2} p_{\alpha k}^{n-1} \]

It could be concluded from Eq. (17) that temperature and degree of cure should be iterated simultaneously in the whole Newton-Raphson iteration. Solving the \( \delta U^n_{i,k} \) increment, the solution on the node is updated as:
\[ U_{i,k+1}^n = U_{i,k}^n + \delta U_{i,k}^n \] (17)

The iteration is stopped when the iteration result is less than the preset iteration error.

Results and Discussion

Model verification

The finite element program calculating curing process of thermoset composite materials is coded combining finite element software ABAQUS and subroutines in FORTRAN. Employing the data from literature \([10]\) for validation, \([0/90]\) glass/polyester laminate is studied and the material property is listed in Table 1. The composite curing kinetic equation is:
\[ \frac{d\alpha}{dt} = A \exp(-\Delta E / RT) \alpha^n (1-\alpha)^n \] (18)

**Tab. 1.** Thermal properties of glass/polyester composite.

<table>
<thead>
<tr>
<th>( \rho )</th>
<th>( C_p )</th>
<th>( K_{xx} )</th>
<th>( K_{yy} = K_{zz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg·m(^{-3})</td>
<td>J·kg(^{-1})·K(^{-1})</td>
<td>W·m(^{-1})·K(^{-1})</td>
<td>W·m(^{-1})·K(^{-1})</td>
</tr>
<tr>
<td>1890</td>
<td>1260</td>
<td>0.4326</td>
<td>0.2163</td>
</tr>
</tbody>
</table>
The values of parameters of above equation are listed in Table 2, where $R$ is universal gas constant, $T$ is absolute temperature, $m$ and $n$ are exponents, $A$ is pre-exponential coefficients, and $H_r$ is the total heat of reaction.

**Tab. 2.** Cure kinetics parameters for glass/polyester composite.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$/min$^{-1}$</td>
<td>$3.7 \times 10^{22}$</td>
</tr>
<tr>
<td>$\Delta E$/J·mol$^{-1}$</td>
<td>$1.674 \times 10^5$</td>
</tr>
<tr>
<td>$m$</td>
<td>0.524</td>
</tr>
<tr>
<td>$n$</td>
<td>1.476</td>
</tr>
<tr>
<td>$R$/kJ·kg$^{-1}$·mol$^{-1}$·K$^{-1}$</td>
<td>8.31434</td>
</tr>
<tr>
<td>$H_r$/J·kg$^{-1}$</td>
<td>77500</td>
</tr>
</tbody>
</table>

The dimension of the composite laminate in the example is 15.24×15.24×2.54 cm. The heat convection coefficients on the top and bottom surfaces are 37.636 W·m$^{-2}$·K$^{-1}$ and 54.075 W·m$^{-2}$·K$^{-1}$, respectively. In addition, insulated boundary conditions were employed on the sides to isolate through the thickness effects. Figure 2 gives the comparison of temperature between calculation results and experimental results from the literature, located in the center of the laminate, from which the validation of the model in this paper is verified. It can be also concluded from Figure 2 that the results from the model in this paper is closer to experimental data than the calculation results from the literature [10].

![Fig. 2. Temperature profiles at the center point of 2.54 cm thickness laminate.](image)

The cure kinetic model of the epoxy resin was obtained using the Netzsch DSC204 F1. The isothermal scanning tests were conducted with constant temperatures. The reaction rate expression for the epoxy resin was given as Eq. (20). Figure 3 shows comparison between the heat flow rate measured during the isothermal scanning and those calculated by the cure kinetic model of Eq. (20). The developed cure kinetic model agreed well with the experimental results. The thermal properties and cure kinetic parameters of the epoxy resin are presented in Table 3 and Table 4 respectively.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1-\alpha)^n$$  \hspace{1cm} (19)
where \( k_1 \) and \( k_2 \) and defined by the Arrhenius rate expressions:

\[
k_1 = A_1 \exp(-\Delta E_1 / RT)
\]

\[
k_2 = A_2 \exp(-\Delta E_2 / RT)
\]

(20)

**Fig. 3.** Cure rate versus degree of cure for epoxy.

**Tab. 3.** Thermal properties of epoxy.

<table>
<thead>
<tr>
<th>( \rho/)</th>
<th>( C_p/)</th>
<th>( K_{xx}= K_{yy}= K_{zz}/)</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg.m(^{-3})</td>
<td>J-kg(^{-1})-K(^{-1})</td>
<td>W-m(^{-1})-K(^{-1})</td>
</tr>
<tr>
<td>1225</td>
<td>967</td>
<td>0.191</td>
</tr>
</tbody>
</table>

**Tab. 4.** Cure kinetics parameters for epoxy.

<table>
<thead>
<tr>
<th>( A_1/)min(^{-1})</th>
<th>1246.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_2/)min(^{-1})</td>
<td>49.26</td>
</tr>
<tr>
<td>( E_1/J-mol^{-1})</td>
<td>38330</td>
</tr>
<tr>
<td>( E_2/J-mol^{-1})</td>
<td>20000</td>
</tr>
<tr>
<td>( m)</td>
<td>0.786</td>
</tr>
<tr>
<td>( n)</td>
<td>3.207</td>
</tr>
<tr>
<td>( R/kJ-kg^{-1}-mol^{-1}-K^{-1})</td>
<td>8.31434</td>
</tr>
<tr>
<td>( H/J-kg^{-1})</td>
<td>277000</td>
</tr>
</tbody>
</table>

Because the glass mould is very thin, it was assumed that the resin part contacted with exterior environment directly. The epoxy cylinder part with 12 cm diameter and 1.2 cm height was subjected to cure cycle temperature history indicated in Figure 4 with specified \( h=5 \) W-m\(^{-2}\)-K\(^{-1}\). Figure 4 illustrates the comparison of temperature between calculation results and experimental results of the epoxy concerned, located in the center of the cylinder part, from which the validation of the model is verified.
Fig. 4. Temperature profile of epoxy cylinder part.

**Boundary condition effects**

The internal oven environment can profoundly influence the heat transfer to the resin and may ultimately alter the curing process within the part. The surface temperature variation of the part may be significantly different from the prescribed cure cycle temperature. While convective heat transfer due to heat flow within the oven is not modeled explicitly, flexibility with the convective heat transfer coefficient enables the influence of the effective heat transfer to the part on the curing process to be investigated.

Fig. 5. Influence of $h$ on temperature profiles in an epoxy part.

The following example demonstrates the influence $h$, can have on the curing process. An epoxy casting part as described above was subjected to cure cycle temperature
history indicated in Figure 5 with specified \( h = 5 \text{ W/m}^2\text{K}^{-1} \) and \( h = 20 \text{ W/m}^2\text{K}^{-1} \) on the surfaces respectively. Model calculated temperature profiles at the surface point (in this paper surface point means the point on the cylinder side with half height) and center point of the epoxy part are shown in Figure 5. The higher \( h \) permits a more rapid transfer of heat into the part, causing the part to heat up and cure faster. This also allows more heat to escape from the part during the exotherm, resulting in an overall lower exotherm and lower value of maximum center point temperature minus maximum surface point temperature.

Figure 6 shows the corresponding degree of cure profiles, demonstrates the significant influence \( h \) can have on the curing process. Higher \( h \) decreases degree of cure gradients during the exotherm. The effective heat transfer across the part surface plays an important role in the development of residual stress and warpage during processing.

![Graph showing temperature profiles](image)

**Fig. 6.** Influence of \( h \) on degree of cure in an epoxy part.

*Cure cycle temperature ramp effects*

The cure cycle temperature ramp can strongly influence the temperature and degree of cure gradients that develop during the cure. The effect of the temperature cure cycle ramp on the degree of cure gradients is examined in an epoxy part described above exposed to various cure cycle temperature ramps. The epoxy part with specified temperature and convective boundary conditions (\( h = 5 \text{ W/m}^2\text{K}^{-1} \)) on all the surfaces is used here respectively. The temperature cure cycle is illustrated in Figure 7. Predicted values of the degree of cure at the center point minus the degree of cure at the surface point of the part (\( \alpha_c - \alpha_s \)), are plotted in Figure 8 and Figure 9 as a function of cycle time for the various temperature ramps investigated, respectively. Both Figure 8 and Figure 9 show a negative peak and the absolute peak value in Figure 9 exceeded in Figure 8. This could be due to that heat transfer by diffusion is low, the surface cure reaction took place earlier than center point, and the heat transfer with temperature boundary condition is more rapid than with convective boundary condition. It is also concluded that with the temperature ramp increasing, the final value of (\( \alpha_c - \alpha_s \)) rise.
Fig. 7. Temperature cure cycle ramps.

Fig. 8. Effect of the temperature ramp on non-uniform curing in epoxy part with temperature boundary condition.

Figure 8 and Figure 9 were local amplified when the curves deviated from each other. It indicated that the value of \((\alpha_c - \alpha_s)\) steadily increased from negative value to positive value for convective boundary condition. While for the temperature boundary condition, the value of \((\alpha_c - \alpha_s)\) decreased from positive value to negative value, and then increased to positive value again. Otherwise, with the temperature ramp increasing, the absolute negative peak value rise. Consequently, the surface temperature initiates the cure reaction. The exothermic reaction accelerates the cure and as a result creates non-uniform degree of cure field interior to the part. Non-uniform curing potentially entraps voids and volatile byproducts of the cure reaction and enhances warpage and residual stress development. It can be concluded that,
the temperature ramp can significantly influence the quality and in-service performance of epoxy plate.

**Fig. 9.** Effect of the temperature ramp on non-uniform curing in epoxy part with convective boundary condition.

**Effects on hardness**

Since normal mechanical testing cannot reflect the mechanical property of single point of epoxy part, Shore hardness is used here to evaluate the mechanical property of single point of epoxy part. The tested positions are showed in Figure 10, and the hardness of which (average value of 5 times test) is listed in Table 5. Samples for measurement are the epoxy casting part described above cured at the temperature cycle illustrated in Figure 5, with convective boundary conditions \( h = 5 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1} \) on all the surfaces. It was assumed that epoxy resin with higher degree of cure could have better mechanical property, but the data listed in Table 5 does not obey this simple rule. Consequently, the mechanical property is not only related to the degree of cure but to the thermal history during cure process.

**Fig. 10.** Hardness measurement point of epoxy part.

Figure 11 illustrates the thermal history for each point. Without considering the postcure process, the value of temperature peak decreased for point A to point F,
while point D has the highest Shore hardness. The high temperature overshoot can cause the problem of a runaway thermal reaction, resulting in material degradation and mechanical property decline. Otherwise, excessive low temperature causes low degree of cure, decrease mechanical property as well. It is essential for epoxy resin casting part that designs a proper temperature cycle neither causes temperature overshoot nor results in incomplete cure. With the objective to improve the mechanical property of epoxy resin casting part, the cure cycle optimum design technique will be studied in our next paper.

![Fig. 11. Temperature profiles of epoxy part.](image)

<table>
<thead>
<tr>
<th>Position</th>
<th>Point A</th>
<th>Point B</th>
<th>Point C</th>
<th>Point D</th>
<th>Point E</th>
<th>Point F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final degree of cure/10³</td>
<td>926.115</td>
<td>926.104</td>
<td>926.091</td>
<td>926.040</td>
<td>925.874</td>
<td>925.346</td>
</tr>
<tr>
<td>Hardness</td>
<td>76</td>
<td>76</td>
<td>82</td>
<td>90</td>
<td>80</td>
<td>74</td>
</tr>
</tbody>
</table>

**Tab. 5.** Final degree of cure and Hardness of epoxy part.

**Conclusions**

In this paper, a 3-dimensional finite element model based on general finite element software ABAQUS was developed to study the temperature and degree of cure distribution in epoxy casting part during cure process. The present model is validated by example from literature and experimental data. The predicted results show good agreement with literature example and measured data, and are even more accurate than the simulation of literature. By applying present model, the influences of heat convection coefficients and temperature cure cycle ramps have on the temperature and degree of cure gradient are investigated. Moreover, the effect of non-uniform temperature and degree of cure field within epoxy casting part on mechanical properties is demonstrated. The non-linear internal heat source and heat transfer process causes non-uniform temperature and degree of cure field in internal epoxy part. By comparing the calculated temperature profile and degree of cure with Shore hardness of a series of internal locations, it indicates that mechanical property not
only depends on the degree of cure but on the thermal history during cure process. This work, therefore, represents an accurate and novel method that allows further insight into the process of cure for epoxy resin, which can improve mechanical property and in-service performance of the finished component by reducing warpage and residual stress during the cure process. The cure cycle optimum design technique for improving the mechanical property of epoxy resin casting part will be studied in our next paper.

**Experimental**

**Materials and sample preparation**

The resin used in this paper was obtained by mixing Diglycidyl ether of bisphenol-A(DGEBA)-based epoxy (E-51 and E-20 from Wuxi resin factory) and cure agent DAMI (Long chain flexible aromatic amine, developed by advanced polymer materials institute, Nanjing university of technology). The mixture was prepared at 130 °C with continuous stirring, and then poured into the cylindrical glass-mould of 12 cm diameter.

**Temperature and mechanical property measurements**

The cylindrical glass-mould with the resin sample was put in an oven heated by air with preset temperature profile. The temperature profiles at various locations within the epoxy casting part were measured by thermocouple, and recorded by computer. The hardness values of samples were tested by Shore D-type hardness instrument.

**References**