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Effects of key thermophysical properties on the curing uniformity of carbon fiber reinforced resin composites

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Abstract: Key thermophysical properties of the thermosetting resin, including density, conductivity coefficient and specific heat that evolve with resin curing, are related to temperature and curing degree fields of the fiber/resin composite material. However, their effects on heat transfer inside composite materials, consequently on the curing non-uniformity in thick-section laminates, are not well understood. The focus of this study is on the effects of key thermophysical properties of resin on the curing uniformity of AS4/3501-6 composite by means of the coupled thermochemical analysis with the method of numerical simulation. The results clearly indicate that the conductivity coefficient and specific heat of resin have obvious influence on curing uniformity, especially for thick laminates, while the density of resin has no noticeable effect on the curing uniformity. The simulation results can help to guide the material preparation of industrial production.

Keywords: carbon/epoxy composites; curing uniformity; thermochemical model; thermophysical property.

1 Introduction

Undesired cure-induced residual stresses are an inherent issue within the fiber/epoxy composite curing process (1). With wide range applications of carbon fiber/epoxy composites in aerospace, military, ship industries and civil infrastructure, influencing factors of process-induced residual strain and stress that can deteriorate the mechanical properties and dimensional stability of the final industrial structures have received much interest in published literatures (2–6). Bogetti and Gillespie analyzed the effects of processing history, composite thickness, resin cure shrinkage and layup style on the evolution of curing deformation and residual stress during the curing process (2). Johnston et al. (3) analyzed the effects of laminate layup and tool/part interaction on the spring-back angles for angle laminates. Kim et al. (4) investigated the effects of cure cycle on internal strain during the curing process. Kappel et al. (5) discussed the effects of different layups on process distortions based on experimental studies. Zhang et al. (6) found that higher curing temperature in composite joints would result in an obvious increase of the residual stress.

A number of factors may induce the evolution of residual stress during the curing process. However, thermophysical properties of the thermosetting resin, including density, conductivity coefficient and specific heat, varying with temperature and curing degree, are usually ignored in curing process modeling. In most of the present simulations, above properties of resin were assumed independent of temperature and curing degree (1, 7). Actually, the properties of a fully cured resin could be 30%–40% higher than that of an uncured resin (8). If it was overlooked, such a variation in thermal properties of resin may lead to inaccurate results during curing process simulation. Therefore, from the perspective of the precise prediction about the cure characteristics of the composites, the variation of thermophysical properties should be considered. In the study of Shin and Hahn (9), although variable resin properties were considered in the modeling of temperature field, their effects on the curing uniformity of composites were not well understood.

From the definition formulas of thermal strain ($\varepsilon_{th} = \text{CTEs} \cdot \Delta T$) and chemical shrinkage strain ($\varepsilon_{th} = \text{CTE} \cdot \Delta\alpha$) (1, 2), it can be clearly noted that non-uniform temperature field and curing degree field are important reasons for the evolution of residual stress. Thermophysical properties that are related to the thermal characteristics of fiber/resin composite in non-isothermal environment may lead to curing non-uniformity within composite and then indirectly affect the residual stress and curing deformation. In this paper, with the aid of the software COMSOL, the simulation is organized to analyze the effects of key thermophysical

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properties on the temperature field uniformity and curing degree field uniformity, which can provide a theoretical foundation for further research.

2 Theoretical models

The governing equation with the non-linear heat generation for heat transfer model is described by the following equation (1, 10):

$$\rho_c C_{pc}\frac{\partial T}{\partial t}=\left(k_{xx}\frac{\partial^2 T}{\partial x^2}+k_{yy}\frac{\partial^2 T}{\partial y^2}+k_{zz}\frac{\partial^2 T}{\partial z^2}\right)+\frac{\partial H}{\partial t}, \quad [1]$$

where ρ_c and C_{pc} denote the composite density and specific heat, respectively. k_{xx}, k_{yy} and k_{zz} are the conductivity coefficient of composite in x, y and z directions, respectively. α is curing degree. T denotes the absolute temperature. $\frac{\partial H}{\partial t}$ defines the rate of internal heat generation within the composite, which can be obtained by the following formulation [1]:

$$\frac{\partial H}{\partial t}=\rho_m(1-V_f)H_m\frac{d\alpha}{dt}, \quad [2]$$

where ρ_m is the resin density, V_f is the volume fraction of fiber, $d\alpha/dt$ is the cure rate of resin and H_m is the total heat release per unit mass of resin.

The relationship among $d\alpha/dt$, T and α for the specific resin system 3501-6 is based on semiempirical expression, which can be described by the Arrehenius equation as [1]:

$$\frac{d\alpha}{dt}=\begin{cases}(K_1+K_2\alpha)(1-\alpha)(0.47-\alpha) & (\alpha\le 0.3)\\ K_3(1-\alpha) & (0.3\le\alpha)\end{cases} \quad [3]$$

$$K_i=A_i e^{\frac{-\Delta E_i}{RT}}, \quad [4]$$

where K_i and ΔE_i are the rate constants and the Arrhenius activation energies, respectively. A_i is the pre-exponential constants. ΔE_i and A_i are determined by experiment. R is the universal gas constant. Cure kinetic parameters for 3501-6 resin are included in Table 1 (1, 2, 11).

From the equation [1], it can be known that density, conductivity coefficient and specific heat of the composite are the key input parameters to predict the temperature and curing degree fields of composite. The thermophysical properties of the composite have to be well known in order to understand the thermocuring characteristics of the composite accurately.

Composite density can be obtained by rule of mixture (12):

Table 1: Material properties of AS4/3501-6 composite (1, 2, 9, 11).

Parameters	Numerical values
A_1 (min^{-1})	2.101×10^9
A_2 (min^{-1})	-2.014×10^9
A_3 (min^{-1})	1.960×10^5
E_1 (J/mol)	8.07×10^4
E_2 (J/mol)	7.78×10^4
E_3 (J/mol)	5.66×10^4
H_m (J/kg)	1.986×10^5
ρ_m (kg/m^3)	1.26×10^3
ρ_f (kg/m^3)	1.79×10^3
V_f	50%
C_m (J/kg K)	1.26×10^3
C_f (J/kg K)	7.12×10^2
k_m (W/m K)	0.167
k_f (W/m K)	26

$$\rho_c=V_f\rho_f+(1-V_f)\rho_m, \quad [5]$$

where ρ_c, ρ_f and ρ_m are densities of composite, fiber and resin, respectively. V_f is the volume fraction of fiber.

Similarly, using the rule of mixture, the specific heat of composite can be evaluated (12):

$$C_{pc}=V_fC_f+(1-V_f)C_m, \quad [6]$$

where C_{pc}, C_f and C_m are specific heat capacities of composite, fiber and resin, respectively.

AS4/3501-6 composite can be considered transversely isotropic. Conductivity coefficients are expressed by longitudinal and transverse conductivity coefficients k_{xx} and k_{yy}. Using the rule of mixture, k_{xx} is determined as follows (13):

$$k_t=\frac{k_m-k_f}{k_m+k_f+V_f(k_m+k_f)} \quad [7]$$

$$k_{xx}=V_fk_f(1+V_mk_t)+V_mk_m(1-V_fk_t), \quad [8]$$

where k_f and k_m are conductivity coefficients of fiber and resin, respectively. V_m is resin volume fraction.

Transverse conductivity coefficient k_{yy} is calculated using the Springer-Tsai model (14, 15):

$$\frac{k_{yy}}{k_m}=\left(1-2\sqrt{\frac{V_f}{\pi}}\right)+\frac{1}{B}\left[\pi-\frac{4}{\sqrt{1-\frac{B^2V_f}{\pi}}}\tan^{-1}\frac{\sqrt{1-\frac{B^2V_f}{\pi}}}{1+B\sqrt{\frac{V_f}{\pi}}}\right] \quad [9]$$

$$B=2\left(\frac{k_m}{k_f}-1\right) \quad [10]$$

3 Finite element model and its verification

AS4/3501-6 composites are chosen in this paper due to their widely use and large existing knowledge base. The most frequently used material parameters used for AS4/3501-6 composites are cited from the literature (1, 2, 9, 11). The simulation is implemented in the software COMSOL Multiphysics 4.3a. The dimensions of a flat plate are 15.24 cm × 15.24 cm × 2.54 cm or 15.24 cm × 15.24 cm × 7.62 cm. The desired temperature cycle shown in Figure 1 is applied to the top and bottom surfaces of the AS4/3501-6 composite.

A 2.54-cm laminate with layup style (0/90/90/0), previously studied by White and Kim (16), is taken as an example of verification. The development curves of the curing degree at the central point during curing process are shown in Figure 1, which shows a good agreement between the present result and that obtained by White and Kim (16).

4 Simulation results and discussion

4.1 Curing parameters evolution

Before studying the effects of key thermophysical properties on the composites curing uniformity, an example is designed for the simulation of the curing process. The input key thermophysical properties are included in Table 1 (1, 2, 9, 11). Figure 2 shows the temperature and curing degree of the surface point and central point for

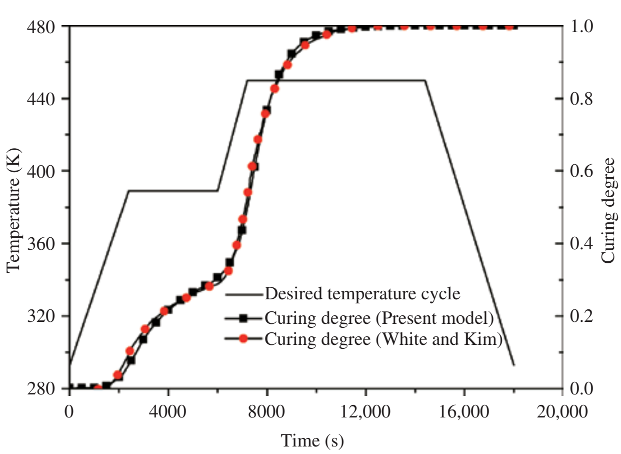

Figure 1: Desired temperature cycle and comparison of the curing degree at the central point between the present model and the previous model.

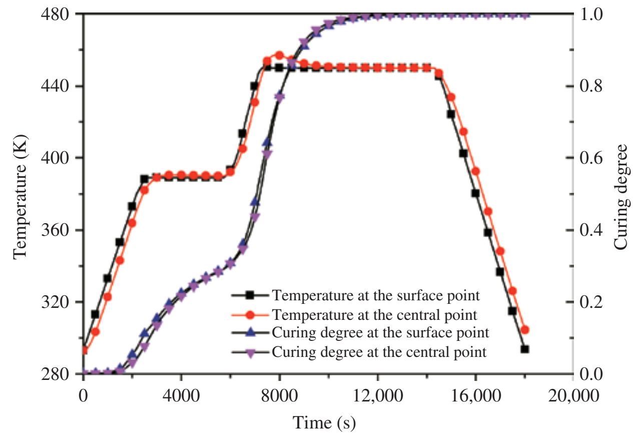

Figure 2: Comparison of the temperature and curing degree of the surface and central points for 2.54 cm plate.

2.54 cm unidirectional plate. Surface point and central point are upper surface center and body center of composite plate, respectively. At the initial stage of curing process, the temperature of the surface point increases more rapidly than the central point because of the low conductivity coefficient of the composite. With the curing reaction, the temperature of the central point reaches to a high value than that of surface point because of the exothermal curing reaction. However, the difference is small owing to the small height and low heat release of the composite. The development curves of the curing degree in Figure 2 follow the similar rule to that of the temperature, which can be explicated by the relationship between the temperature and the curing degree, as shown in equation [3].

4.2 Effect of density of resin on curing uniformity

In paper of Shin and Hahn (9), the non-cured resin density and cured resin density, ρ_m, were tested 1232 kg/m^3 and 1272 kg/m^3, respectively. Combining above densities with Table 1, we choose densities of resin values of 1232, 1242, 1252, 1260 and 1272 kg/m^3 and discuss the effects of these densities on temperature and curing degree. The other parameters remain the value in Table 1. In order to enrich the results, two kinds of laminates with thickness of 2.54 cm and 7.62 cm are simulated to reveal the sensitivity of the results to the thickness of the laminate.

As shown in Figure 3, at the initial stage of the curing process, the temperature of the thick laminate increases more slowly than the thin laminate because of the low conductivity coefficient of the composite. The temperature of the thick laminate rises to a higher value than thin laminate

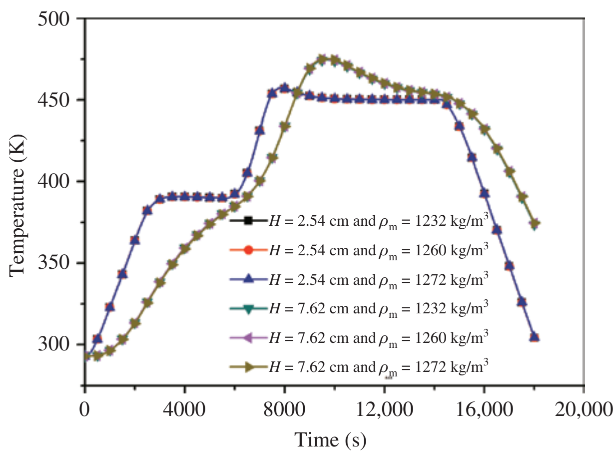

Figure 3: Development of temperature at central point of laminate with different densities of resin.

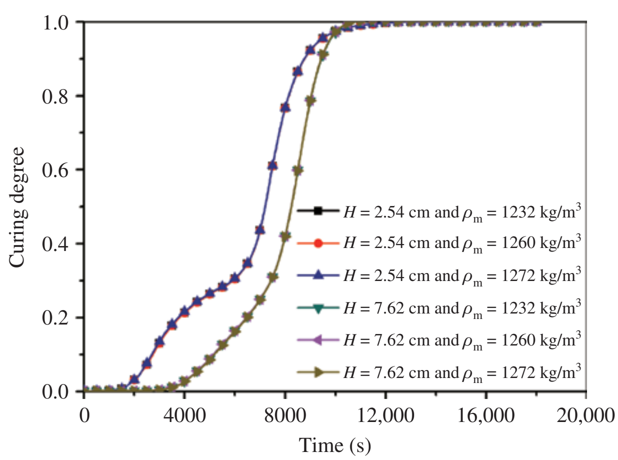

Figure 4: Development of curing degree at central point of laminate with different densities of resin.

because of the exothermal curing reaction and the low conductivity coefficient of the composite. In view of the relation between the temperature and the curing degree, the development of the curing degree shown in Figure 4 can be easily understood. For the laminate with the same thickness, the result does not show much difference when changing the density of resin. The result shows that the resin density in the tested range has no obvious effect on the temperature and curing degree in the cure process.

To investigate the influence of density on curing uniformity, the maximum temperature difference and the curing degree difference under different conductivity coefficients are plotted in Figure 5. It is observed that with the increasing of the density of resin, the temperature difference and the curing degree difference are basically unchanged. This indicates that the density of resin has no obvious effect on the curing uniformity.

4.3 Effect of conductivity coefficient of resin on curing uniformity

The conductivity coefficient of carbon/epoxy composite varies obviously during the transformation of the resin, which has a considerable effect on heat transfer within a thick composite in the process. In the study of Chern et al. (17), in the temperature range of 300–500 K and degree-of-cure range of 10%–100%, the conductivity coefficient of 3501-6 resin was in the range (0.19–0.32) W/(m K) ± 11.8%. In the findings of Farmer and Covert (18), the conductivity coefficient of 3501-6 resin was found to be 0.255, 0.270 and 0.283 W/(m K) at 368, 418 and 448 K, respectively, at the curing degree 0.98. In another paper (19), for neat 3501-6 resin with the curing degree ranging from 0.8 to 0.98 and

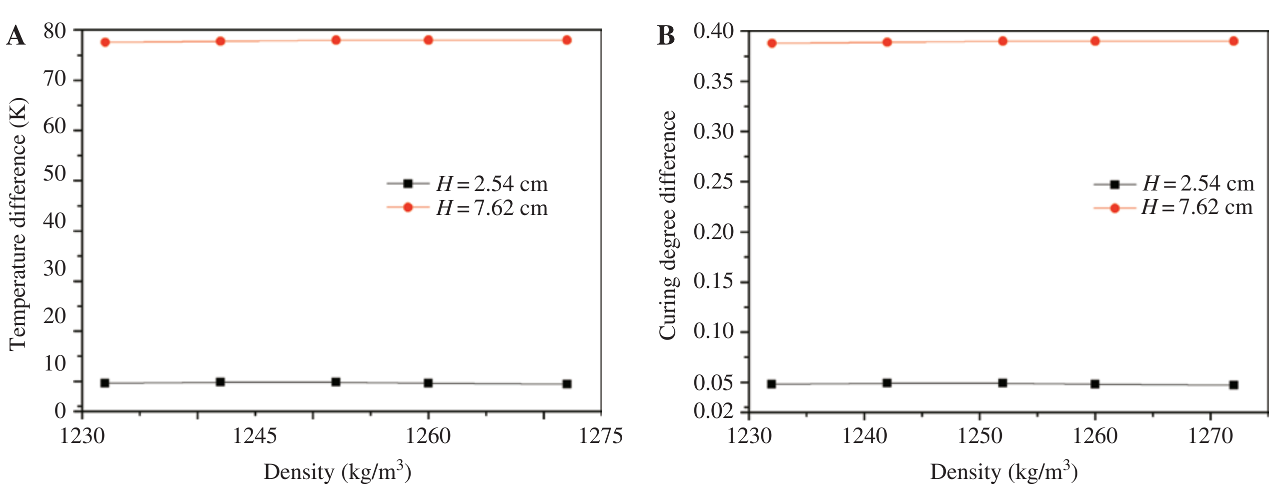

Figure 5: Effects of density on curing uniformity: (A) temperature difference vs. density, (B) curing degree difference vs. density.

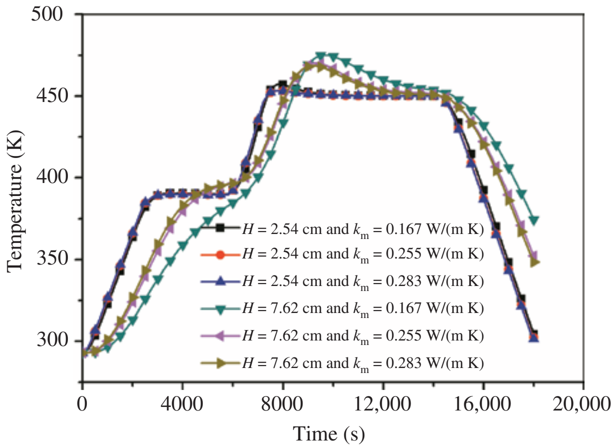

Figure 6: Development of temperature at central point of laminate with different conductivity coefficients.

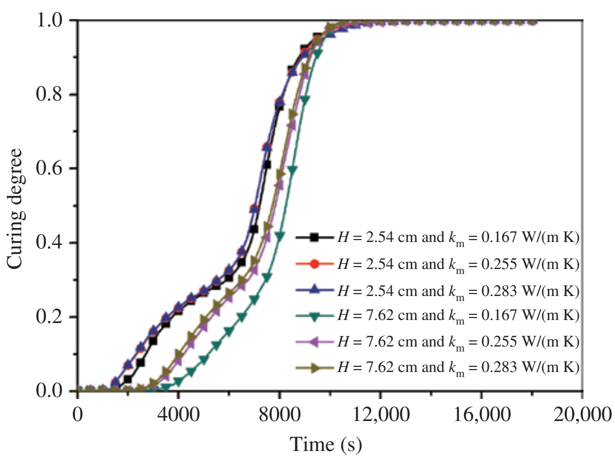

Figure 7: Development of curing degree at central point of laminate with different conductivity coefficients.

temperature ranging from 313 to 450 K, the conductivity coefficient varied in the range of 0.17–0.20. Combined with the value in Table 1, conductivity coefficients of 0.167, 0.2, 0.255, 0.27 and 0.283 W/(m K) are considered and other parameters remain unchanged.

The developments of temperature and curing degree at central point are presented in Figures 6 and 7. Similar to Figures 3 and 4, the simulation result is more sensitive to the thickness of the laminate. The temperature peak is higher because the exothermic reaction heat is not easy to transfer out in thick laminate.

Different from the effect of density on temperature and curing degree, for the laminate with the same thickness, the effect of conductivity coefficient on temperature and curing degree is obvious. As shown in Figure 6, the temperature of the laminate with low conductivity coefficient increases more slowly than that with high conductivity coefficient. Similar development rule can be seen from the result of curing degree shown in Figure 7.

To investigate the influence of conductivity coefficient on curing uniformity, the maximum temperature difference and curing degree difference under different conductivity coefficients are plotted in Figure 8. As the conductivity coefficient increases, the temperature difference decreases. The low conductivity coefficient makes the internal exothermic reaction not easy to transfer out, which increases the temperature difference. On the contrary, the high conductivity coefficient promotes the fast transfer of the exothermic reaction, which reduces the temperature difference. It is easy to know that the temperature difference and curing degree difference increase with the growth of the thickness of the laminate on the basis of the above analysis. Meanwhile, a general conclusion that

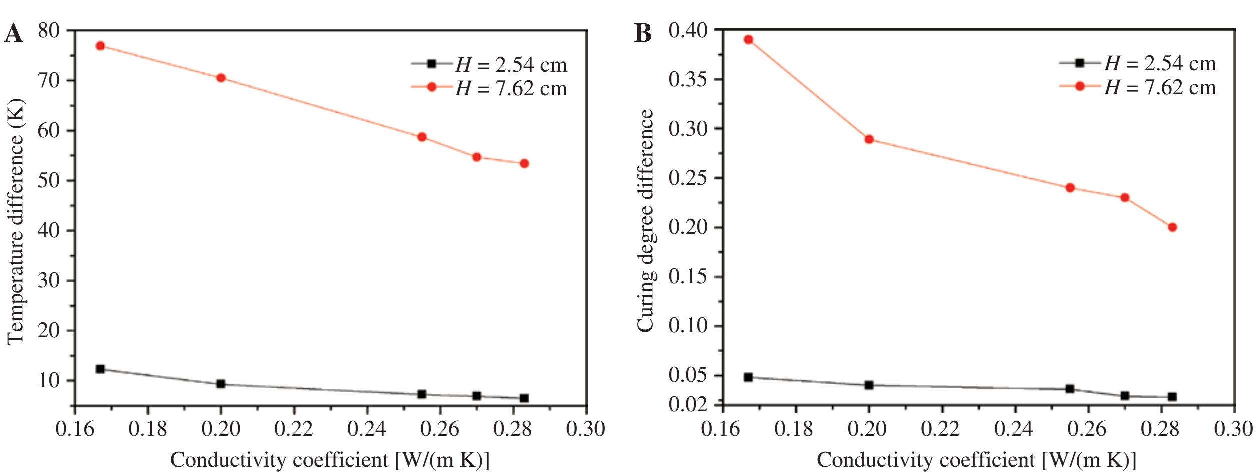

Figure 8: Effects of conductivity coefficient on curing uniformity: (A) temperature difference vs. conductivity coefficient, (B) curing degree difference vs. conductivity coefficient.

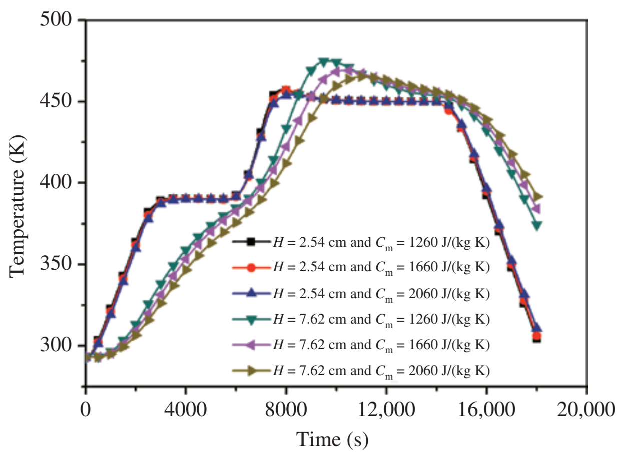

Figure 9: Development of temperature at central point of laminate with different specific heat capacities.

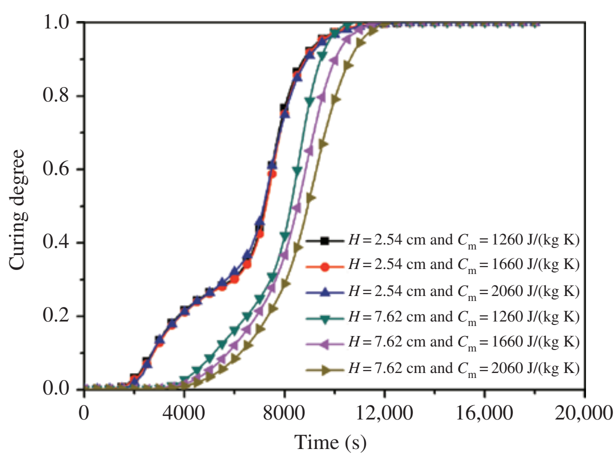

Figure 10: Development of curing degree at central point of laminate with different specific heat capacities.

the temperature difference and curing degree difference are more sensitive to conductivity coefficient with the increasing of the thickness might be obtained by observing the slope of the curves.

4.4 Effect of specific heat of resin on curing uniformity

Chern et al. (17) pointed out that the specific heat of 3501-6 resin increased in the range of 1300–2300 J/(kg K) with a temperature range of 320–550 K. Combined with Table 1, the specific heat increases from 1260 to 2260 J/(kg K) by the increment of 200 J/(kg K), whereas other parameters remain unchanged.

The evolution characteristics of temperature and curing degree are plotted in Figures 9 and 10. For the thin laminate, it can be observed that the temperature at the central point does not change obviously with the increase of specific heat. For the thick laminate, the difference becomes more obvious for different specific heat capacities. An interesting phenomenon that can be seen from Figure 9 is that before the temperature reaches the maximum value, it reduces with the rising specific heat, which the rule turns over after the temperature reaches the maximum value. For this phenomenon, it can be easily explained by the physical meaning of specific heat, which characterizes the relationship between heat and temperature change. In detail, at the heating stage, the temperature increment increases with the decrease of specific heat with the same heat, whereas at the cooling stage, the temperature increment decreases with the growth of specific heat in the case of the same heat. The characteristic

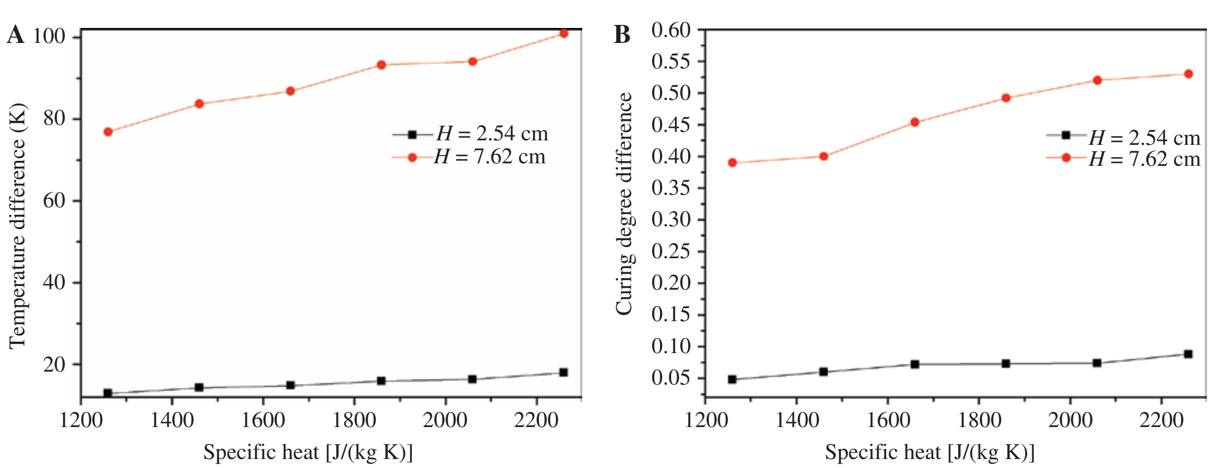

Figure 11: Effects of specific heat on curing uniformity: (A) temperature difference vs. specific heat, (B) curing degree difference vs. specific heat.

shown in Figure 10 is easy to understand because higher temperature results in a faster cure.

In order to study the effects of specific heat on curing uniformity, the maximum temperature difference and curing degree difference under different specific heat capacities are plotted in Figure 11. Different from the negative relationship between curing uniformity and conductivity coefficient, the relationship between cuing uniformity and specific heat presents a positive correlation. Specifically speaking, the temperature difference and curing degree difference increase with the rise of specific heat, which is easily analyzed from the above analysis for Figure 10. When the two curves shown in Figure 11A are observed by contrast, the influence degree of specific heat on curing uniformity is sensitive to thickness of laminate by observing the slope of the curves.

5 Conclusions

A process simulation model for heat transfer and cure kinetic is presented. The accuracy of this model is validated with the results of previous studies. The effects of key thermophysical parameters of epoxy resin on curing uniformity are numerically analyzed. Several conclusions can be obtained as follows:

1. With the increase of the density of resin, the temperature difference and the curing degree difference are basically unchanged. That is, the density of resin in the range from non-cured state to fully-cured state has not obvious effect on the curing uniformity. In view of the conclusion, constant density can be used in the simulation of temperature and curing degree fields to simplify calculations.
2. The effect of resin conductivity coefficient on curing uniformity is evident. With the increasing conductivity coefficient, the curing uniformity is enhanced effectively. Accurate conductivity coefficient of resin should be used in the simulation. Relevant measures can be adopted to improve conductivity coefficient on the premise of not affecting the curing kinetics.
3. With the increase of specific heat of resin, the curing uniformity is reduced. Accurate measurement of specific heat is important for the reasonable simulation of temperature and curing degree.
4. The effects of conductivity coefficient and specific heat are more evident on the thick laminate than the thin laminate.

In the further work, to make the simulation model of curing process more rigorous, variable thermophysical properties of resin should be carefully evaluated for being suitable to the non-isothermal curing condition. And then the effects of thermophysical parameters on residual stress due to non-uniform temperature and curing degree in the cure process can be analyzed.

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