Taylor & Francis
Taylor & Francis Group

Materials Research Innovations

ISSN: 1432-8917 (Print) 1433-075X (Online) Journal homepage: http://www.tandfonline.com/loi/ymri20

Simulation analysis of resin-based composites on temperature and degree of cure fields by thermoforming process considering the influence of temperature distribution inside the autoclave

F. Sun, D. M. Liao, Z. C. Zhang, L. Cao & J. X. Zhou

To cite this article: F. Sun, D. M. Liao, Z. C. Zhang, L. Cao & J. X. Zhou (2015) Simulation analysis of resin-based composites on temperature and degree of cure fields by thermoforming process considering the influence of temperature distribution inside the autoclave, Materials Research Innovations, 19:sup5, S5-53-S5-58, DOI: 10.1179/1432891715Z.0000000001336

To link to this article: https://doi.org/10.1179/1432891715Z.0000000001336

Simulation analysis of resin-based composites on temperature and degree of cure fields by thermoforming process considering the influence of temperature distribution inside the autoclave

F. Sun, D. M. Liao*, Z. C. Zhang, L. Cao and J. X. Zhou

The curing process is critical in the production of composite materials. In this paper, a heat transfer and curing kinetics of the two-way coupling model reflecting the resin-based composite curing process was built. The degree of curing and temperature fields simulation programme using the finite difference method independently was also developed. With this programme, a numerical simulation for a flat plate was conducted. The distributions of temperature and degree of curing fields were obtained. The simulation results indicated that temperature distribution plays an important role in the resin curing process. The internal temperature of autoclave is inhomogeneous. The temperature of the composite has a non-linear relationship with the gradient temperature distribution in the autoclave. Moreover, the existence of temperature difference inside the autoclave can have a more significant influence at a low temperature than that of a high one. This research provides a certain basis for optimising the moulding process parameters, mould design and product quality control.

Keywords: Resin-based composite, Numerical simulation, Thermoforming, Autoclave

Introduction

Resin-based composites are one of the most-advanced composite materials. They are widely used as aerospace material because of excellent properties, such as high specific strength, high specific modulus, strong design ability, fatigue resistance and corrosion resistance.[1] The curing process is important during the production of composites. The internal temperature distribution depends on the heat, released from the cure reaction of the resin matrix, and the heat transfer of the materials. The non-uniform temperature field is responsible not only for causing residual stress and residual deformation, but also for the early damage of the composite layer.[2] However, the relationship between the temperature distribution and the curing degree is not sufficiently understood. Hence, it is necessary to study the distribution of temperature and curing degree during the curing process of the composites to design reasonable technology parameters.

Researchers have proposed simulation methods for curing processes of resin-based composites. By calculus of the differences, Bogetti[3] reported two-dimensional numerical simulations of thermosetting composite materials' curing process. Sung[4] proposed a curing process simulation by using the finite element method of non-linear heat conduction without considering the flow of the resin. Using the finite element method, Zhang Zuoguang[5] analysed the effect of the specific heat capacity, thermal conductivity, density and packaging materials on the temperature field and curing degree field in the hot forming process of composite materials.

There are many limitations of the models mentioned. For example, the simulation only considered two dimensions, which missed the two-way-coupled relationship of resin curing and heat transfer. Also, the boundary conditions are needed, especially in the case of not considering the effect of actual asymmetrical temperature distribution in autoclave moulding for the curing process. This paper established a three-dimensional transient numerical analysis model for the curing process in resin-based composites moulding, which obtained the temperature and curing field simulation results of a flat plate. Considering the asymmetrical temperature distribution inside the autoclave, the influence of temperature on a flat plate curing process was discussed.

State Key Laboratory of Materials Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China

*Corresponding author, email liaodunming@hust.edu.cn

Received 20 October 2014; accepted 12 December 2014
DOI 10.1179/1432891715Z.0000000001336

Mathematical model

In the thermoforming consolidation process of composite materials, the heat passes from the external of composite to the internal with the growing-up air in the autoclave. Meanwhile, the resin cures gradually.[6] In this process, the temperature of the resin matrix affects its curing rate. The heat from the curing resin also affects the temperature distribution. Figure 1 shows the relationship between them.

Thus, it can be seen that the temperature and curing degree of resin are correlated. To make their relationship clear, it was necessary to comprehend the chemical model, including a heat transfer model and a cure kinetic model. Considering the complexity of the real situation, this study had the following premises:

(i) resin and fibre were treated as a whole material, which was a homogeneous anisotropic material on the macroscale;
(ii) the heat transmission caused by resin flowing was ignored;
(iii) the temperature of the resin and fibre was the same when they were located in the same internal of the composite materials;
(iv) the influence of the internal composite porosity was ignored.

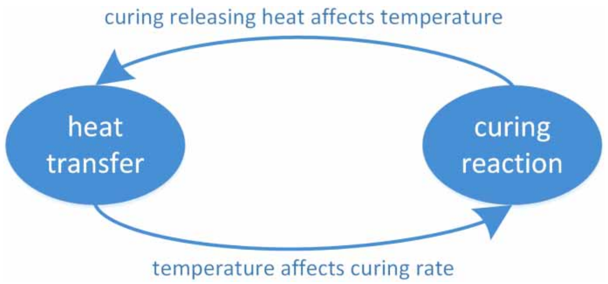
Heat transfer model

The temperature field of the resin-based composite curing was a heat conduction issue with a non-linear inner heat source. The inner heat source came from the exothermal reactions of the resin matrix. Therefore, the Fourier heat equation and the energy conservative relations to were used to establish the three-dimensional transient equation of heat conduction.[7] It was given by equation (1) as follows:

$$\rho C_{\mathrm{p}} \frac{\partial T}{\partial t} = k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} + k_z \frac{\partial^2 T}{\partial z^2} + \dot{q} \qquad (1)$$

where ρ is the density of the material, C_{p} is the specific heat capacity of the material, T is the temperature, t is the time, k_x, k_y and k_z are three heat transfer coefficients in three main directions, and $\dot{q}$, which relates to the curing rate, is the heat released from the resin curing in unit time. The definition of $\dot{q}$ is shown as equation (2).[8]

$$\dot{q} = \rho(1 - V_{\mathrm{f}}) H_{\mathrm{R}} \frac{\mathrm{d}\alpha}{\mathrm{d}t} \qquad (2)$$



1 Relationship between heat transmission and curing reaction in the hot-press process

where V_{f} is the fibre volume content and H_{R} is the total reaction heat released from the curing of a unit quantity. α is the degree of resin curing and $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ is the resin curing rate.

According to the two equations, it could be seen that the degree of curing and temperature couple with each other. Furthermore, the density and specific heat capacity of composite materials were obtained by using the mixing law. The heat conductivity of composite material depended primarily on the combination of the resin and fibre. And, it was generally anisotropic and could be calculated using the volume weighted average method.[8] The calculation method is shown as the following formulas:

$$\rho_{\mathrm{p}} = V_{\mathrm{f}} \rho_{\mathrm{f}} + (1 - V_{\mathrm{f}}) \rho_{\mathrm{r}} \qquad (3)$$

$$C_{\mathrm{p}} = V_{\mathrm{f}} C_{\mathrm{f}} + (1 - V_{\mathrm{f}}) C_{\mathrm{r}} \qquad (4)$$

$$k_{\mathrm{p}} = V_{\mathrm{f}} k_{\mathrm{f}} + (1 - V_{\mathrm{f}}) k_{\mathrm{r}} \qquad (k = k_x, k_y, k_z) \qquad (5)$$

where ρ_{p}, C_{p} and k_{p} are the density, specific heat capacity and heat transfer coefficients of the composite. ρ_{f}, C_{f} and k_{f} are the density, specific heat capacity and heat transfer coefficients of the fibre. ρ_{r}, C_{r} and k_{r} are the density, specific heat capacity and heat transfer coefficients of the resin matrix. V_{f} is fibre volume content.

Curing kinetic model

The curing process for composite materials is a complex chemical reaction. The resin goes through a complex changing process from viscous flow state to gel state, then glassy state, and eventually to a solid state, along with the phenomenon of chemical exothermic. Until now, the kinetic model has been divided into two main models, the phenomenological model and the mechanism model.[9–11] The former one is widely applied. Based on the curing future, Kamal[12] proposed the following autocatalytic model:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n \qquad (6)$$

$$K_i = A_i e^{-\frac{E_i}{RT}} \qquad (i = 1, 2) \qquad (7)$$

where K_i is the speed constant and A_i is the pre-exponential factor. E_i is the activation energy. m and n are reaction orders.

In this model, when m plus n equals two, meaning that the reaction order is two, the above equations were widely used to describe the isothermal curing reaction kinetics of unsaturated polyester resin and epoxy resin. It was necessary to measure two curing kinetic parameters of the equation, the curing state and curing rate, at the same time. A method that is often used to measure these two curing kinetic parameters is thermo analysis technology, such as differential scanning calorimetry.[13] When the kinetic parameters were obtained, they were used to predict the degree of cure for any temperature history by the following formula:

$$\alpha = \int_0^t \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t} \right) \mathrm{d}t \qquad (8)$$

Numerical method

In this study, the finite difference method (FDM) was used to detect the mathematical models, and get the heat balance equation of all nodes in the system, assuming that the system had a total of n nodes. Then, the nth order linear algebraic equations were obtained as follows:

$$\begin{cases} a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = b_1 \\ a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = b_2 \\ \cdots \\ a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n = b_n \end{cases} \tag{9}$$

These equations are represented in the form of matrices and vectors, that is,

$$AX = b \tag{10}$$

In the above formula, coefficient matrix A characterises the nature of the problem to solve. It is related to physical parameters of the system. Matrix b characterises the initial conditions and boundary conditions. Meanwhile, the curing exotherm of resin can be considered in Matrix b. By solving the equation, the distribution of the temperature field and the curing degree at next moment were obtained.

According to the numerical model, a universal curing simulation programme was developed. The calculation process is shown in Fig. 2, and the details are as follows:

(i) Set the relevant parameters, such as the boundary conditions, initial conditions and calculation parameters, etc. Then assemble coefficient matrix A;

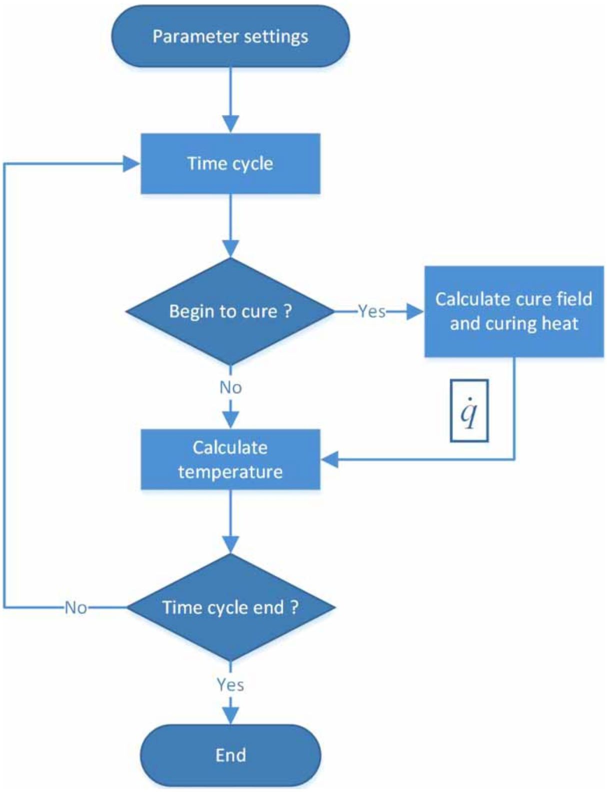
(ii) According to the autoclave heating specification, calculate the applied temperature loads at current time step. Then assemble matrix b;

(iii) Determine whether the resin is beginning to cure in the current temperature field. If the curing start conditions are met, proceed to step 4, otherwise go to step 5;

(iv) Calculate the curing degree's change at the current time step and get the distribution of the curing degree field. At the same time, calculate the heat $\left(\dot{q}\right)$ released by resin according to the curing rate. Considering the coupled relationship between curing degree and the temperature field, we put the heat in the matrix b from step 2;

(v) Calculate equations $Ax = b$ to get the systems' temperature field distribution at current time step;

(vi) Determine whether the time cycle is complete. If reached, then stop the calculation. Otherwise, return to step 2 for the next time step calculation.



2 Numerical calculation process

Structure and parameters

Structure of the numerical model

The autoclave is the key equipment of hot-press forming process for resin-based composites. And autoclave moulding has been adopted widely in advanced aerospace composite materials preparation as it has the following characteristics: the uniformity of pressure and temperature inside, stable and reliable moulding process, the relatively simple mould, and high efficiency.[14] In this moulding process, the air or inert gas was used as a heat carrier medium to complete the process of heating and pressurising so that the resin was gradually curing. Before the process, some encapsulation processes needed to be done. One complete system structure diagram after encapsulation is shown in Fig. 3.

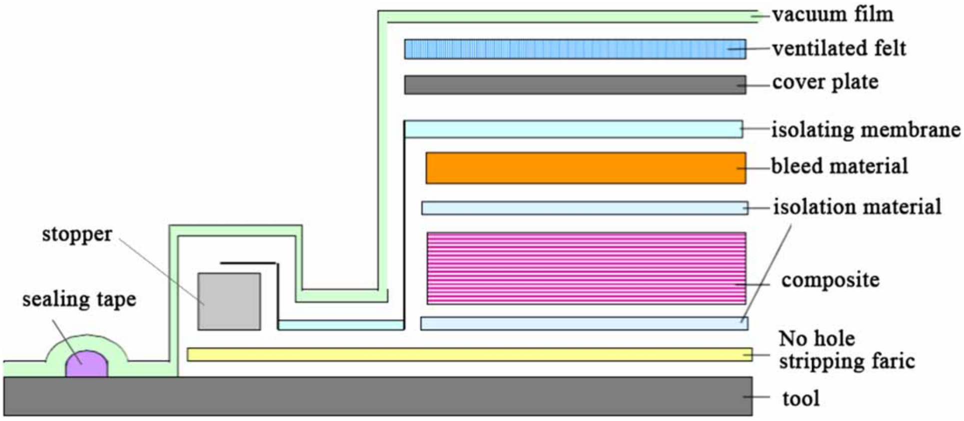
By simplifying the encapsulation structure of composites in Fig. 3 and considering the effects of tools and auxiliary materials, the structure of the numerical model was established and shown in Fig. 4.

Calculation parameters

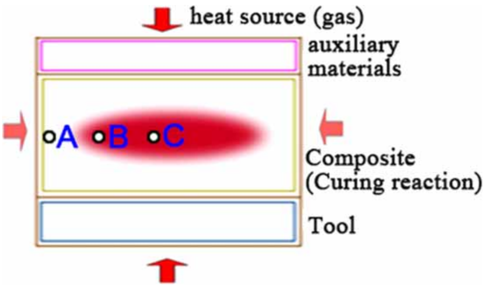
In this paper, the FDM was used to detect the mathematical model described and the corresponding thermal curing simulation programme was developed. The nonuniform grid technology was adopted to mesh the structure shown in Fig. 4. The adopted autoclave temperature cycle presented in Fig. 5 is a two-stage cycle.

The composite material used for simulation was the AS4/3501-6 graphite/epoxy resin system with the thickness of 30 mm and the length and width were both 300 mm. The material properties of AS4/3501-6 graphite/epoxy are given in Table 1. The curing kinetics parameters are given in Table 2. The curing kinetics equation is as follows:[15]

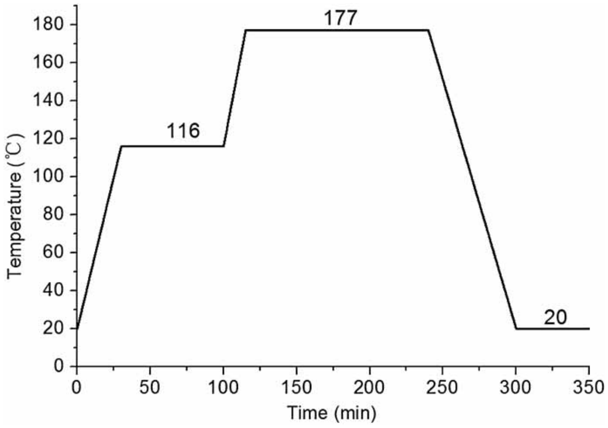
$$\begin{cases} \dfrac{\mathrm{d}\alpha}{\mathrm{d}t} = (K_1 + K_2\alpha)(1-\alpha)(0.47-\alpha) \quad \alpha \le 0.3 \\ \dfrac{\mathrm{d}\alpha}{\mathrm{d}t} = K_3(1-\alpha) \quad \alpha > 0.3 \\ K_1 = A_1 e^{-\frac{E_1}{RT}}; \quad K_2 = A_2 e^{-\frac{E_2}{RT}}; \quad K_3 = A_3 e^{-\frac{E_3}{RT}} \end{cases} \tag{11}$$



3 **A complete system structure of composite after encapsulation**



4 **Structure of the numerical model**



5 **Autoclave temperature cycle**

Table 1 Material properties of AS4/3501-6 graphite/epoxy

Parameters (unit)	Value
Density ρ (kg m^{-3})	1578
Polymer specific heat C_p [J (kg K)$^{-1}$]	862
Thermal conductivity k_z [W (m K)$^{-1}$]	0·4135
k_x, k_y, k_z	1, 5, 10

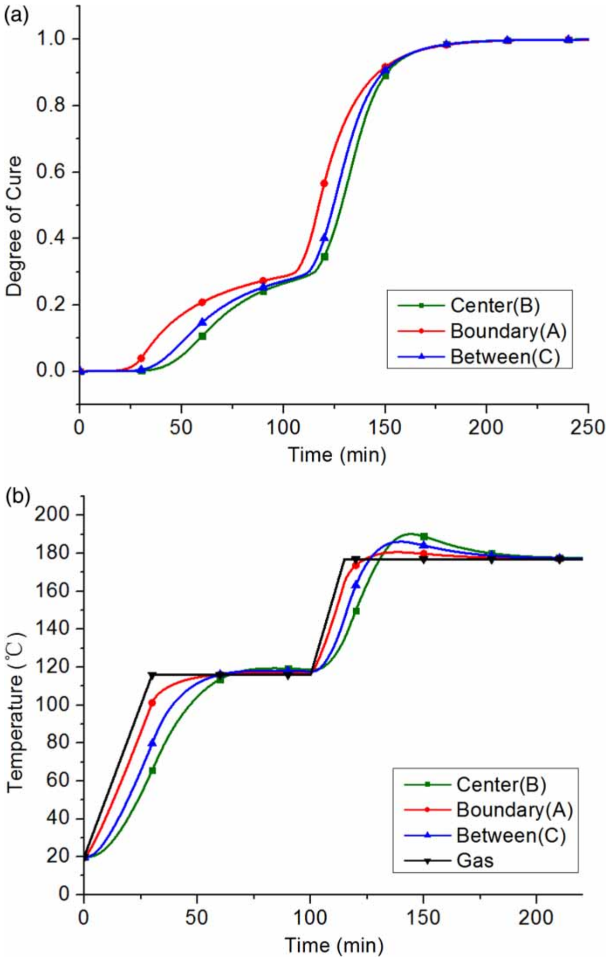
Table 2 Cure kinetics parameters for AS4/3501-6 graphite/epoxy

Parameters (unit)	Value
A_1 (min^{-1})	$2{\cdot}102\times10^{9}$
A_2 (min^{-1})	$-2{\cdot}014\times10^{9}$
A_3 (min^{-1})	$1{\cdot}960\times10^{5}$
E_1 (J mol^{-1})	$8{\cdot}07\times10^{4}$
E_2 (J mol^{-1})	$7{\cdot}78\times10^{4}$
E_3 (J mol^{-1})	$5{\cdot}66\times10^{4}$
R [J (mol K)$^{-1}$]	8·3143
H_R (J kg^{-1})	$198{\cdot}6\times10^{3}$
V_f	0·5

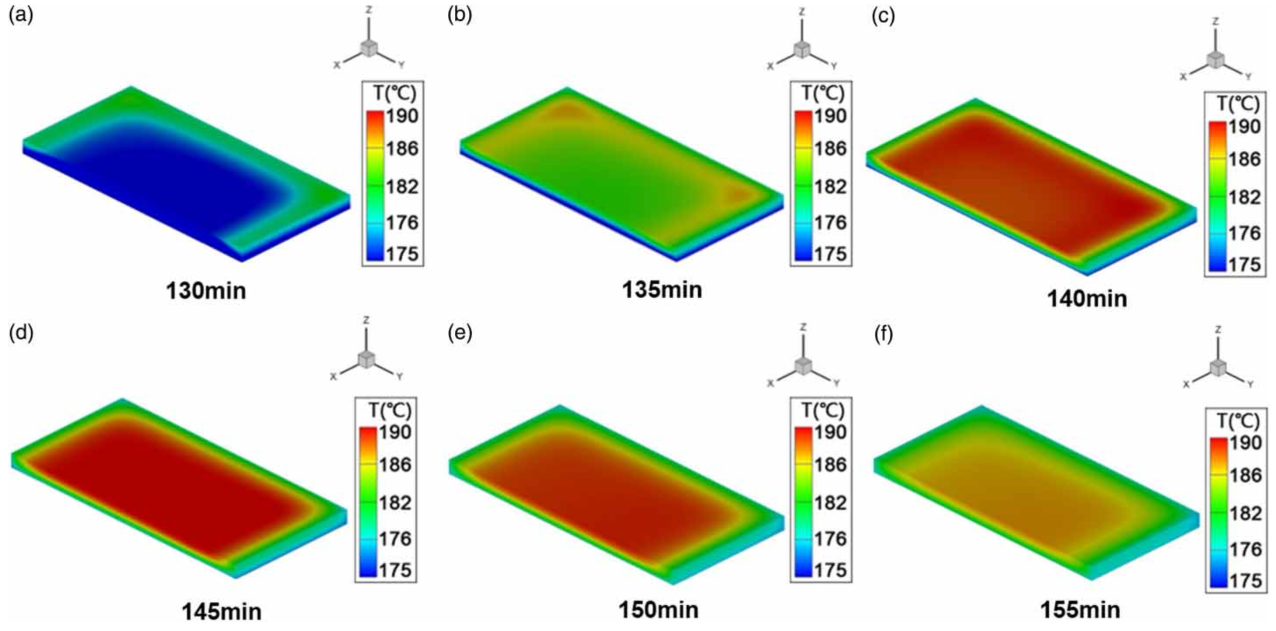
Results and discussions

Uniform temperature distribution

Degree of cure and the temperature profiles are shown in Fig. 6, which had three points in the horizontal centre flat plate of the composites: the boundary point, the centre point and the point between them, i.e. A, B and C points shown in Fig. 4. Through the three degrees of cure profiles, the curing process was divided into two stages by the point that the degree of cure was equal to 0·3. It was consistent with the epoxy resin curing kinetics



6 **Degree of cure and temperature profiles at different points (*a* degree of cure, *b* temperature)**

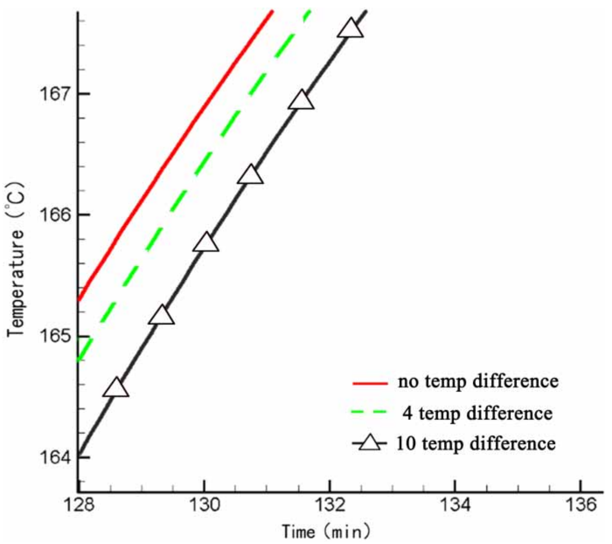


7 **Temperature field distribution at different times (one-fourth composite plate)**

of equation (11). In addition, it could be seen from the degree of cure profiles that the curing starting time at the centre point was later than the point on the boundary. Since at the early stage of the curing, the curing rate was low and degree of cure at the centre was smaller than the boundary, the composite material was cured gradually from the boundary to the centre. However, as the resin was cured constantly, especially at the time of the second heating up stage, the curing reaction near the centre was very strong and emitted a large amount of heat. The heat promoted the progress of the resin curing, which resulted in the rapid increased curing speed at the centre, and the resin at the centre completed curing at the same time as the boundary at last.

It can be seen from the temperature profiles that the temperature rising at the centre showed an obvious delay from the boundary. This was mainly because the boundary of the composites was closer to the heated gas inside the autoclave. The heat from the gas to the composite system used convection heat transfer and then moved by heat conduction means from the boundary to the centre of the composites. In this process, the resin gradually completed the curing process. In addition, through the profiles, there were two obvious exothermic peaks in two stages. Since the curing rate was low at the first stage, the heat released by the resin curing reaction was less. The peak could be not obviously seen at the first stage. While at the second stage, a clear peak temperature in the profiles could be seen because the heat released was much greater than the first stage as the curing rate was higher. Relative to the boundary, the surrounding resin at the centre is rich. And the released heat is greater and the peak owing to the exothermic curing was more prominent. By measuring the centre point, the peak temperature of the first stage was higher than the autoclave air of 5°C and the second stage was higher than the autoclave air of 14°C.

To clearly see this phenomenon of internal curing of composite materials, the temperature field was displayed in the interception of the one-fourth composite plate according to the symmetry, as shown in Fig. 7, where the exothermic phenomenon is very obvious.



8 **Temperature of the centre of inner composite under different temperature difference (local zoom)**

Non-uniform temperature distribution

In the actual production, the temperature in the autoclave was not uniform. In order to simulate the actual autoclave production, the simulations with 4 and 10 temperature difference in the axial direction along the cylinder were performed.

Magnifying the temperature curve around 128 minutes, as shown in Fig. 8, the temperature under the condition with four temperature difference differed about 0·5°C with the condition with no temperature difference. And the temperature under the condition with 10 temperature difference differed about 1·3°C under the condition with no temperature difference. So it could be deduced that if the temperature difference was increased in the autoclave, the actual composite temperature would have a linear relationship with the condition with no temperature difference.

Compared to the first temperature rising process, the temperature gradient in the second process was not very significant. The reason was that the average temperature of the system was higher in the second process, and the temperature difference had a smaller proportion with the average temperature. So the conclusion could be drawn that the higher temperature the system has, the smaller the effect of the temperature difference will be.

Because the actual temperature gradient in autoclave is usually tiny, the effect that the temperature has on the composite temperature field and the degree of curing field can be ignored. And, the temperature difference has no obvious effect on the uniform temperature field of the whole composite system.

Conclusion

This paper presented a two-way coupled model of heat transfer and curing kinetics in resin-based composite curing process. Based on the finite difference method, simulation programme was developed to simulate the curing and temperature fields. The simulation results of a flat plate illustrated the significant two steps of AS4/3501-6 graphite/epoxy resin systems. The curing time of the centre part material was later than the boundary at the beginning. However, the temperature growth in the centre was higher during the curing process. The asymmetrical temperature difference inside the autoclave increased gradually. Thus, the actual resin-based composite had a linear relationship with no temperature difference. This was more obvious at a low temperature situation. Moreover, with the higher temperature of the system, the effect of the temperature difference was smaller. The model and programme developed in this research have a general application in the curing process. They are not limited in a certain product shape or forming process.

Acknowledgements

This research was financially supported by Programme for New Century Excellent Talents in University (No. NCET-13-0229) and the Fundamental Research Funds for the Central Universities (HUST: 2012TS010).

References

1. C. Soutis: ‘Fibre reinforced composites in aircraft construction’, *Prog. Aerosp. Sci.*, 2010, **42**, 143–151.
2. L. G. Zhao, N. A. Warrior and A. C. Long: ‘A thermo-viscoelastic analysis of process-induced residual stress in fibre-reinforced polymer-matrix composites’, *Mater. Sci. Eng. A-Struct.*, 2007, **452**, 483–498.
3. T. A. Bogetti and J. W. Gillespie: ‘Two-dimensional cure simulation of thick thermosetting composites’, *J. Compos. Mater.*, 1991, **25**, 239–273.
4. S. Yi, H. H. Hilton and M. F. Ahmad: ‘A finite element approach for cure simulation of thermo setting matrix composites’, *Comput. Struct.*, 1997, **61**, 383–388.
5. C. B. Xin, Y. Z. Gu and M. Li: ‘Experimental and numerical study on the effect of rubber mold configuration on the compaction of composite angle laminates during autoclave processing’, *Compos. Part. A-Appl. Sci.*, 2011, **42**, 1353–1360.
6. R. Andrews and M. C. Weisenberger: ‘Carbon nanotube polymer composites’, *Curr. Opin. Solid St. M.*, 2004, **8**, 31–37.
7. C. Bernardin and S. Olla: ‘Fourier’s law for a microscopic model of heat conduction’, *J. Stat. Phys.*, 2005, **121**, 271–289.
8. T. Behzad and M. Sain: ‘Finite element modeling of polymer curing in natural fiber reinforced composites’, *Compos. Sci. Technol.*, 2007, **67**, 1666–1673.
9. F. Boey and W. Qiang: ‘Experimental modeling of the cure kinetics of an epoxy-hexaanhydro-4-methylphthalicanhydride (MHHPA) system’, *Polymer*, 2000, **41**, 2081–2094.
10. P. I. Karkanas and I. K. Partridge: ‘Cure modeling and monitoring of epoxy/amine resin systems. I. Cure kinetics modeling’, *J. Appl. Polym. Sci.*, 2000, **77**, 1417–1431.
11. J. L. Martin, A. Cadenato and J. M. Salla: ‘Comparative studies on the non-isothermal DSC curing kinetics of an unsaturated polyester resin using free radicals and empirical models’, *Thermochim. Acta*, 1997, **306**, 115–126.
12. M. R. Kamal: ‘Thermoset characterization for moldability analysis’, *Polym. Eng. Sci.*, 1974, **14**, 231–239.
13. D. Rosu, C. N. Cascaval and F. Mustat: ‘Cure kinetics of epoxy resins studied by non-isothermal DSC dat’, *Thermochim. Acta*, 2002, **383**, 119–127.
14. G. Fernlund, N. Rahman and R. Courdji: ‘Experimental and numerical study of the effect of cure cycle, tool surface, geometry, and lay-up on the dimensional fidelity of autoclave-processed composite parts’, *Compos. Part. A-Appl. Sci.*, 2002, **33**, 341–351.
15. M. I. Naji and S. V. Hoa: ‘Curing of thick angle-bend thermoset composite part: curing process modification for uniform thickness and uniform fiber volume fraction distribution’, *J. Compos. Mater.*, 2000, **34**, 1710–1755.