Deformation and residual stresses during curing of hot-melt impregnated phenolic resin/glass fabric composite

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Key words： Phenolic resin, Hot-melt impregnated method, Finite element method, Curing deformation, Residual stresses

ABSTRACT

The environmentally friendly and low-cost hot-melt impregnated method was utilized to prepare phenolic resin/glass fabric (MPF/GF) prepreg and composite. The curing kinetics and model of the hot-melt phenolic resin (MPF) were characterized. The viscosity of MPF as a function of cure temperature was investigated using the Arrhenius model. Based on the mutual interactions of heat transfer-cure, flow-compaction and stress-distortion during the curing process of hot-melt MPF/GF composite, as well as by taking into account the viscoelastic effect, three-dimensional finite element analysis model for the numerical simulation and prediction of the deformation and bending modulus of MPF/GF composite was established. Via calculating the temperature distribution and degree of cure of MPF/GF composite in different locations and at any cure time, the curing cycle including heating rates, holding time and different cooling rates can be optimized with finite element method. As a result, both the curing deformation and the residual stress of MPF/GF composite were reduced by 6.37% and 2.4%, respectively.

1 INTRODUCTION

Phenolic resin composite has been regarded as one of the key materials for aeronautic utilities owing to the characteristics of lightweight, high strength, good designability, mechanical property, electric performance and chemical corrosion resistance[1]. Phenolic resin composite is usually obtained from its prepreg through the autoclave[2]. Traditional preparation of prepreg using solution impregnation process, which causes large amount of solvent evaporation, environmental pollution and jeopardizing the operator's safety. In addition, the volatile of the solvent increases the porosity of the composite and results in causing the nonuniform distribution of the resin and the unstability of product batch[2]. Whereas, hot-melt impregnated technology can not only avoid the deficiency of solution impregnation, but also can effectively improve the quality of composite. Therefore, design and preparation of modified phenolic resin that meets the requirement of hot-melt impregnated technology, has been aroused widespread attention.

Due to the integrated effect of curing heat, heterogeneous of material and curing system, diversity of component design and mold during the autoclave curing process, the uneven distribution of the internal temperature field, temperature gradient and the greater internal stress in the local can not be avoided[3-5], and expansion and curing shrinkage of composite occurred. The release of stress after demolding the composite resulted in a deviation in the size and shape of the composite between the design and the expectation, which results in the curing deformation and seriously affects the quality of the product.

In order to reduce the curing deformation and residual stress of composite, traditionally, repeated experiments and compensatory design based on experience are adopted[6]. However, for complex shapes or new composite, traditional empirical method may be useless, and experimental iteration efficiency is relatively low. As an alternative, numerical simulation evokes widespread attention to study the curing deformation and residual stress of composite[7, 8, 9, 10]. Recently, numerical simulation is the most widely used method to predict the curing deformation and residual stresses of composite by consisting of three sub-modules: heat transfer-cure, flow-compaction and stress-distortion. The heat conduction-curing module mainly studies the temperature distribution in the composite material. The flow-compaction module mainly calculates V_f of the composite and variation of composite material thickness. While the stress-distortion module mainly calculates curing deformation and residual stresses of composite. However, most of the existing studies only consider one or two modules. For example, Shin. et al.[11] have proposed a process simulation model for heat transfer and compaction along the bleeder-composite assembly, which can predict a higher fiber volume fraction for given effective stress, considering heat transfer-cure and flow-compaction modules. Çınar, K. et al[12]. have proposed a methodology for predicting the residual stress development during the curing, considering heat transfer-cure and stress-distortion.

Besides, earlier researchers take into account curing deformation and residual stresses in resol composite materials only in the cooling stage, assuming that no stress occurs during the heating and holding stage[13,14]. In fact, with the deepening of research, researchers find that curing deformation and residual stresses cannot be ignored before the stage. Hubert P. et al.[15] have found the effects of gelation on the parameter of the composite are blindingly obvious and yet ignored. Before the gel time, transference of force between resin and fiber is weak, because the resin is liquid, the deformation of the resin has no effect on the curing deformation and residual stresses of the composite[16, 17]. During gel-vitrification stage, the resol resin shows a strong viscoelasticity and curing shrinkage. Nevertheless, curing shrinkage and thermal expansion of resol resin has no impact on residual stresses but influences curing deformation, because the modulus of the resin is decreased.[18]. As the resin continues to cure, the composite reaches the glass, and degree of cure of resin remains basically unchanged. This makes no contribution to curing deformation and residual stresses[19,20]. While curing deformation and residual stresses are obvious during the cooling stage.

In this paper, MPF is prepared and utilized to fabricate MPF/GF prepreg, and the MPF composite is obtained through the molding process of autoclave. Three-dimensional finite element analysis model of 100mm*80mm*40mm is established via analyzing the mutual interactions among temperature fields and stress field during the curing process of MPF/GF composite. The temperature of the center point of the composite during the curing process is simulated by aforesaid method and is compared with the temperature curve measured by experiments as well to validate the rationality of the model. Besides, the curing parameters, such as holding time, heating and cooling rate, are simulated and optimized, which are used to calculate the corresponding curing deformation and thermal stress of MPF/GF composite.

2 EXPERIMENTAL

2.1 Preparation of MPF and MPF/GF prepreg

As shown in Figure 1, hot-melt impregnated technology was utilized to prepare MPF/GF prepreg, and MPF/GF composite was obtained through the molding process of autoclave.

Fig1: The fabricated process of MPF/GF composite

2.2 Characterization of the reaction kinetics of MPF

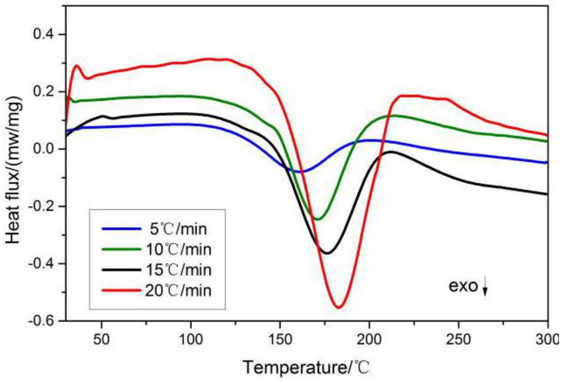

Fig. 2 DSC of MPF under different heating rates

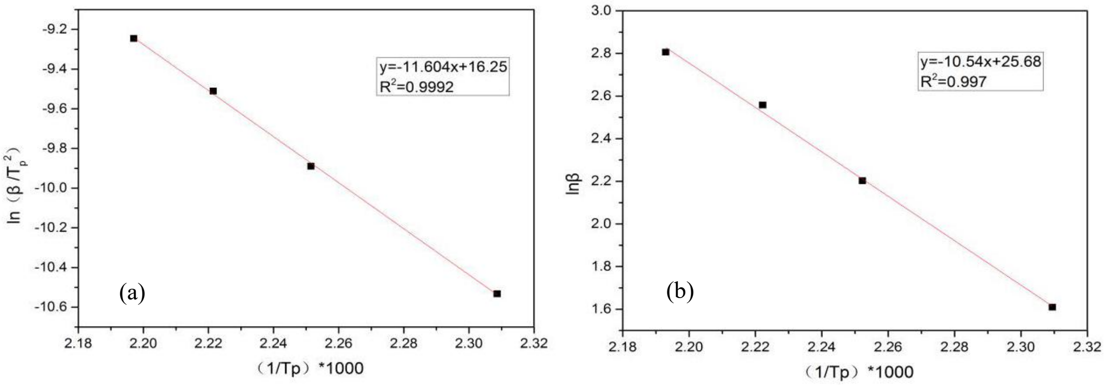

Fig. 3 Linear fitting of the reaction kinetics of MPF

It's easy to obtain the reaction kinetics of MPF throgh model-fitting by Kissinger method as indicated in Fig. 3.

$$\frac{d\alpha}{dt} = 4.89\times10^{10}\exp(-92938/RT)(1-\alpha)^{1.06} \quad (1)$$

2.3 Characterization of the viscosity of MPF

The viscosity and rheological properties of hot-melt resin are very important for the processing of film, which are directly affected by temperature and time. The Arrhenius model is widely used in viscosity prediction.

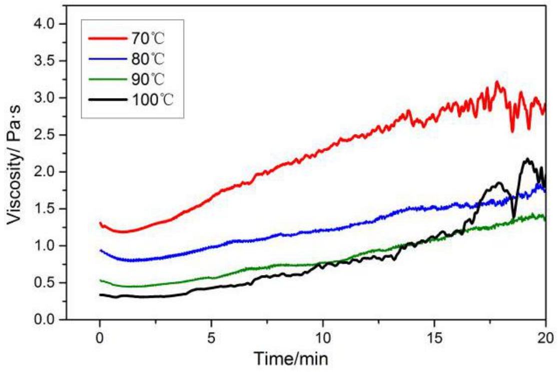

Fig. 4 The viscosity-time curve of MPF at different temperature

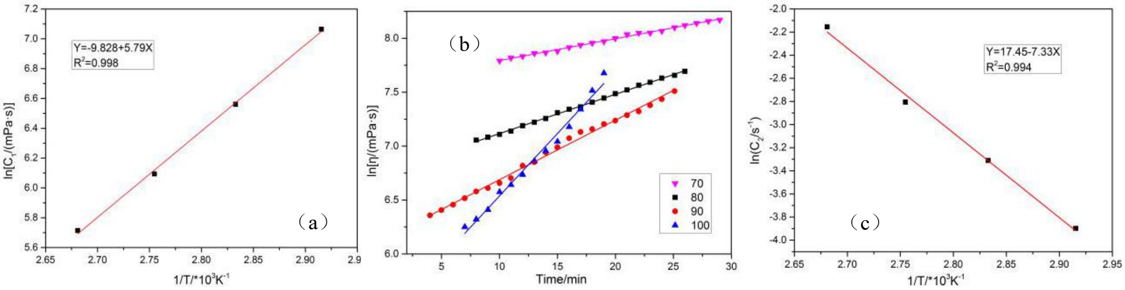

Fig. 5 Linear fitting of the viscosity of MPF

The viscosity of MPF can be presented as follows:

$$\ln\eta = -9.828 + 5790/T + t\exp\left(17.45 - 7330/T\right) \tag{2}$$

$$\eta = \exp\left\{-9.828 + 5790/T(t) + \int_0^t \exp\left(17.45 - 7330/T(t)\right)dt\right\} \tag{3}$$

3 NUMERICAL SIMULATION

3.1 Heat transfer-curing

$$\frac{\partial}{\partial x}[k_x\frac{\partial T}{\partial x}] + \frac{\partial}{\partial y}[k_y\frac{\partial T}{\partial y}] + \frac{\partial}{\partial z}[k_z\frac{\partial T}{\partial z}] + \rho Q = \rho C_T\frac{\partial T}{\partial t} \tag{4}$$

$$Q = \rho_r(1-V_f)H_f\frac{d\alpha}{dt} \tag{5}$$

where ρ is the density of composite; C_T is the specific heat of composite; k_x、k_y、k_z are anisotropic conductivity of the composite in the x, y, z direction, respectively; t is the time; T is transient temperature of the composite at time t; Q is the matrices resin reaction heat, generated from the cross-linking polymerization of it.

3.2 Flow-compaction

$$\frac{1}{\eta m_v}\left[k_x\frac{\partial^2 P_r}{\partial x^2} + k_y\frac{\partial^2 P_r}{\partial y^2} + k_z\frac{\partial^2 P_r}{\partial z^2}\right] = \frac{\partial P}{\partial t} \tag{6}$$

$$\bar{\sigma} = P + p \tag{7}$$

Eq. (6) is the basic differential equation of seepage, derived from Darcy's law. Eq. (7) is the effective pressure principle. Where k_i is the permeability in the i direction of composite; η is the resin viscosity; σ is the externally pressure; p is the effective pressure, beared by fiber; P is the pore pressure withstood by resin. The main purpose of flow-compaction model is to determine the V_f of the composite before the gel point. Moreover, due to the viscosity of the resin is related to temperature and the degree of cure, as equation (3).

3.3 Stress-deformation

The viscoelasticity constitutive equation of MPF/GF composite can be rewritten as follows:

$$\sigma_i(t) = \int_{-\infty}^{t} C_{ij}\left(\alpha, T, t-\tau\right)\frac{\partial\varepsilon_j^{eff}}{\partial\tau}d\tau \tag{8}$$

where σ_i indicates stress vector; C_{ij} is stiffness matrices of material; which reflects the viscoelasticity mechanics parameter of materials changes with time, temperature and degree of cure; t and τ are the history of time and past reduced time, respectively; ε_j^{eff} is the effective strain vector composed of the total strain, which can be indicated as follows:

$$\varepsilon_{\mathrm{j}}^{\mathrm{eff}} = \varepsilon_j - \varepsilon_{th} - \varepsilon_{ch} = \varepsilon_j - CTE_j \Delta T - CSE_j \Delta \alpha \tag{9}$$

where ε_j represents the total strain; ε_j *and* ε_j are the thermal strain and chemical shrinkage strain, respectively. CTE and CSE are the coefficient of thermal expansion and the coefficient of shrinkage expansion in each direction, respectively.

3.4 Simulation process

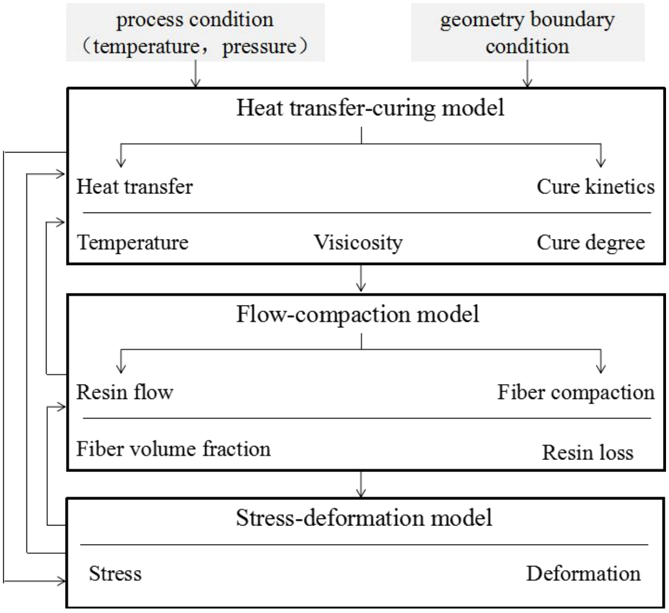

Fig. 6 Simulation process

3.5 RESULT

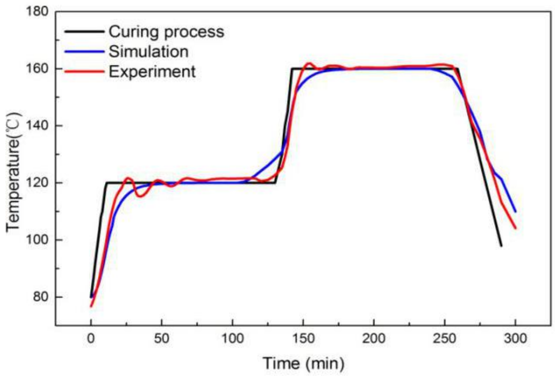

Fig.7 Verify the finite element model

As shown in Fig. 8, the temperature field distribution at 131min and at 161min of MPF/GF composite is calculated by the finite element method. To optimize the curing parameters, the simulated curing parameters of MPF/GF composite under different holding time, heating and cooling rate are analyzed and as indicated in Fig. 9. The existing curing process (heating rate of 4 ºC/min, holding time of 120min, cooling rate of 2 ºC/min) should be optimized as the cycle with the heating rate of 2 ºC/min, holding time of 120min and cooling rate of 0.5ºC/min based on the results of finite element simulation. The curing deformation and thermal stress of three representative locations in the model are calculated respectively under the two optimized curing parameters as shown in Table 1.

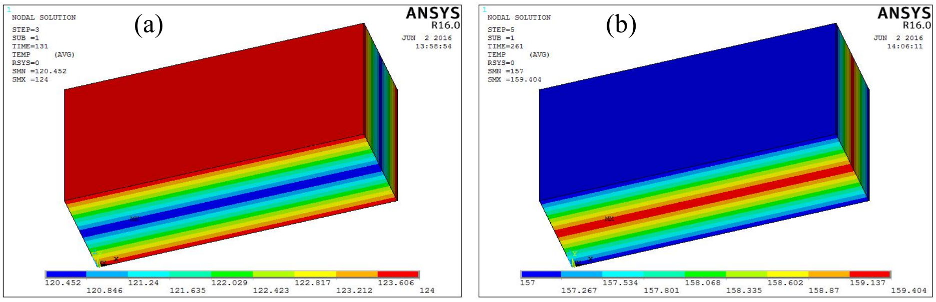

Fig.8 Temperature field distribution (a) at 131min; (b) at 161min of the composite

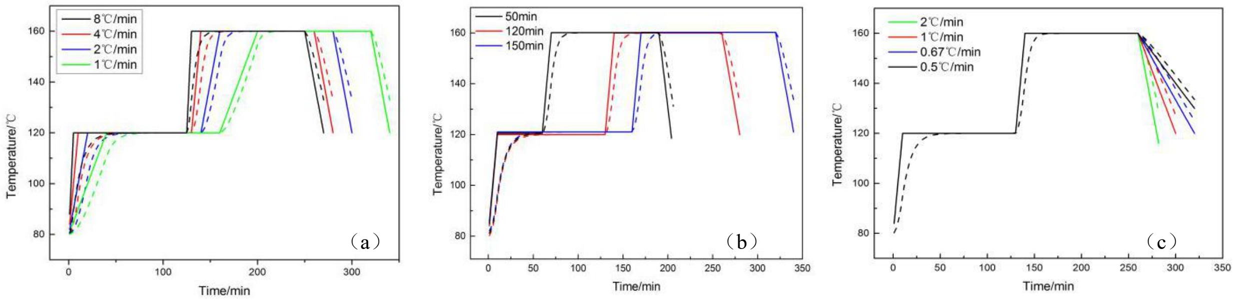

Fig. 9 Temperature changes of upper and lower surface and center point under (a) different heating rates; (b) different holding time; (c) different cooling rates. (solid lines show the surface temperature and dotted lines shows the center point temperature)

In summary, via calculating the temperature distribution and degree of cure in the composite at any cure time by finite element method, the curing cycle including heating rates, holding time and different cooling rates can be optimized. As a result, the residual stress of MPF/GF composite can be obtained as shown in Fig. 10. In addition, both the curing deformation and the residual stress of the optimized process MPF/GF composite are reduced by 6.37% and 2.4% , respectively, compared to the current process.

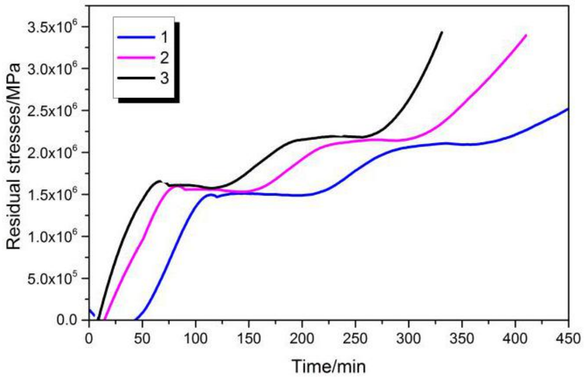

Fig.10 Temperature field distribution (a) at 131min; (b) at 161min of the composite

	Maximum deformation/mm			Maximum thermal stress/GPa		
	1	2	3	1	2	3
Current process	5.17e-4	3.40e-3	4.06e-3	2.13	1.75	1.56
Optimal process	4.77e-4	3.22e-3	3.81e-3	2.08	1.71	1.52
	7.74%	5.29%	6.09%	2.35%	2.29%	2.56%
		6.37%			2.4%	

Table 1: The corresponding curing deformation and thermal stress of MPF/GF composite

4 CONCLUSION

1. A novel hot-melt phenolic resin (MPF) is successfully prepared. The curing kinetic of MPF is characterized and modeled. The viscosity of MPF is investigated as a function of cure temperature using the Arrhenius model.

2. The existing curing process (heating rate of 4 °C/min, holding time of 120min, cooling rate of 2 °C/min) can be optimized with the heating rate of 2 °C/min, holding time of 120min and cooling rate of 0.5°C/min according to the result of finite element simulation.

3. The mathematical simulation allows for formulating a suitable cure cycle in autoclave processing. As a result, the curing deformation and thermal stress of MPF/GF composite are effectively reduced by 6.37% and 2.4%, respectively.

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