Study on the Cure Kinetics of Epoxy Resin Prepreg in Fiber Metal Laminates

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Abstract. To better analysis the curing behavior of a new kind of high temperature curing epoxy resin prepreg in fiber metal laminates (FMLs), dynamic differential scanning calorimetry (DSC) method was used to make the research on the curing process of the prepreg. The characteristic temperature of curing reaction and curing kinetics parameters of epoxy resin prepreg were systematically researched, and the cure kinetics equation was built. The cure kinetics model of the epoxy resin in the prepreg was determined by autocatalytic reaction model. The results showed that the reaction activation energy of the epoxy resin was 62.178kJ/mol and the reaction orders were 0.314 and 1.2157, the total reaction order was 1.5297. The optimum curing process was set at 180℃ under 0.6Mpa pressure for two hours, and the interlaminar shear strength (ILSS) of FMLs result was 69.75Mpa. The model can well describe the curing behavior of the prepreg, which will provide theoretic basis for the further studies on the thermodynamic properties of epoxy resin prepreg and the quality control of fiber metal laminates during the curing process.

1 Introduction

Fiber metal laminates are new hybrid composite structure materials which consist of the metal sheet and fiber reinforced polymeric materials, forming under a certain temperature and pressure according the needs [1]. FMLs combines the advantages of the metal and fiber reinforced resin composite. Compared with the traditional materials, FMLs have excellent fatigue and corrosion characteristics and impact resistance [2]. Due to their advantages, FMLs are widely used in most commonly in aerospace applications, now being used as structural materials for the wing skin panels, fuselage panels, fin box and rudder box. These material systems are the typical representative of advanced aerospace composites in the future.

The T800/epoxy resin used in the FMLs is a novel advanced composite materials with high toughness which developed by the Cytec company [3, 4]. Compared with traditional carbon fiber reinforced resin matrix composites, its application range is expanded to the primary structures, which can obviously reduce the weight of aircraft structure and improve the economic efficiency.

The quantitative analysis research of curing kinetics based on the change of functional groups in the reaction or the change of thermal effect. The most frequently used methods are fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) and DSC [5]. DSC method can directly measure the temperature change and observe the whole process than other methods. The DSC

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method can be divided into the non-isothermal method and isothermal method. Compared to the isothermal method, the non-isothermal method can not only avoids these problems, but also has the advantages of using less sample, saving time and getting more information.

Previous researches focused on the cure kinetics of pure epoxy resin. Using isothermal and non-isothermal DSC methods, Liu[6] studied the cure kinetics of 3234 epoxy resin system. However, Guo[7] et al. found that the cure kinetics of fiber reinforced composite prepreg was definitely different from the pure epoxy resin. Although the fiber did not change on the cure reaction mechanism, the fiber in the prepreg restrained ability of molecular during the curing process. Usually, the prepreg are directly applied for the FMLs. Up to now, the researches mainly focused on the processability and service performance of the T800/epoxy resin composite, ignoring the cure kinetics and quality control during the curing process [8, 9]. Studies on the cure kinetics of T800/epoxy resin in FMLs are rarely relevant reported at home and abroad.

In this paper, the cure kinetics of T800/epoxy resin prepreg was systematically investigated through non-isothermal DSC method, getting the cure kinetics equation and the curing related parameters. The results will find out the thermodynamic properties and provide the basic theory for the further investigation of FMLs during the forming process, expanding the application range of FMLs.

2 Experimental

Carbon fiber/epoxy resin prepreg was provided by the Shenyang Aircraft Company. The reinforcement body was T800 carbon fiber and the initial fiber volume fraction was 65%. Aluminum alloys 2524-T3 sheets were supplied by Southwest Aluminum Company.

FMLs consists of thin layers of aluminum and carbon fiber/epoxy prepreg. It was 3/2 lay-up with three layers of aluminum and two layers of prepreg, bonding with autoclave.

Thermal analyzer STA449C, Netzsch. Universal material testing machine CTM5000, SUST. Optical microscope DSX 500, Olympus.

Weighing 15-20mg sample seals puts in the aluminum crucible every time. Scanning samples uses the different heating rates of 2, 4, 6, 8 and 10K/min, respectively. Before each experiment, using standard samples of indium and zinc to calibrate instrument, setting scanning temperature range from 293.15K to 573.15K.The input rate of nitrogen with high purity is 100mL/min, and recording the DSC curves.

The ILSS was done according to ASTM D2344. There were five specimens for each experiment condition and the dimensions of the sample were 12.0mm × 5.0mm × 2.0mm (length × width × thickness). The testing machine using a speed at 1.0mm/min.

3 Results and discussion

3.1 Analysis of the cure kinetics DSC curves and characteristic temperature of the curing process

Fig.1 (a) shows the T800/epoxy resin prepreg DSC curves at different heating rates. We can find that there is only one single exothermic peak in each of the heating rate during the curing process. With the increase of heating rate, the exothermic peak gradually shifts to right, the peak temperature increases and the peak becomes steep. The main reason is that the samples have enough time for curing at low heating rates. As the heating rate increases, the thermal inertia and the temperature difference also increase.

The degree of cure and curing rate with temperature changes at different heating rates were shown in Fig.1 (b). The figures show that the degree of cure with temperature changes trend is the same as the curing rate. In the lower temperature, the curing rate is slow because of the induction period of reaction. After a period of time, the temperature increases with reaction, and then the curing rate reaches maximum value. At last the curing rate decreases gradually. The curing degree and temperature change as “S” curve during whole process.

Analyzing the DSC curves at different heating rates in Fig.1 (b), we can see the characteristic temperature of the initiative curing temperature T_i, the peak top temperature T_p and the finish curing reaction temperature T_f. They were listed in Table 1.

Using linear fitting method between the different heating rates of T_i, T_p, T_f and the heating rate β deals the experimental data. When the heating rate is zero, we can calculate the isothermal curing temperature through epitaxial method. According to the linear regression equation, the prepreg curing reaction temperature T_{i0}, T_{p0} and T_{f0} is 416.12K, 455.77K and 511.21K, respectively. That is the theoretical gel temperature T_{gel}, theoretical cure temperature T_{cure} and post treatment temperature T_{treat}.

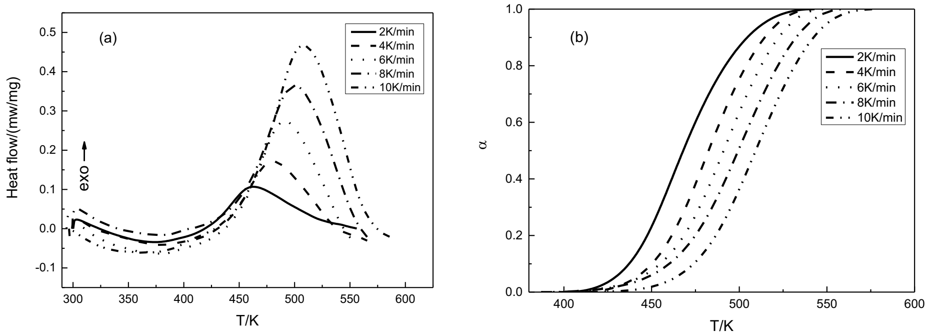

Figure 1. (a)Dynamic DSC curves of T800/epoxy resin prepreg at different heating rate(b)The degree of cure-temperature curves at different heating rate

Table 1. Characteristic temperature of T800/ epoxy resin prepreg at different heating rate

Characteristic temperature	2K/min	4K/min	6K/min	8K/min	10K/min
T_i/K	421.62	436.12	445.79	451.38	458.15
T_p/K	462.79	480.37	492.28	500.07	507.74
T_f/K	519.28	534.52	541.06	553.27	560.9

3.2 The cure kinetics model

In this paper, the phenomenological model was used to describe the curing process of T800/epoxy resin prepreg. The relationship between the curing degree and time, temperature can be clearly described by setting up the cure kinetics equation during curing process.

The autocatalytic reaction model belongs to the phenomenological model:

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1-\alpha)^n \tag{1}$$

The temperature dependence of the reaction rate is described by the Arrhenius equation:

$$k(T) = A\exp(-\frac{E}{RT}) \tag{2}$$

Where “A” is the rate constant, “E” is the activation energy, “R” is the gas constant.

Fig.2 shows that the cure reaction model of T800/epoxy resin met the autocatalytic reaction model. It can be described by the autocatalytic reaction model.

3.3 The cure kinetics parameters and curing model

The activation energy of curing reaction can be obtained by Kissinger equation as follows:

$$\ln\frac{\beta}{T_p^{\,2}} = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p} \qquad (3)$$

In the Eq.3, "β" is the heating rate, "T_p" is the peak top temperature, "A" is the rate constant and "R" is the gas constant. The curve of $\ln(T_p^2)$-$1/T_p$ was drawn according to the Eq.3 and shown in the Fig.2. Fig.2 shows that the correlation coefficient is $R^2=0.999$ which indicates that the fitting precision is very high. According to its slope, we can get E=62178.45J/mol.

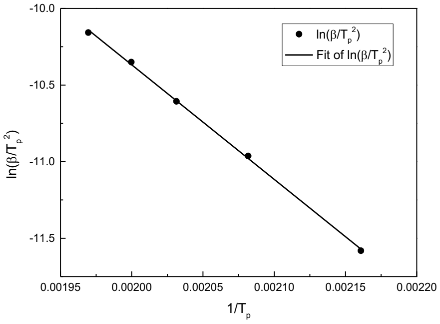

Figure 2. $\ln(\beta/T_p^2)$-$1/T_p$ fitting result of prepreg's curing process

The curing kinetics parameters of T800/epoxy resin prepreg at different heating rate are shown in Table 2. According to the autocatalytic reaction model and other known parameters, we can get the cure kinetics equation of T800/epoxy resin prepreg as follows:

$$\frac{d\alpha}{dt} = 17392.14\exp\left(-\frac{62178.45}{RT}\right)\alpha^{0.314}(1-\alpha)^{1.2157} \qquad (4)$$

Table 2. The curing kinetics parameters of T800/epoxy resin prepreg at different heating rate

β(K/min)	A(s^{-1})	m	n	R^2
2	17320.95	0.35066	1.63896	0.9976
4	17646.67	0.32288	1.30196	0.9973
6	16072.09	0.27509	1.06857	0.9886
8	14531.83	0.21784	1.01624	0.9851
10	21389.14	0.40377	1.34977	0.9928
average	17392.14	0.314	1.2157	

3.4 The curing process and ILSS results

During the FMLs forming process, the point is to control the temperature of prepreg. Appropriate temperature can directly affect the flowing ability of resin, and ensuring the interface of metal and fiber are soaked with resin. In order to improve the performance of the FMLs, the appropriate curing temperature and time are needed to cure the resin completely.

According to the cure kinetics equation, the curing cycle were done at a heating rate at 1.5℃/min up to 150℃ or 180℃ under 0.6Mpa pressure for two hours. The ILSS test results was shown in the Fig.3. Fig.4 presents the interface of FMLs which final temperature was held at 180℃.

The maximum value is 69.75Mpa and 62.56Mpa. The stress is 11 percent over the other when the curing temperature is 180℃. Because the soakage, fluidity and viscosity are better than another. There are less voids and bubbles in the interface of metal and fiber, as we can see in Fig.4. The higher bonding strength of resin with metal and fiber, the better the mechanical capabilities could be gained of FMLs.

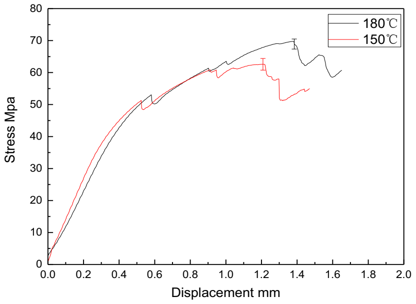

Figure 3. The ILSS test results

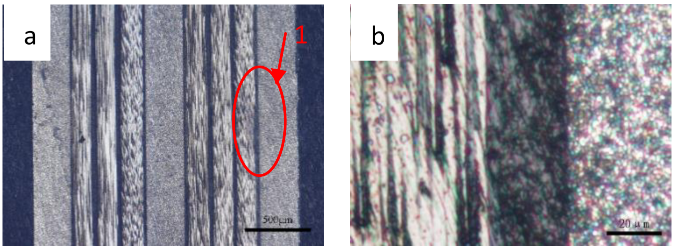

Figure 4. (a) The interface of FMLs optical image, (b) Larger image of area 1

Based on the ILSS tests, It’s better to take the curing process with a temperature growth rate of 1.5℃ /min up to 180℃ under 0.6Mpa pressure for two hours. The cure kinetics equation of T800/epoxy resin prepreg provides theoretic basis for the manufacturing FMLs.

4 Conclusion

(1) In this paper, the curing reaction rate with temperature change was obtained by analyzing the DSC curves of the T800/epoxy resin prepreg. The results showed that the cure kinetics model of the T800/epoxy resin prepreg was accordant with the autocatalytic reaction model.
(2) By non-iso DSC experiment of T800/epoxy resin prepreg, we could get an equation which expressing cure kinetics of resin as: $\frac{d\alpha}{dt} = 17392.14\exp(-\frac{62178.45}{RT})\alpha^{0.314}(1-\alpha)^{1.2157}$.The results of the model agreed well with the experiment results.
(3) Through the cure kinetics of the T800/epoxy resin prepreg, the curing temperature was set to 180℃ under 0.6Mpa pressure for two hours. The ILSS results was 69.75Mpa. This outcome will provide the theoretical basis for the selection and optimization of the FMLs forming.

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