QUANTITATIVE EVALUATION OF CURING SHRINKAGE IN POLYMERIC MATRIX COMPOSITES

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Abstract

The aim of this study is to measure the cure shrinkage of epoxy resin system used in the CFRP. First, the cure kinetics of Bisphenol A type epoxy resin system was studied by Differential Scanning Calorimetry measurement. From the dynamic DSC measurement, the total heat of cure of the epoxy was determined as 293 [kJ/g]. Also, curing condition and the extent of cure were determined by the isothermal DSC and TGA measurement. By controlling the curing condition, immature cured epoxy bar-shaped specimen was moulded.

The cure shrinkage was measured by using the laser confocal displacement meter without any contact with the bar-shaped specimen. Comparing the specimen size after each cure, cure shrinkage of the bar-shaped specimen was measured.

1 Introduction

CFRP possesses excellent mechanical properties, chemical resistance, heat resistance, electrical properties, and so on. From these advantages, CFRP are widely used in aerospace, automotive structural materials as a substitute for metal materials. From the high coefficient of thermal expansion (CTE), CFRP came under review for precision machinery components and large structures. Applying CFRP to such materials, long-time high dimensional stability must be secured. For attaining the super-dimensional accuracy, moisture absorption, cure shrinkage, residual stress relaxation, and visco-elastic deformation such as creep are presumable to be the leading disturbance factors yielding the micro-deformation. These deformation factors might be very small, so that we need to evaluate quantitatively these factors individually. From these factors, we focus on the cure shrinkage of the CFRP in the present study. Because that the cure shrinkage of CFRP occurs in the matrix, we focused on the cure shrinkage of epoxy resin used in the CFRP matrix.

Neat epoxy resin used in this study is 4,4'-isopropylidenediphenol (Bisphenol A type) and the hardener is modified aliphatic polyamines. There are numerous techniques to determine the cure kinetics of epoxy resin system, for example thermal analysis as Differential Scanning Calorimetry (DSC) (1), Infrared spectroscopy (IR), Fourier Transform IR (2), Nuclear Magnetic Resonance (NMR), and simply by measuring mechanical properties. Among these techniques, DSC measurement was selected in this study from its sensitivity and its similarity to the moulding in means of thermal effects.

In this study, thermal behavior of epoxy resin system was studied by means of DSC measurement (3). Dynamic DSC measurement was conducted to determine the total heat of reaction. Also, the heat of reaction during the cure was measured by isothermal DSC measurement. Both values were quoted to define the extent of cure. To evaluate the cure behavior, typical kinetic model was applied to predict the extent of cure for epoxy resin system.

Numerous methods for the determination of cure shrinkage have been reported including mercury dilatometry, water dilatometry, linear contraction measurements, density measurement and calculations based on degree of conversion measurements. From the deformation mode of the bar-shaped specimen, the cure shrinkage was evaluated using laser confocal displacement meter in this study. Cure shrinkage of the specimen from the given extent of cure and to the further cure was measured. By measuring the cure shrinkage after each cure, the micro-dimensional changes concurrent with the cure was evaluated.

2 Experimental

2.1 Materials

The materials used in this study are Bisphenol A type epoxy resin (4,4'-isopropylidenediphenol), jER 834, and the hardener (modified aliphatic polyamines), jER cure 3080, both supplied by Japan Epoxy Resin. The mixture ratio of the epoxy resin and the hardener was determined from the value of phr of the hardener. There are a large number of epoxy resin systems used in researches, but this system was selected from its slow rate of cure and its viscosity. From these properties, the cure reaction would be easily controlled by its cure condition compared to other epoxy system.

2.2 TGA measurement

In order to determine the cure temperature of the epoxy resin system, thermo-gravimetric analysis was conducted. The temperature of the thermal decomposition and the pyrolysis of the epoxy resin system were investigated by thermo-gravimetric as shown in figure 1.

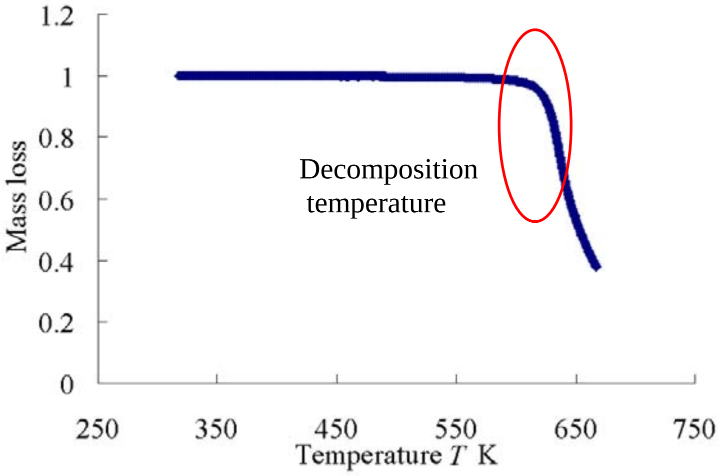

Fig. 1 Thermo-gravimetric curve

The TGA curve falls abruptly when the temperature reaches 573[K]. From the TGA measurement, the maximum temperature available for this epoxy resin system was determined as $T_{\max} = 573[K]$.

2.3 DSC measurement

The cure of epoxy resin was studied under differential scanning of calorimetry, TA Q-200. Both dynamic scans and isothermal scans were conducted for the epoxy resin. The dynamic DSC scanning was performed at 10 [K/min] from 293 to 523 [K]. The scanning temperature was determined by the TGA analysis. The total heat of complete cure reaction, ΔH_{rxn}, was obtained by integrating the area between the dynamic DSC curve and the base

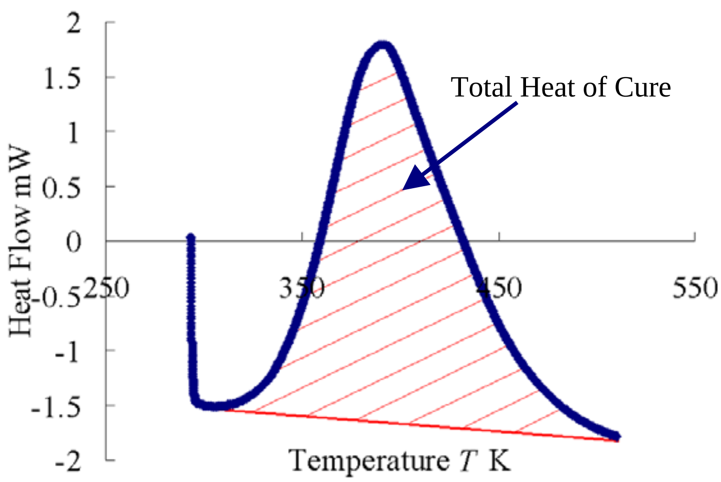

Fig. 2 Dynamic DSC curve and the total heat of cure

line as shown in figure 2.

After the dynamic DSC scanning, another dynamic scanning was conducted to determine the glass-transition temperature, T_g. The typical DSC curve for measuring T_g is shown in figure 3.

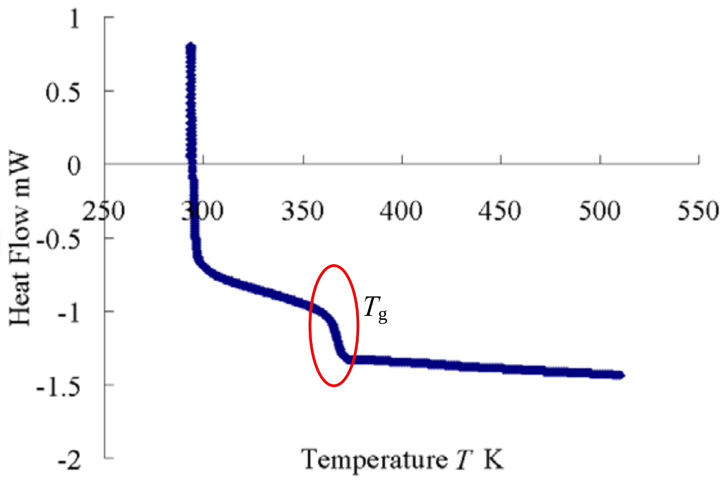

Fig. 3 the Dynamic DSC scanning of glass-transition temperature

Isothermal DSC analysis was performed at cure temperatures, T_{cure}, ranging from 343 to 373 [K] in 10 [K] increments. The heat evolution during the cure reaction, ΔH_{iso}, was obtained by integrating the heat flow between the isothermal DSC curve and the base line as shown in figure 4.

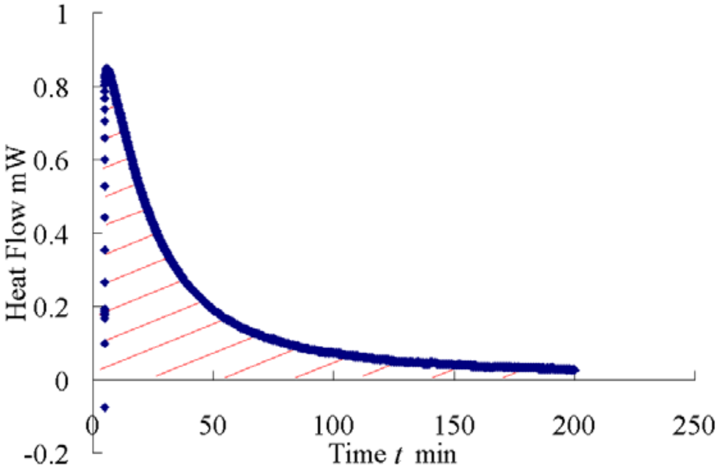

Fig. 4 Isothermal DSC curve and the heat during the cure

2.3 Dimensional Measurement

The dimension of the epoxy bar-shaped specimen used in the measurement is shown in figure 5. The dimensional measurement was conducted in high degree of accuracy using the laser confocal displacement meter, Keyence KS-1100, without any contact against the specimen.

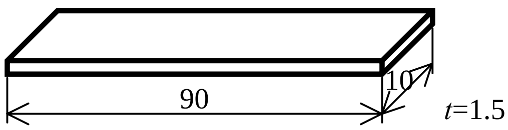

Fig. 5 Specimen geometry

First, the epoxy resin specimen was cured incompletely by the deficient cure condition. The cure condition of the epoxy specimen was determined from the DSC measurement. After the incomplete cure, specimen size was measured to check the geometry before the cure shrinkage occurs. Cure shrinkage occurs concurrent with the further cure. By comparing the specimen size after each cure, cure shrinkage could be measured. From this method, micro-shrinkage concurrent with the cure was determined.

The typical dynamic DSC curve of incompletely cured epoxy specimen is shown in figure 6. The heat flow between the DSC curve and the linear line is the residual heat of cure reaction ΔH_{res}.

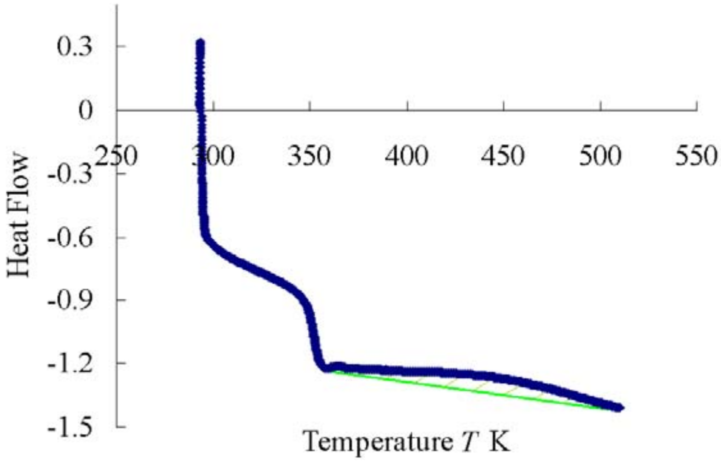

Fig. 6 Dynamic DSC curve of the incompletely cured specimen

3 Results and Discussion

3.1 Total Heat of Reaction

The total heat of cure reaction, ΔH_{rxn}, was obtained from the heat flow, hatching part of the figure 1. The total heat of cure reaction of this epoxy resin used in this study was obtained by integrating the heat flow, ΔH_{rxn} =293[kJ].

3.2 Extent of Cure Reaction

The heat evolution during the cure reaction can be assumed equal to the extent of cure [1]. We defined the extent of cure, x, as a function of the heat of reaction, ΔH, measured by DSC measurement as equation (1):

$$x = \frac{\Delta H_{rxn} - \Delta H_{res}}{\Delta H_{rxn}} = \frac{\Delta H_{iso}}{\Delta H_{rxn}} \qquad (1)$$

where ΔH_{rxn} is the total heat evolving during the complete cure obtained by the dynamic DSC scan, ΔH_{iso} is the heat of partially cured sample obtained by isothermal DSC scan, and ΔH_{res} is the residual heat of cure reaction obtained by dynamic DSC scan. The extent of cure x for the epoxy resin is shown in figure 7.

To evaluate the cure shrinkage, the extent of cure must be predicted at given cure condition. We applied the reaction kinetics commonly used in the epoxy resin system, in order to determine the extent

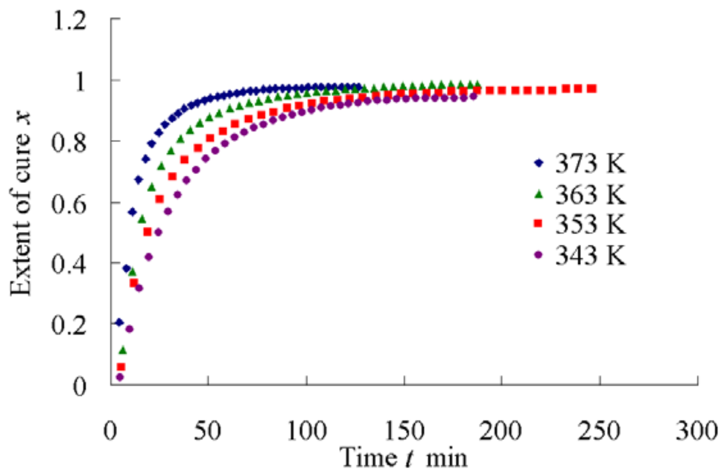

Fig. 7 Extent of cure against time

of cure [2]. Arrhenius model shown in equation (2), was applied to predict the rate of cure reaction.

$$\frac{dx}{dt} = A\exp\left(-\frac{E}{RT_{cure}}\right)x^m(1-x)^n \qquad (2)$$

where A is the reaction rate constant, E is the activation energy, R is the gas constant, and both m, n are the kinetic parameters.

The activation energy E for the epoxy cure reaction is expressed as equation (3).

$$\ln\frac{t}{t_{373}} = \frac{E}{R}\left(\frac{1}{T_{\mathrm{cure}}} - \frac{1}{T_{373}}\right) \qquad (3)$$

where T_{cure} is the curing temperature, $T_{373} = 373[\mathrm{K}]$, t is the time required to reach the peak in each curing temperature, t_{373} is the time required to reach the peak when T_{cure} =373[K]. Arrhenius plot for the

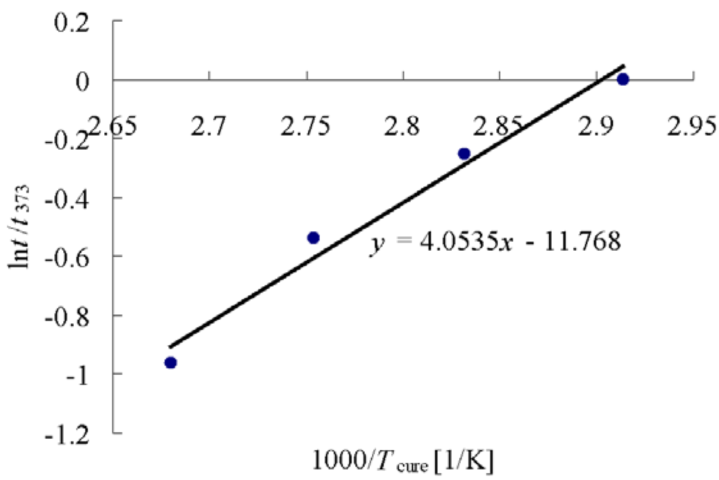

Fig. 8 Arrhenius plot for the epoxy resin

epoxy resin system is shown in figure 8. The activation energy, E, was determined from the linear least-square fit on $\ln t/t_{373}$ vs. $1000/T$ data in the Arrhenius plot as $E = 33.7\,[\mathrm{kJ/g}]$.

The comparison of the extent of cure from the kinetic model from equation (2) and the experiment is shown in figure 9. The parameters used in the Arrhenius model are given in table 1.

Table 1 Arrhenius parameters

Reaction rate constant A [sec^{-1}]	0.0025
Reaction Energy E [kJ/g]	33.7
Gas constant R [kJ/mol]	8.31
Kinetic parameter m	0.36
Kinetic parameter n	1.8

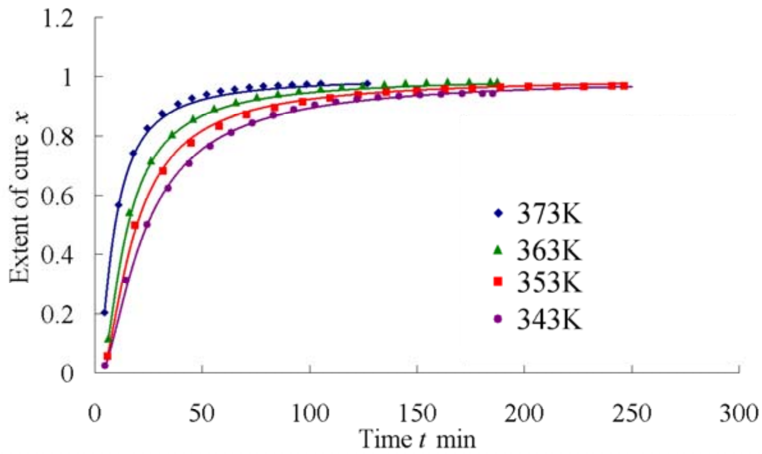

Fig. 9 Comparison of experimental plots and theoretical lines against time

3.3 Cure shrinkage

From the Arrhenius model, the immaturely cured bar-shaped specimen was moulded. By measuring the specimen size after each cure, the cure shrinkage was determined. The cure shrinkage is defined as equation (3).

$$\varepsilon_{\mathrm{cs}} = \frac{\Delta\lambda}{l_0} \qquad (3)$$

where $\Delta\lambda$ is the decrease in the specimen size and l_0 is the basic specimen length. The cure shrinkage was measured in the x direction of the bar-shaped specimen as shown in figure 10. By defining the basic specimen length as the specimen length of an half cured specimen (x=0.5), the cure shrinkage was measured as figure 11.

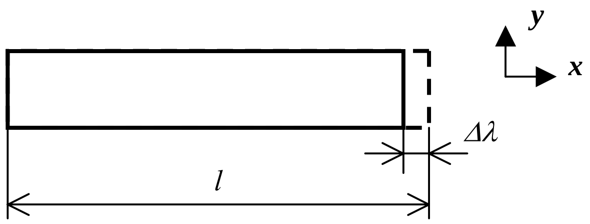

Fig.10 Measurement direction of the cure shrinkage

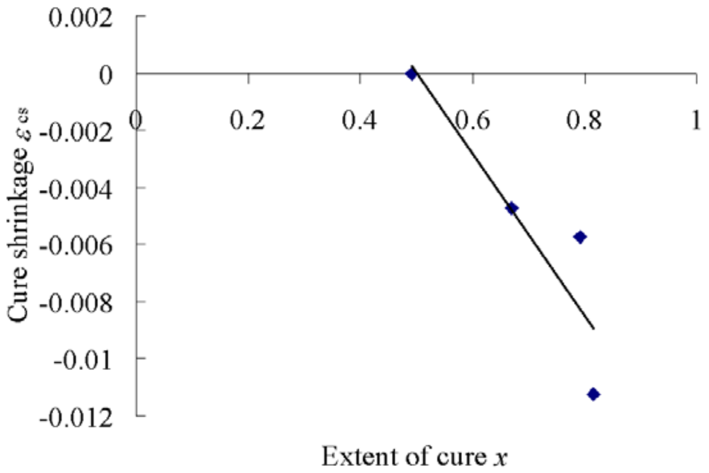

Fig. 11 Cure shrinkage against the extent of cure

4. Concluding Remarks

The cure kinetics of the epoxy resin system was analyzed by DSC measurement and evaluated by Arrhenius model. The total heat of cure $\varDelta H_{rxn}$ of the epoxy resin system was determined as 293[kJ].

From the thermal analysis, the extent of cure of the bar-shaped specimen was predicted. By curing the immaturely cured specimen, the cure shrinkage was observed. By curing the half cured specimen (x=0.5), the cure shrinkage was measured as $\varepsilon_{CS} = -0.012$.

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