IN-SITU MONITORING AND SIMULATION OF CURE-PROCESS OF CFRP USING OPTICAL FIBER SENSORS

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Abstract

In-situ measurement method using embeddable sensors is an attractive method to investigate the optimum molding condition of FRP. In the present study, Fresnel-based fiber-optic sensors were used for cure monitoring of CFRP. Refractive index of matrix resin can be measured by the sensor and degree-of-cure can be calculated from the value because the refractive index varies with cure reaction. First, degree-of-cure curves of resin were measured by the fiber-optic sensors and DSC analysis. Comparing these curves by fiber-optic sensors and DSC analysis, it appeared that the degree-of-cure curves by the two methods agreed well with each other. Second, the cure monitoring of textile CFRP was conducted with heating temperature of 80 °C. It was found that the degree-of-cure curve of CFRP was almost the same as that of matrix resin. Therefore, it appeared that the sensing system can measure precise degree-of-cure of CFRP. Cure process simulation was conducted using a kinetic model obtained from DSC analysis and optical fiber sensors. Since the simulated results showed good agreement with the experimental results, it appeared that the kinetic model using data measured by optical fiber sensors has very good performance to predict cure process.

1. Introduction

Recently, large and complex-shaped thermosetting composite structures have been applied to varieous engineering products such as aircraft fuselage and wings, automotive shaft and bodies. Difficulty of manufacturing of large thermosetting composites is to hold uniformity of temperature distribution overall products since the non-uniform temperature causes inhomogeneous distribution of degree-of-cure. Thus, the optimum temperature condition is essential to achieve high performance of composites products. Additionally, designing the optimum condition, molding process time can be minimized. However, since optimization of molding condition is conducted by a trial-and-error method today, development of molding process of large composites cost very high. Therefore, more efficient and low coast method for obtaining the optimum molding condition for composites molding is desired commercially.

In-situ sensing method using embeddable sensors is an attractive solution to investigate optimum molding condition of FRP [1]. Among embeddable sensors, optical fiber sensors are very promising to measure cure process of thermosetting composites due to thin fiber shape, flexibility, high strength, high functionality and high durability. Many kinds of physical parameters can be measured by optical fiber sensors such as infrared absorption spectrum [2-5], refractive index [6-8] and strain. A fiber-optic infrared spectroscopy-based cure monitoring is a method to estimate molecular structures by measuring infrared absorption spectrum of reactive molecules of resin. Although this technique is able

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to monitor progress of cure reaction in detail, it is difficult to measure degree-of-cure accurately due to large noise. On the other hand, a refractive-index sensor, which is a technique to measure degree-of-cure of resin from Fresnel's reflection at interface between glass fiber and resin, is inexpensive due to simple optical system. Additionally, this sensor can measure both fast and slow cure reactions, and the measurement area, that is equivalent to beam diameter (typically 10 μm for a single-mode fiber), is very small. A refractive-index sensor has been proven to be applicable to monitor progress of cure reaction of epoxy resin form start to finish [6].

In the present study, Fresnel-based fiber-optic sensors were employed to measure degree-of-cure of resin and CFRP molded by VaRTM process. At first, degree-of-cure curves of resin and CFRP were measured by DSC(Differential Scanning Calorimeter) and the optical fiber sensors in order to confirm measurement performance of our system. Next, a precise kinetic model was made from experimental results. Then, the process simulation was conducted and the results are compared with the experimental results in order to discuss measurement and prediction performance of our present method.

2. Theory for Measurement of Degree-of-Cure

A schematic view of an optical fiber sensor and a sensing system used in this study is illustrated in Fig.1. The light from a light source enters in the resin through a circulator. At the surface between optical fiber and resin, the light causes Fresnel's reflection due to the difference of refractive index between the glass and resin. The reflection light is sent to the optical receiver through a circulator again and the light intensity is measured by the receiver.

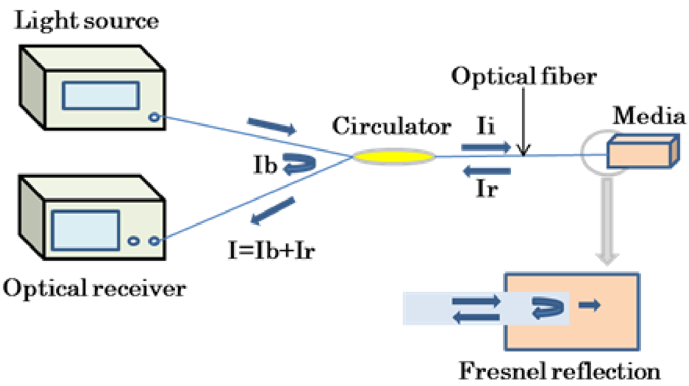


Figure 1. Schematic view of refractive index measurement of resin by an optical fiber.

Refractive index variation Δn of resin is calculated by the following equations from the measured optical power.

$$\frac{\Delta n}{n_{eff}+n_s}=\frac{\eta_s(1+\eta_s)+\eta_{air}^2\nu\pm(1+\eta_s)\sqrt{\eta_s^2+\eta_{air}^2\nu}}{1-\left(\eta_s^2+\eta_{air}^2\nu\right)} \tag{1}$$

$$\eta_{air}=\sqrt{R_{air}}=\frac{n_{eff}-1}{n_{eff}+1},\quad \eta_s=\sqrt{R_s}=\frac{n_{eff}-n_s}{n_{eff}+n_s}.$$

$$\nu\simeq\Delta I/I_{air}$$

Here, ν is normalized optical intensity variation, n_{eff} is the effective refractive-index of glass, n_S is the initial refractive-index of resin, ΔI is variation of the measured light intensity and I_{Air} is light intensity reflected from the air.

When the refractive index variation $\Delta n(\alpha,T)$ is defined as a function of degree of cure α and temperature T, the temperature dependencies of the refractive index of the resin are expressed in the following equations when the degree of cure is constatnt.

$$\Delta n(\alpha,T)=\Delta n(\alpha,T_0)+\frac{dn}{dT}(\alpha)(T-T_0)\,. \tag{2}$$

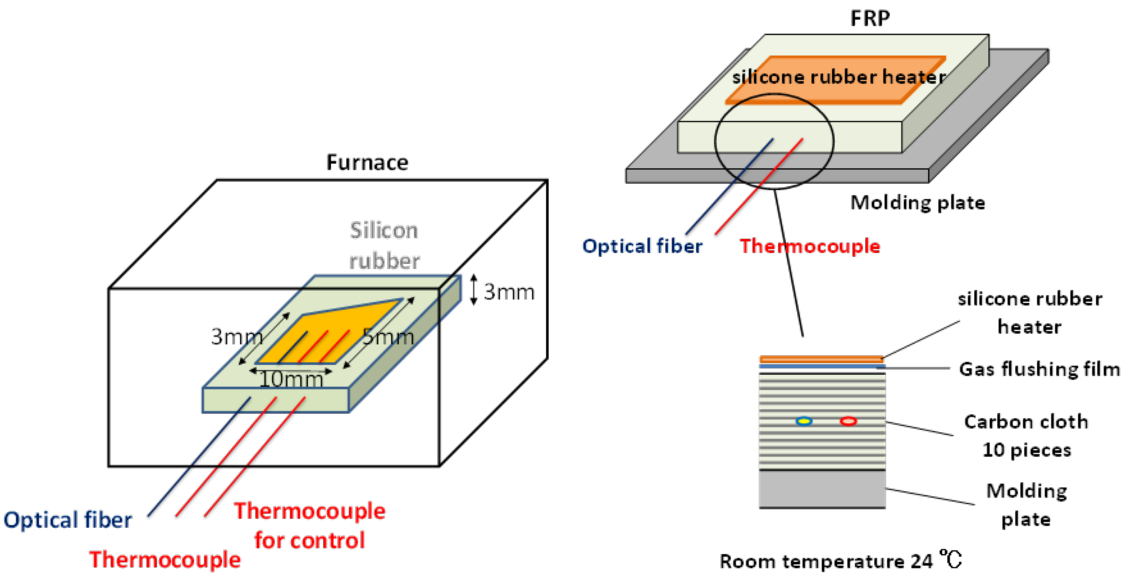
Here, dn/dT(α) is the temperature dependency of the refractive index and T_0 is the reference temperature. We suppose that the refractive index variation Δn is defined as the following formula using degree-of-cure α as a linear transition factor during cure reaction.

$$\Delta n(\alpha,T)=\Delta n(0,T)(1-\alpha)+\Delta n(1,T)\alpha\,. \tag{3}$$

From the about equations of (2) and (3), degree-of-cure can be calculated by removing the temperature dependency of the refractive index.

$$\alpha=\frac{\Delta n(\alpha,T)-\dfrac{dn}{dT}(0)(T-T_S)}{\Delta n(1,T_0)+\left\{\dfrac{dn}{dT}(1)-\dfrac{dn}{dT}(0)\right\}(T-T_0)}\,. \tag{4}$$

Where, T_s is the temperature where the calculation of degree of cure starts where $\Delta n = 0$.



(a) Monitoring of Resin (b) Monitoring of CFRP

Figure 2. Experiment set-up for measuring degree-of-cure of resin and CFRP

3. Experimental Methods

3.1. Materials and experimental set-up for measuring degree of cure of the resin

For manufacturing FRP, epoxy resin (ARALDITE LY5052, hardening: ARADUR 5052 CH) was employed as matrix resin and carbon cross of thickness 0.2mm, as reinforcement. Figure 2(a) illustrates an experimental set-up for measuring refractive index of resin. We prepared a silicon mold which has a trapezoid shape and 3mm thickness as shown in the Fig. 2(a). The silicon mold was filled with liquid resin and an optical fiber sensor and a thermocouple were embedded in the resin. The light source is a SLD light whose wavelength is 1310 nm. The heating rates of the molding temperature conditions were 0.5, 1, 2, 3 and 5 °C/min. where the respective maximum temperatures were 150, 150, 170, 180 and 200 °C. In addition, we conducted room-tempearture cure and single-step heating cure tests (we named it isothermal condition in the present paper) where the heating rate was 2°C/min. and the maximum constant temperature was 60, 70 and 80 °C.

Using a DSC (MAC SCIENCE PSL3100), heat flow curves by cure reaction of the epoxy resin were measured. The temperature conditions were the same values as the experiment of cure monitoring by the optical fiber sensors at the constant heating condition.

3.2. Experimental set-up for measuring degree of cure of the CFRP

The experimental set-ups for measuring degree-of-cure of the CFRP is shown in Fig.2(b). The textile CFRP was manufactured by a VaRTM (Vacuum assisted Resin Transfer Molding). Before vacuum packing process, an optical fiber sensor and a thermocouple were embedded into the center layer of the carbon textile preform which is consist of ten textile layers. Then, the resin diffusion media was placed on the carbon preform. By dragging the air after packing process, the preform was impregnated with the liquid epoxy within a few minutes. After VaRTM process, the CFRP was heated by a silicon rubber heater attached on the upper surface of packed material. A single-step heating conditions where the heating rate was 2°C/min. and the maximum constant temperature was 60, 70 and 80 °C were used for the manufacturing process.

4. Results and Discussions

4.1. Comparison between degree of cure curves of resin by the DSC and by the optical fiber sensor

The relationship between refractive index variation of epoxy resin and temperature for several temperature conditions were plotted in Fig.4. The heating rates of the data were 0.5, 1, 2, 3 and 5 °C/min. In addition, the results obtained under the single-step temperature conditions were plotted in the figure. The refractive index decreased in proportion to temperature before cure reaction started. After cure reaction begins, the temperature dependency of Δn became nonlinear and turned to increase. Then, the temperature dependency became linear again when cure reaction completed. From the figure,

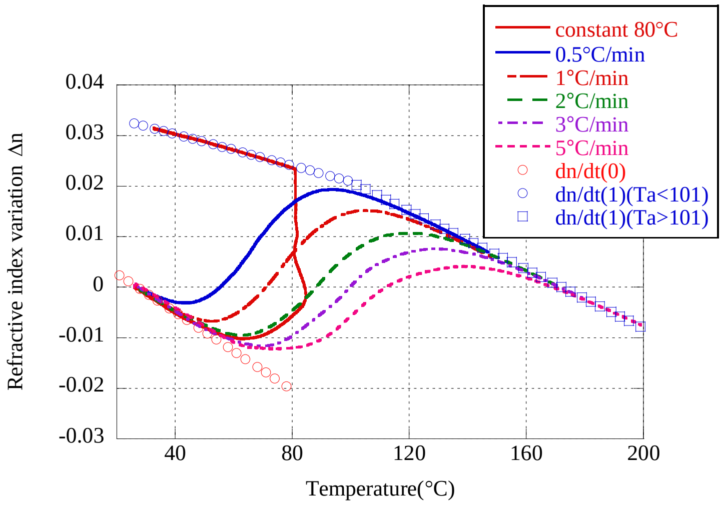


Figure 3. Relationship between refractive index variation of epoxy resin and temperature for several temperature conditions

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it appeared that the all measured curves of the epoxy showed the same temperature dependent curve after cure reaction. It means that this sensor can estimate degree-of-cure precisely using the equation (4) at any molding temperature condition. The material constants for calculating degree-of-cure was obtained from the results and listed at Table. 1. Using these constants, we can obtain degree-of-cure at real time.

The degree-of-cure was calculated from the experimental Δn curves using the equation (1). Figure 4 shows relationships between degree-of-cure obtained by optical fiber sensors, degree-of-cure by DSC and temperature. Here, lines show data measured by the DSC and marks show data measured by optical fiber sensors. From the results, it was revealed that the degree-of-cure curves measured by the optical fiber sensors agreed very well with that by DSC analysis. Thus, the degree-of-cure measured by the optical fiber sensors was considered to be equal to that by DSC analysis

Table 1. Material constants of epoxy resin for cure monitoring

$dn/dT(0)$ [1/K]	-5.24×10^{-4}
$dn/dT(1)$ ($T<T_0$) [1/K]	-1.82×10^{-4}
$dn/dT(1)$ ($T>=T_0$) [1/K]	-3.81×10^{-4}
$\Delta n(1,T)$	2.42×10^{-2}
T_0 [°C]	101

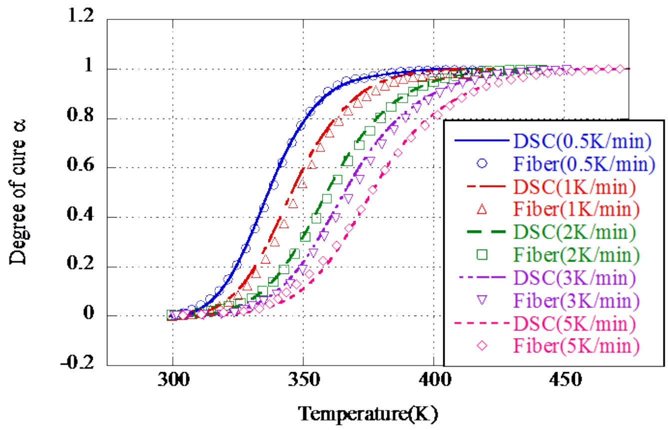

Figure 4. Degfee-of-cure curves of epoxy measured by optical fiber sensors and done by DSC, plotted against molding temperature

4.2. Comparison between degree-of-cure of resin and textile CFRP

A textile CFRP was manufactured by VaRTM method and cured under the single-step temperature conditions. Degree-of-cure was measured by the embedded optical fiber sensor. The relationship between the degree-of-cure, temperature and curing cycle time is plotted in Fig.5. Here, the line plots shows the results of monitoring CFRP and the dot plots does the results of monitoring resin-only. From the figure, it appeared that the both degree-of-cure curves agreed very well with each other. Thus, it is thought that the carbon cross does not affect the degree-of-cure measurement of the matrix resin. This means that photoelastic changes in refractive index of the matrix resin caused by carbon fibers which restrict matrix, is negligible during cure process. Therefore, constants for calculation of degree-of-cure of CFRP can obtained from the cure monitoring tests of resin.

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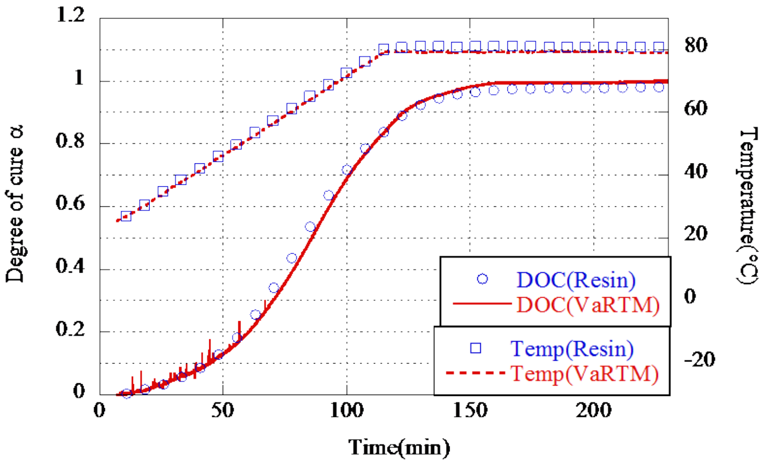

Figure 5. Degree-of-cure curves of CFRP (VaRTM) and resin-only cured at 80℃

4.3. Making kinetic model of cure reaction for process simulation

In this section, the kinetic model of cure reaction of matrix resin is obtained using the Kamal model and experimental degree-of-cure curves [9]. The Kamal model was described as,

$$\frac{d\alpha}{dt}=\left(k_1+k_2\alpha^m\right)\left(1-\alpha\right)^n \tag{5}$$

$$k_1=A_1e^{-\frac{E_1}{RT}},\ k_2=A_2e^{-\frac{E_2}{RT}}.$$

Where, R is a gas constant, E_1 and E_2 are activation energy, m, n are order of reaction, A_1 and A_2 are constants. The parameters of Kamal model were obtained using measured data by DSC under the condition of constant heating rate and by optical fiber sensors under the condition of isothermal heating (25, 60, 70, 80°C). These parameters are listed in the table 2. Here, it supposed that k_1 is negligible and set to 10^{-6} because relationship between rate of degree-of-cure and temperature showed shape of single peak mountain.

Table 2. Parameters of Kamal model for the epoxy resin obtained from DSC analysis and optical fiber sensors

m	0.104114
n	1.10086
E_2	50.78 kJ/mol
A_2	39152.7
k_1	10^{-6}

The degree-of-cure was simulated under the single-step temperature conditions. Figure 6 shows the simulated degree-of-cure curves of CFRP with the experimental results when the isothermal temperature was 80°C. The figure shows that that the simulated curve agreed well with the experimental curves.

In the present paper, we propose the method of real-time estimation of degree-of-cure using combination of real-time measurement and simulation of degree-of-cure. When the degree-of-cure was more than 0.2, the value was estimated using the kinetic model where the initial value of degree-of-cure was measured by the optical fiber sensors.

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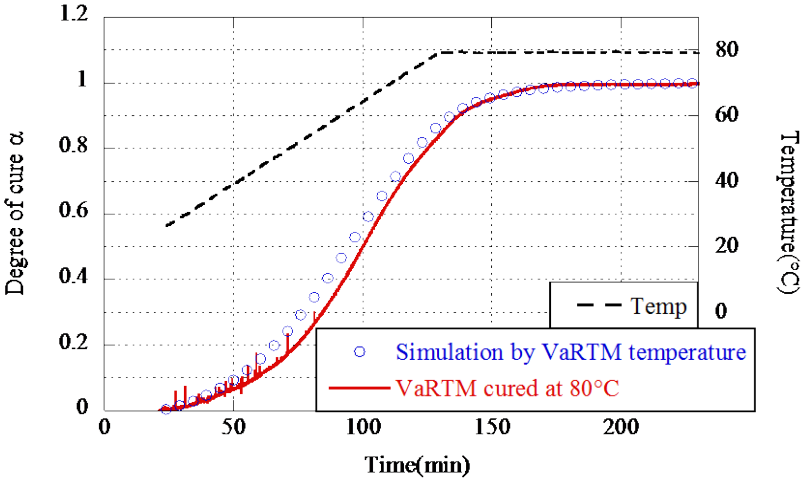

Figure 6. Degree-of-cure curves of CFRP by the simulation, measured by fiber-optic sensor and temperature plotted against time

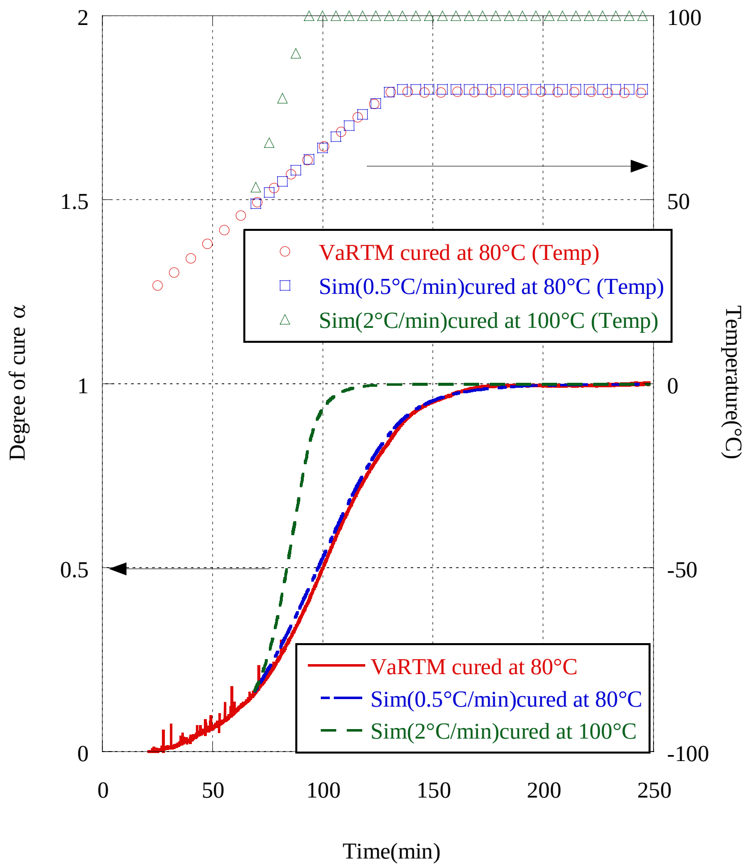

Figure 7. Degree-of-cure curves of CFRP and temperature curves where the isothermal temperatures were 80°C(0.5°C /min) and 100°C (2°C /min)

The simulated result was compared with the experimental results in Fig.7. From these results, it appeared that degree-of-cure could be estimated precisely at real-time by an accurate kinetic model for cure reaction and in-situ monitoring result of degree-of-cure. Using this method, we can control molding temperature so that degree-of-cure becomes 1.0 at the time we desired. For example, the temperature control using this method was demonstrated in Fig.7. It is shown that cure reaction finished at 110 minutes by changing heating rate and isothermal temperature.

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4. Conclusions

In the present paper, *in situ* monitoring and prediction method of degree-of-cure using Fresnel-based optical fiber sensors was applied to monitor cure reaction of epoxy resin and CFRP. From the experimental and simulated results, we can obtain the following conclusions.

(1) Carbon reinforcements do not influence measurement performance of degree-of-cure of CFRP.
(2) A precise kinetic model of cure reaction of resin can be obtained using combination of degree-of-cure data measured by DSC and the optical fiber sensors.
(3) Degree-of-cure can be estimated precisely in real time by an accurate kinetic model for cure reaction and *in-situ* monitoring results of degree-of-cure.

This monitoring system is helpful to conduct real-time control of molding temperature. In future, multiple-points measurement function will integrated into the system in order to monitor distribution of degree-of-cure.

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