Key Engineering Materials. Vols. 297-300, p. p2903 -2908
online at http://www.scientific.net

Smart Cure Monitoring Method of Carbon/Epoxy Laminates using Electric Capacitance Change with Applied Alternating Current Frequency

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Keywords: Degree of cure, Cure monitoring, Carbon/epoxy composite, Dielectric constant, Frequency dependency

Abstract. Authors have developed an electric resistance change method for delamination monitoring of carbon/epoxy composite laminates. The method employs reinforcement fibers as sensors; electrodes are co-cured. Co-cured electrodes for delamination monitoring are adopted in the present study as sensors for monitoring the degree of cure. This study proposes a new method using electrical capacitance change for monitoring the degree of cure without using additional sensors. Applying alternating current between electrodes during the cure process provides dielectric properties of carbon/epoxy composites. As with the conventional cure monitoring method using extra dielectric sensors, the degree of cure of composites is monitored by measuring the dielectric constant of composites. The dielectric constant of epoxy resin changes concomitant with change of frequency of applied alternating current (AC). Using dependency of the applied AC frequency of the dielectric constant, the degree of cure is measured directly. The proposed method is applied to single and multi-ply carbon/epoxy composite laminates. The method demonstrates excellent estimations of the degree of cure without additional sensors.

Introduction

Carbon/epoxy composites have been employed widely for aerospace structures and other transportation vehicles. Several processing methods have been adopted to fabricate composite structures, including autoclave molding and resin transfer molding. Cure monitoring of composite structures is crucial for quality control and improvement of mechanical properties of structures.

Several cure monitoring methods have been investigated in recent years. Most use change of dielectric properties to estimate viscosity change of epoxy resin. For example, the dissipation factor of dielectric properties is often used to measure resin viscosity and to determine the gel point [1-3]. However, there are only a few studies that address the relationship between the degree of cure and dielectric properties. Kim et al. compared dissipation factors from dielectric properties with the degree of cure from differential scanning calorimetry (DSC) data; they derived the relationship between the dissipation factor and the degree of cure [4]. They also investigated sensitivity of dielectric sensors for cure monitoring using finite element method [5]. Bartolomeo et al. used the Williams-Landel-Ferry (WLF) equation to extract resin conversion from dielectric data [6]. Other cure monitoring methods that do not use dielectric property changes have also been reported. Urabe et al. presented a cure monitoring method with a high frequency electromagnetic wave transmission line [7]. They investigated applicability of the method by comparing experimental results with those of calculations. Oshima et al. presented a method utilizing the impedance change of piezoelectric ceramics embedded in composites [8].

Several kinds of sensors have been investigated to measure dielectric properties of composites during curing. Among them, a small planar interdigital capacitor sensor system is already available commercially [4,5]. Methods other than the dielectric method require extra sensors, such as optical fiber sensors and piezoelectric sensors, to measure properties required for cure monitoring. However, conventional cure monitoring methods using sensors may reduce mechanical properties of the structure owing to embedded sensors.

In the present study, a smart cure monitoring method with co-cured electrodes is proposed. Since the method employs carbon fiber itself as a sensor, it needs no additional sensor for cure monitoring. The present method utilizes dependency of the dielectric constant of resin on the frequency of applied alternating current. Also, co-cured electrodes can be used for delamination monitoring after cure monitoring of carbon/epoxy laminated structures [9]. The present method is applied to estimates the degree of cure of single and multi-ply carbon/epoxy composite laminates; results are discussed in comparison with those obtained from the conventional method with DSC.

Cure Monitoring Theory using Frequency Dependency of Dielectric Constant

As noted in Ref. [10], the dielectric constant of resin depends on the frequency of applied alternating current. In general, the dielectric constant shows frequency dependence caused by dielectric relaxation, and it is expressed as

$$\varepsilon^* = \varepsilon_\infty + \Delta\varepsilon / (1 + i\varpi\tau) \tag{1}$$

where ε_∞ is the limit value of the dielectric constant at high frequency region, $\Delta\varepsilon$ is the dielectric increment associated with relaxation of dipoles, ϖ is alternating current frequency, and τ is the time for relaxation. The real part of the complex dielectric constant ε' is expressed as follows.

$$\varepsilon' = \varepsilon_\infty + \Delta\varepsilon / (1 + \varpi^2\tau^2) \tag{2}$$

Because the term $\varpi^2\tau^2$ is much greater than unity in the high frequency region, Eq. 2 can be rewritten as follows.

$$\varepsilon' = \varepsilon_\infty + \Delta\varepsilon / (1 + \varpi^2\tau^2) \approx \varepsilon_\infty + \Delta\varepsilon / (\varpi^2\tau^2) \tag{3}$$

By means of Taylor series expansion around ϖ_0, Eq. 3 can be rewritten as

$$\varepsilon' \approx \varepsilon_\infty + \frac{\Delta\varepsilon}{\varpi_0^2\tau^2} - \frac{2\Delta\varepsilon}{\varpi_0^2\tau^2}\Delta\varpi = b_0 + b_1\Delta\varpi \tag{4}$$

where $\Delta\varpi$ represents a minute of frequency.

Levita et al. showed experimentally that ε' and/or ε'' are individually linearly dependent on the degree of cure of epoxy resin at a proper alternating current frequency [10], where ε'' is dielectric loss. The following equation is derived.

$$\varepsilon' = a_0 + a_1\beta \tag{5}$$

The isothermal rate of cure $d\beta/dt$ is derived by means of differentiating both sides of Eq. 5. Differentiation shows that the isothermal rate of cure $d\beta/dt$ is equal to the time derivative of dielectric constant $d\varepsilon'/dt$: $d\varepsilon'/dt = d\beta/dt$. The time derivative of dielectric constant is obtained by means of differentiating both sides of Eq. 4, too. In Eq. 4, only $1/\tau^2$ is time dependent; other terms, such as ε_∞ and $\Delta\varepsilon$, are time independent. That implies the following equation.

$$\frac{d\beta}{dt}=\frac{d\varepsilon'}{dt}\approx\frac{\Delta\varepsilon}{\varpi_0^2}\frac{d(\tau^{-2})}{dt}-\frac{2\Delta\varepsilon}{\varpi_0^2}\frac{d(\tau^{-2})}{dt}\Delta\varpi=\frac{db_0}{dt}+\frac{db_1}{dt}\Delta\varpi \quad (6)$$

Eq. 6 means that each time derivative of coefficient of Eq. 4 is proportional to the isothermal rate of cure as follows.

$$d\beta/dt\propto d\left(\tau^{-2}\right)/dt\propto db_0/dt\propto db_1/dt \quad (7)$$

Eq. 7 enables us to calculate the degree of cure β from Eq. 4. Indefinite integration of db_1/dt is equal to degree of cure β. Because the degree of cure β is a standardized value between 0 and 1, the degree of cure can be obtained by means of standardization as

$$\beta=\int d\beta/dt\,dt=\int\left(db_1/dt\right)dt/A=\int b_1dt/TA \quad (8)$$

where A is an integration result of coefficient b_1 from the start of curing to its end and T represents the total time for curing.

Coefficient b_1, however, also depends on temperature because it is connected with segment mobility. Therefore, the value of b_1 is not zero before and after curing. Therefore, we must integrate only variation of b_1 from the base value at the curing temperature before curing with respect to time from the start of cure to its end.

A unidirectional carbon/epoxy laminate can be represented by parallel arrangement of a capacitance and resistance, as shown in Fig. 1, because resin in composite materials has dielectric properties. Capacitance of a parallel plate capacitor is shown as

$$C=\varepsilon S/d \quad (9)$$

where ε is the dielectric constant and equal to ε'; S and d represent parallel plates' area and distance, respectively. In actual carbon/epoxy laminates, the coefficient S/d is unknown and it may change owing to resin flow during the curing process. However, in a very short time, for instance, the measurement time of capacitances at several AC frequencies, S/d can be considered to be a constant value. In this case, frequency dependence of the dielectric constant is proportional to frequency dependence of capacitance. Therefore, we can measure the degree of cure by measurement of frequency dependency of capacitance of actual carbon/epoxy laminates without considering movement of S/d.

The following steps yield the degree of cure:

(I) Measurement of capacitance of carbon/epoxy laminates with various alternating current frequencies in the narrow frequency band within a short time.

(II) Linear regression of measured capacitances at several frequencies as a function of $\Delta\varpi$.

(III) Integrating the slope of the linear expression obtained in step (II).

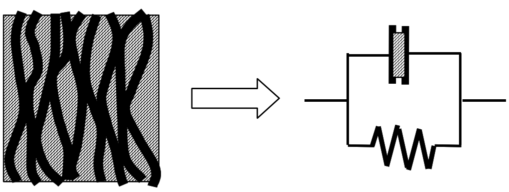

Fig.1 Modeling of carbon/epoxy composite to an equivalent circuit

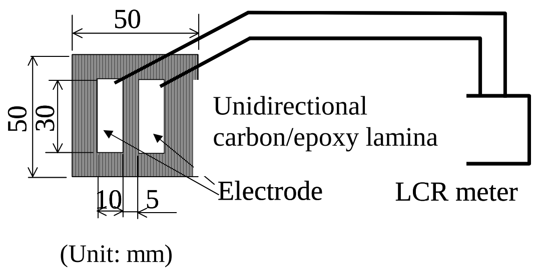

Fig.2 Cure monitoring system for a carbon/epoxy lamina

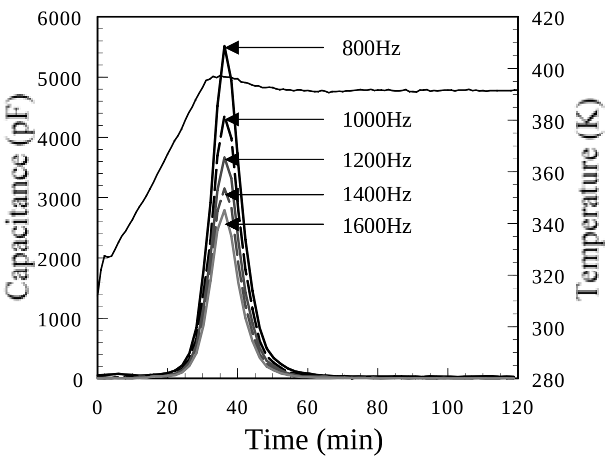

Fig.3 Measured capacitance change of unidirectional lamina $[0]_T$

Of course, db_0/dt is also proportional to $d\beta/dt$, as shown in Eq. (7). However, because the intercept b_0 includes a constant term ε_∞, we cannot determine an indefinite integration constant without knowledge of $\varepsilon_{\infty.}$ In another respect, b_0 corresponds to extrapolation of eq. (4). This means that it may include large experimental error. Because the constant term ε_∞ is not included in b_1 as shown in Eq. (4), the degree of cure β is easily calculated in the manner mentioned above.

Cure Monitoring Results of Carbon /Epoxy Laminates

Unidirectional Lamina. Fig. 2 shows a cure monitoring system for a unidirectional carbon/epoxy lamina. The specimen is made by aligning carbon fibers impregnated with Nikkatol VX-1315 epoxy resin (Nihon Gosei Kako Co., Ltd.) in one direction on the glass/epoxy plate where two electrodes of thin copper film are attached. Capacitance change during curing is measured by applying alternating electric current between electrodes.

The cure monitoring experiment was conducted in an electric furnace with retention temperature of 393 K; capacitance changes were measured with the LCR meter (3522 LCR Hitester; Hioki E. E. Corp.) with five AC frequencies (800 Hz, 1000 Hz, 1200 Hz, 1400 Hz, and 1600 Hz). Actual measurements require 1-2 min for measurements at the five frequencies. Fig.3 shows measured capacitance change during curing at each AC frequency. In this figure, the abscissa represents time, while the ordinate means measured capacitance and temperature. In the experiments, AC is applied perpendicular to the fiber direction. Thereby, capacitance changes are measured clearly, showing strong frequency dependency.

Fig. 4 shows capacitance change at each AC frequency after the furnace temperature reached 393 K. In Fig. 4, the abscissa is $\Delta\varpi$ calculated from the five AC frequencies (base frequency is 800Hz); the ordinate is measured capacitance. A linear relationship between the capacitance value and $\Delta\varpi$ can be observed and regressed linearly; the R^2 of each line is greater than 0.95. Though the S/d value may change during curing, we assume that capacitance change is almost related to dielectric change.

The degree of cure β is obtained by integrating slope b_1 after subtracting initial value b_1 around 393 K and dividing with the integrating value to the cure end time. The degree of cure obtained by the present method is shown in Fig. 5 with open circles. The cure end time is defined as the time at which the slope achieves the mean value between 100 to 120 min. The degree of cure obtained from the process introduced in Ref [4] with DSC analysis data is also shown in the figure with a solid curve. The figure implies that the present method estimates the degree of cure of unidirectional lamina effectively, though coefficient S/d changes owing to resin flow during curing.

Cross-Ply Laminate. Cure monitoring of $[0/90]_T$ laminate is conducted in the same manner as for the experiment of unidirectional lamina. We produced the specimen by aligning carbon fibers impregnated with Nikkatol VX-1315 epoxy resin on a glass-fiber/epoxy plate. In this case, AC is charged perpendicular to the 0° lamina, which is the top layer of the $[0/90]_T$ laminate. That is, the AC applied direction coincides with the fiber direction of the 90° layer, which is the second layer. The electric current mainly passes through the 90° layer, which affects capacitance measurement because electric resistance of a carbon fiber is very small.

The degree of cure obtained by the present method is show in Fig. 6 with open circles. The degree of cure obtained from DSC analysis data is also shown in the same figure with a solid curve. The present method is also inferred to be effective for cure monitoring of cross-ply laminate because the two results are very similar to each other.

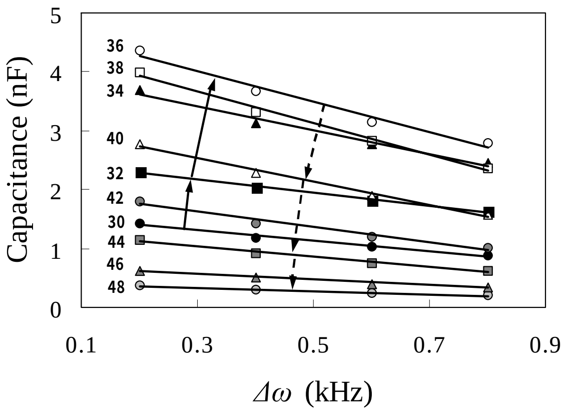

Fig.4 Capacitance change of a unidirectional lamina $[0]_T$ during curing

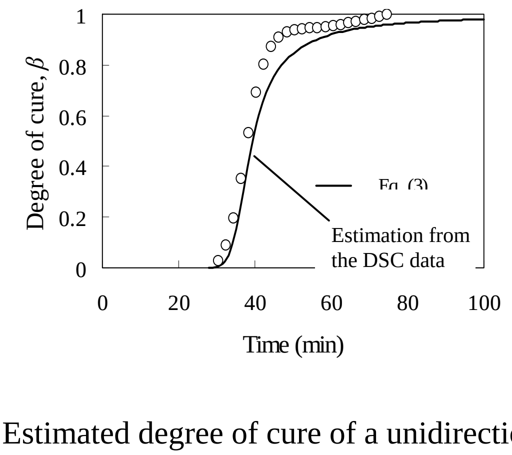

Fig.5 Estimated degree of cure of a unidirectional lamina $[0]_T$

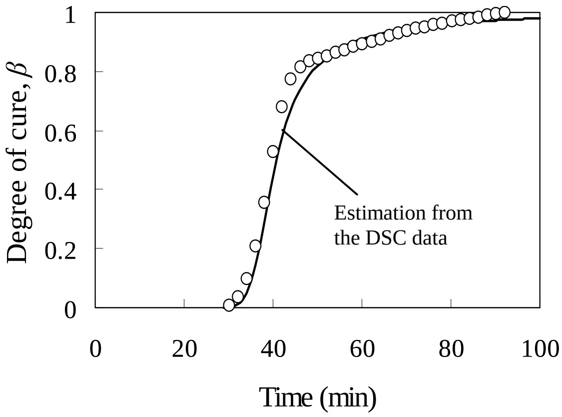

Fig.6 Estimated degree of cure of a cross-ply laminate $[0/90]_T$

Summary

This study describes the smart cure monitoring method using co-cured electrodes. The proposed method does not require additional sensors for cure monitoring; also, co-cured electrodes can be used for damage monitoring after curing. The cure monitoring method uses frequency dependency of applied alternating current of the epoxy resin. This method, therefore, is unaffected by carbon fiber movement during curing caused by resin flow. We must measure capacitance change with several alternating currents in the present method. Relationships between increment of frequencies and capacitances are obtained from measured capacitances. The slope of the relation is integrated to calculate the degree of cure. This measurement of the degree of cure is applied to epoxy resin monitoring and carbon/epoxy composites here. As a result, this method reveals good agreement of the degree of cure obtained with the conventional method using DSC data. Although this method has small errors caused by the decision of the end point of perfect cure, this method does not require DSC measurements and can be applied to actual carbon/epoxy laminates without extra sensors. This convenience constitutes the main advantage of this method.

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