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Smart autoclave processing of thermoset resin matrix composites based on temperature and internal strain monitoring

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Abstract—Cure cycle optimization and process control for autoclave cure of thermoset resin matrix composites based on temperature and internal strain monitoring were studied. Cure of thermoset resin is usually an exothermic reaction, which causes temperature increase of composites during cure. Slowing down the temperature ramp rate is effective in lowering the peak temperature. However, the slower is the ramp rate, the longer the cure time becomes. Therefore, it is desirable to control the ramp rate in order to depress the peak temperature with prolongation of cure time minimized. Besides that, precise determination of cure completion is also required in order to minimize cure time. The procedure for smart processing described above was developed and tried on laminate of carbon fiber/epoxy resin prepreg. In this procedure, temperature ramp rate is controlled so that the peak temperature predicted by Springer's thermochemical model is kept below an allowable value. Cure completion is determined by a cure rate equation and internal strain monitoring with embedded EFPI optical fiber sensors. The internal strain is correlated with specific volume change of the matrix resin caused by cure shrinkage and thermal expansion/contraction. The authors found that the cure shrinkage terminates at a certain degree of cure, and EFPI sensors can detect this point. Although the degree of cure can be calculated by integrating the cure rate equation along temperature history, errors may be accumulated. Therefore, the degree of cure is corrected and integration of cure rate equation is restarted at the cure shrinkage termination point detected by EFPI sensors. Thus, cure completion is determined precisely. This smart autoclave processing procedure was able to depress the peak temperature and determine the end of cure.

Keywords: Smart autoclave processing; EFPI optical fiber strain sensor; cure shrinkage.

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1. INTRODUCTION

In recent years, smart composite materials with embedded sensors and micro actuators have attracted increasing attention. In order to manufacture such smart composite materials, a curing process optimization technique to minimize local temperature increase and residual stress is considered to be essential. In the case of autoclave cure of thermoset resin matrix composites, a smart processing system which includes cure monitoring by embedded sensors, process optimization by model prediction and autoclave control for optimized process is supposed to be effective.

As to the model prediction for autoclave cure, Springer's work is well known [1, 2]. Springer *et al.* proposed a thermochemical model to predict CFRP temperature distribution during autoclave cure based on cure kinetics and heat transfer. Ciriscioli *et al.* showed the effectiveness of cure cycle optimization based on Springer's model by curing thick laminates up to 200 plies [3].

Ciriscioli, Springer, and Lee developed the expert system for autoclave control named 'SECURE' [4]. In this system, temperature of surfaces and center of the laminate, laminate thickness and dielectric properties are monitored. The autoclave heating, cooling and pressure are controlled by simple if-then rules based on the monitored data. Cure completion is detected by ion conductivity measured by dielectric sensors.

Dielectric sensors are well known and widely used as monitoring components for viscosity and degree of cure of thermoset resins [5–7]. Also, autoclave cure control methods by dielectric property monitoring are proposed to determine the time for applying pressure and cure completion [8, 9].

Cure of thermoset resin is usually an exothermic reaction, which causes temperature increase of composites during cure. Especially, in the case of curing thick laminate, composite temperature at the peak of reaction rate may become significantly higher than desired cure temperature. Such high temperature degrades mechanical properties of composites. Slowing down the temperature ramp rate is effective in lowering the peak temperature. However, the slower is the ramp rate, the longer the cure time becomes. Combination of the ramp rate control based on Springer's thermochemical model and precise determination of cure completion is expected to depress the peak temperature with prolongation of cure time minimized.

The authors found a particular resin whose degree of cure cannot be detected by dielectric sensor [10]. In the case of such resin, another tool to detect degree of cure is required. An optical fiber strain sensor is one of the candidates. There are many research works on structural health monitoring by FBG (Fiber Bragg Grating) or EFPI (Extrinsic Fabry-Perot Interferometer) optical fiber strain sensors [11], and both FBG [12] and EFPI [13] sensors can be used for monitoring internal residual strain during cure.

In this work, the authors developed and demonstrated smart autoclave processing which consists of the ramp rate control and degree of cure determination by embedded EFPI optical fiber strain sensors.

2. MODELING FOR SMART AUTOCLAVE PROCESSING

The authors have studied monitoring and modeling for cure process of MR50K/#982 (Mitsubishi Rayon Co., Ltd.) carbon fiber/epoxy resin prepreg which is used for aircraft structure. When 88 ply (12 mm thick) laminate of this prepreg laid up as shown in Fig. 1 is cured at 183°C with 2°C/minute ramp rate, the laminate temperature exceed 200°C at the reaction rate peak. Autoclave temperature, laminate (CFRP) temperature and degree of cure in this case are shown in Fig. 2. Exposing the laminate to such unusual high temperature should be avoided not to cause degradation of mechanical properties. Control of composite parts temperature by thermocouples stuck on the parts or bag surface is usually applied. However, it might be difficult for autoclave cooling facility to control the parts temperature under such significant reaction heat generation.

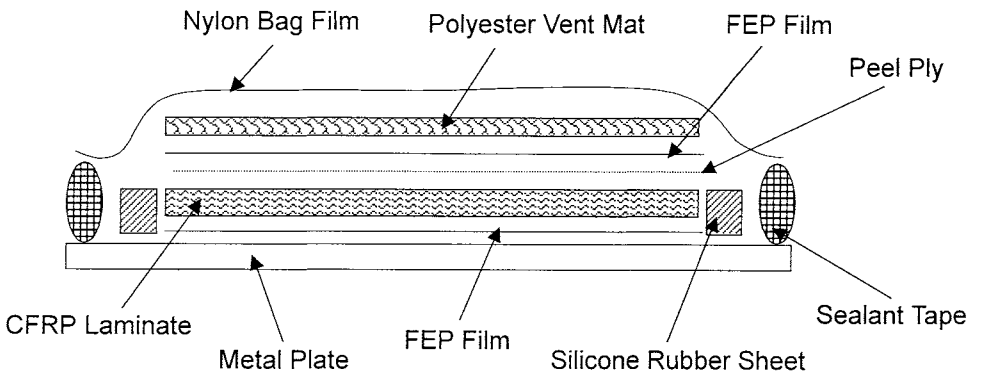


Figure 1. Lay-up for CFRP laminate.

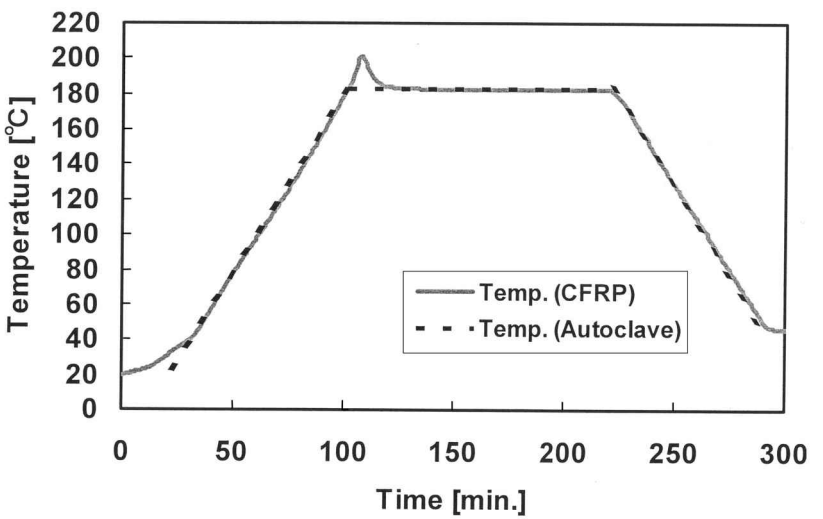


Figure 2. CFRP temperature during curing 88-ply (12 mm thick) laminate.

Lowering temperature ramp rate makes peak reaction rate smaller because the peak reaction rate is achieved at lower temperature. Thus, temperature increase caused by reaction heat can be depressed by lowering temperature ramp rate. However, lowering the ramp rate causes elongation of cure time, which increases energy consumption. Therefore, unless the peak temperature exceeds the desired value, the ramp rate should be as fast as possible.

To depress energy consumption, precise determination of cure completion is necessary. Dielectric sensors are well known and widely used as cure monitoring components for thermoset resins. However, in the case of this resin, a dielectric sensor is not able to indicate the cure completion [10]. After degree of cure reaches approximately 40%, loss factors measured by dielectric sensors with frequency of 1 Hz–1 kHz become almost constant and do not show the end of cure. Although degree of cure can be calculated by integrating the rate equation, error may accumulate near the cure completion. Therefore, an appropriate sensing method will be combined with degree of cure calculation to determine the end of cure precisely.

In the following paragraphs, smart autoclave processing procedures for thick laminate of this prepreg is discussed.

2.1. Peak temperature control by Springer's thermochemical model

By Springer's thermochemical model, temperature distribution in laminate is expressed in the following equation (2).

$$\rho C(\partial T/\partial t) = K\left(\partial^2 T/\partial z^2\right) + \rho H, \tag{1}$$

where ρ and C are the density and specific heat of the laminate, K is the thermal conductivity in the direction perpendicular to the plane of the laminate. H is the rate of heat generated by chemical reactions, and is expressed as follows.

$$H = (\mathrm{d}\alpha/\mathrm{d}t)Hu, \tag{2}$$

Hu is the ultimate heat of reaction during cure and α is degree of cure. The authors obtained a reaction rate equation for matrix resin of MR50K/#982 prepreg from differential scanning calorimetry (DSC) data as follows.

$$\mathrm{d}\alpha/\mathrm{d}t = \left\{5035.7\cdot\exp(-7803.7/T)+1167100\cdot\exp(-9695.7/T)\cdot\alpha^{0.41}\right\}(1-\alpha)^{1.15}. \tag{3}$$

Figure 3 shows calculated temperature distribution in the direction perpendicular to the plane at the peak temperature during cure of 88-ply laminate which is laid up on metal plate and bagged as shown in Fig. 1. At the reaction heat generation peak, metal side surface temperature is the lowest in the laminate, because total heat transfer coefficient between metal side surface and autoclave atmosphere is larger than that between bag side surface and autoclave atmosphere; and laminate temperature at bag side surface is almost same as maximum internal temperature. Therefore, in this case, the peak temperature can be depressed by controlling the temperature at bag side surface. Figure 4 shows changes in temperature calculated

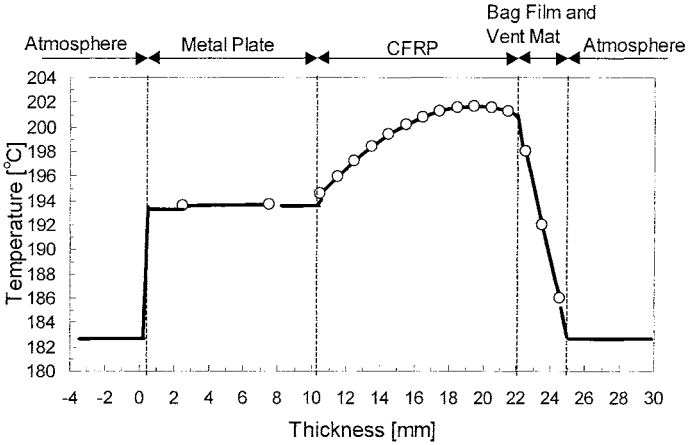


Figure 3. Predicted temperature distribution for 88-ply CFRP laminate at the peak temperature.

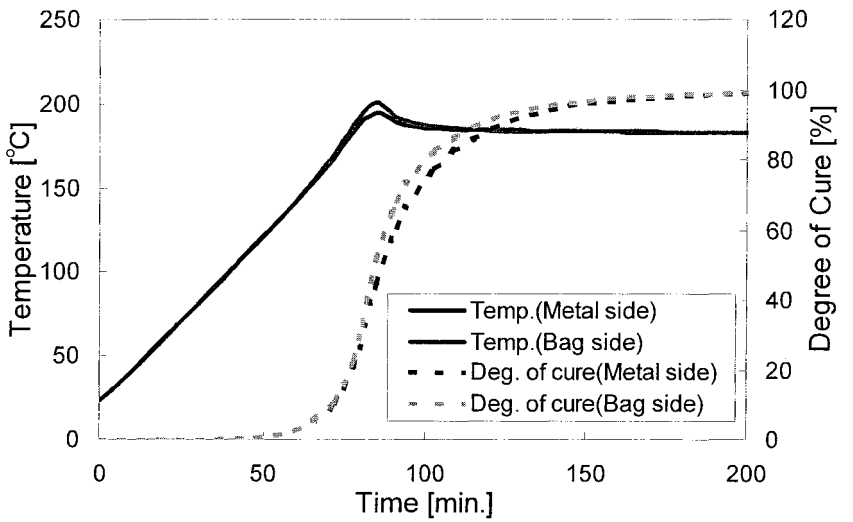


Figure 4. Comparison of temperature and degree of cure between laminate surfaces (bag side and metal side) calculated by Springer's thermochemical model.

by equation (1) and degree of cure calculated by equation (3) at bag side surface and at metal side surface. According to Fig. 4, degrees of cure at both sides correspond at the end of cure. Therefore, the whole laminate is considered to be cured completely when the laminate at bag side surface reaches cure completion. When the laminate temperature is assumed to be approximately uniform and is represented by the bag side surface temperature Tc, heat balance of laminate unit area is expressed as follows.

$$D\rho C(\partial Tc/\partial t) = (h_1 + h_2)(Ta - Tc) + D\rho(\mathrm{d}\alpha/\mathrm{d}t)Hr. \quad (4)$$

Here, h_1 and h_2 are total heat transfer coefficient at bag side and at metal side. Ta is autoclave atmosphere temperature, D is laminate thickness and Hr is reaction heat per laminate unit mass. Then, laminate temperature change is expressed as follows.

$$(\partial Tc/\partial t) = P(Ta - Tc) + Q(\mathrm{d}\alpha/\mathrm{d}t), \tag{5}$$

where parameters P and Q are as follows.

$$P = (h_1 + h_2)/(D\rho C), \tag{6}$$

$$Q = Hr/C. \tag{7}$$

Thus, Tc can be predicted by equation (5) if P and Q are determined.

However, total heat transfer coefficient h_1 and h_2 depend on autoclave atmospheric gas circulation, bag thickness, and so on, and Hr depends on resin content. Therefore, the parameters P and Q should be determined by monitored data of autoclave atmosphere temperature and laminate temperature during cure. Then, future laminate temperature can be predicted by equation (5) with various ramp rate. Thus the maximum ramp rate that keeps peak temperature from exceeding the acceptable upper limit can be determined. Controlling autoclave temperature ramp rate by repeating this procedure can depress laminate peak temperature.

2.2. Determination of cure completion by internal strain measurement

Matrix resin specific volume changes during cure cycle by cure shrinkage and thermal expansion/contraction. Such resin volume change may increase internal strain in the CFRP laminate, which can be measured by optical fiber strain sensors.

To correlate specific volume with internal strain measurement, it is necessary to measure and formulate the specific volume as functions of temperature and degree of cure. Mitani *et al.* developed a method to measure pressure–volume–temperature (P–V–T) characteristics of thermoset resin during cure by using bellows type P–V–T apparatus [14]. Matrix resin specific volume of MR50K/#982 prepreg during cure was measured by this method. Thermal expansion/contraction of the cured resin was also measured. These results of specific volume measurements are shown in Fig. 5 by open circles. Temperatures are indicated by thin solid line and degrees of cure calculated by equation (3) are indicated by bold dotted line. Specific volume change during cure cycle can be divided into three regions: (A) the region where degree of cure is small and specific volume is mainly controlled by thermal expansion/contraction; (B) the region where cure shrinkage progresses as degree of cure increases; and (C) the region where cure shrinkage has terminated and specific volume is completely controlled by thermal expansion/contraction, and it can be formulated for each region. By fitting the measured data in each region to separate functions, the following equations are obtained.

A: Degree of cure is small and specific volume is mainly controlled by thermal expansion/contraction:

$$Vs_1 = 0.6865 \cdot \exp(0.004429 \cdot \alpha - 0.0001722 \cdot \alpha \cdot T + 0.0005963 \cdot T). \tag{8}$$

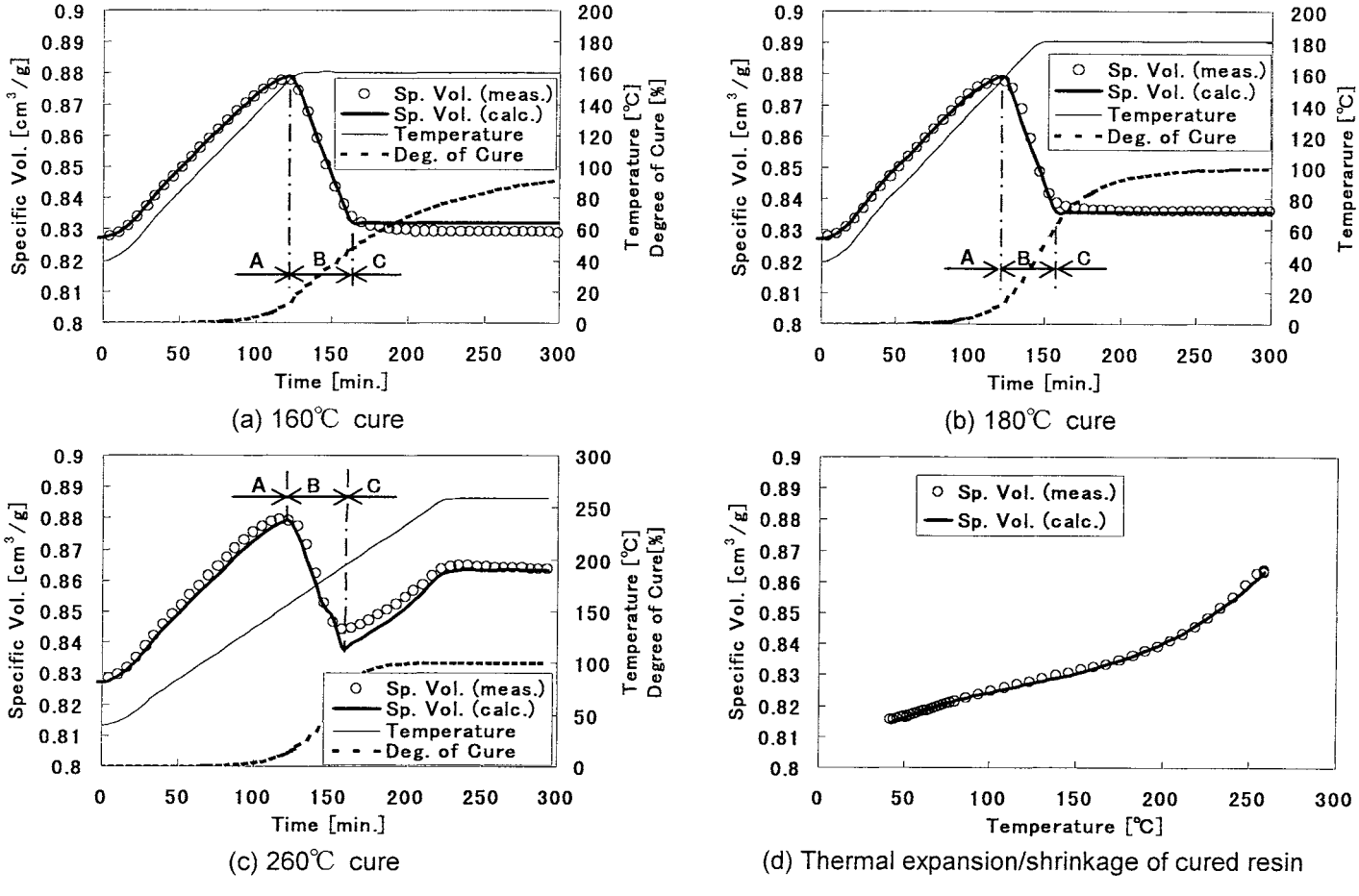


Figure 5. Comparison between measured and calculated specific volume of matrix resin.

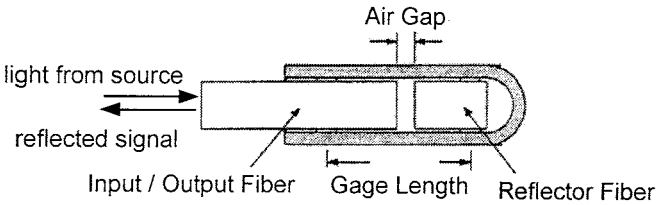


Figure 6. Schematic diagram of EFPI optical fiber strain sensor.

B: Cure shrinkage progresses as degree of cure increases

$$Vs_2 = 1.128 \cdot \exp(-1.613 \cdot \alpha + 0.003312 \cdot \alpha \cdot T - 0.0005122 \cdot T). \quad (9)$$

C: Cure shrinkage has terminated and specific volume is completely controlled by thermal expansion/contraction:

$$Vs_3 = 0.4719 \cdot \exp(8.409 \times 10^{-9} \cdot T^3 - 9.871 \times 10^{-6} \cdot T^2 + 0.004007 \cdot T). \quad (10)$$

Here, Vs_1, Vs_2 and Vs_3 are specific volumes (cm^3/g). T is temperature (K) and α is degree of cure. The bold solid line in Fig. 5 shows specific volume calculated by these equations. Segmentation of region A, B and C is also shown in Fig. 5. It is found that equations (8) to (10) reproduce specific volume measurement.

Internal strains during the cure of quasi-isotropic 16-ply and 88-ply laminates of the prepreg are also measured by EFPI optical fiber strain sensors (FOS-50003-N, FISO Technologies Inc.). Figure 6 shows a schematic diagram of an EFPI sensor. The sensor system detects the air gap distance, which varies correspond to the matrix strain, by interferometry. It is noted that an EFPI sensor can measure internal strain induced by resin curing process [13] as well as internal strain in the structure [11]. The authors embedded EFPI sensors in the center layer of 16-ply laminate, in the center layer of 88-ply laminate and in the layer near the surface of 88-ply laminate. Figure 7 shows comparison between measured strain and calculated specific volume. In this figure, negative strain means compressive strain.

At first, resin specific volume increases by thermal expansion. After cure shrinkage starts, it begins to decrease. Then, it becomes constant under 183°C isothermal cure, when degree of cure reaches approximately 64%. This means cure shrinkage terminates before cure completes. The cure shrinkage termination point is expressed as the point where equation (9) meets equation (10).

On the other hand, strains measured by EFPI sensors are affected by autoclave pressurization and bag vacuum relief at the beginning of the cure cycle. They are not correlated with resin specific volume while resin viscosity is too low to stick to the sensors. After degree of cure reaches approximately 30%, compressive strain increases rapidly as resin specific volume decreases. At this point, indicated as point (a) in Fig. 7, the resin is considered to become viscous enough to stick to the sensors as the cure progresses. This rapid increase of compressive strain continues for 10–20 min. Then, at point (b) indicated in Fig. 7, measured strain becomes

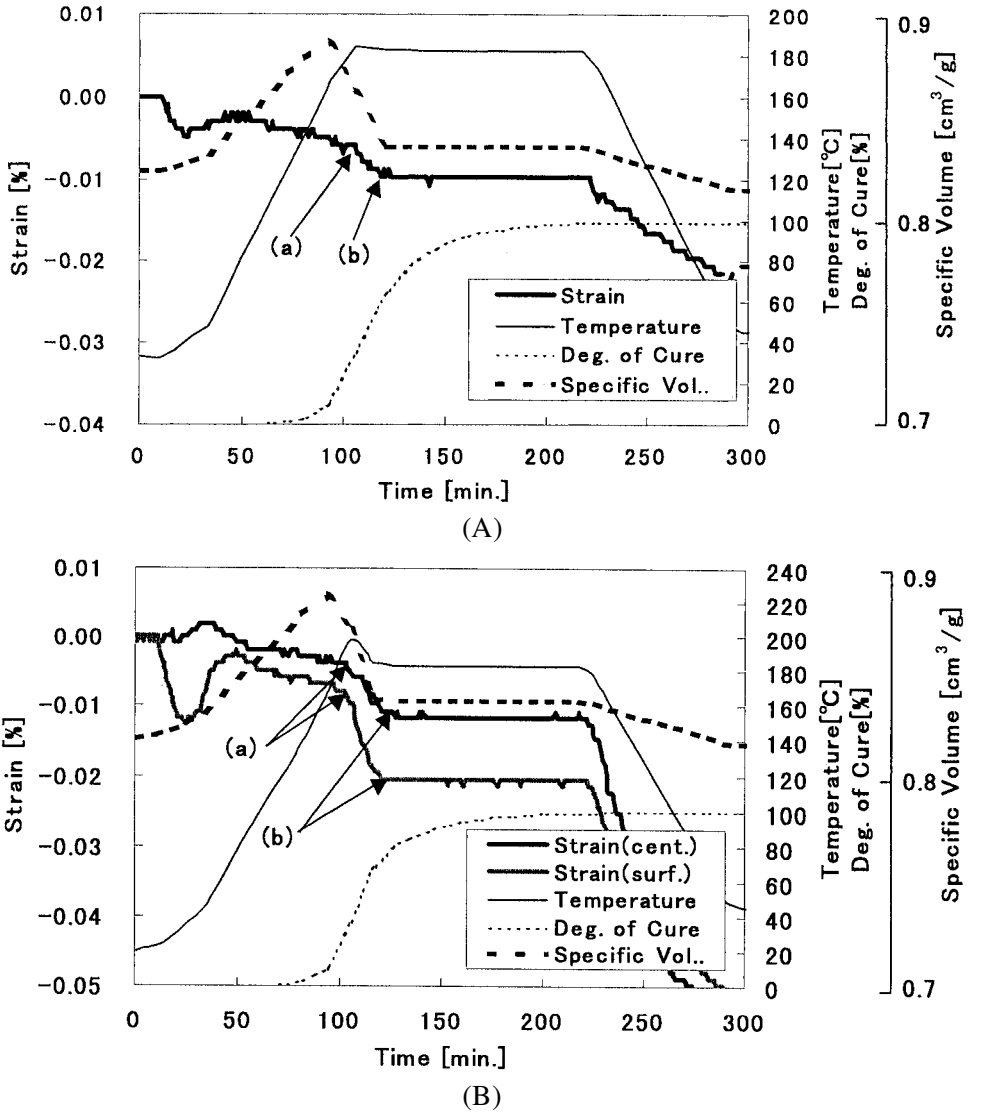


Figure 7. Strain measured by EFPI sensors and specific volume during cure. (A) 16 ply; (B) 88 ply.

constant. At the last of cure cycle, compressive strain increases again because of resin thermal contraction as temperature decreases.

Thus, measured strain becomes constant at point (b) in Fig. 7. This point is approximately as same as the point when cure shrinkage terminates. This shows EFPI sensors can detect cure shrinkage termination point, which identifies a certain degree of cure. In other words, degree of cure calculated by integrating reaction rate equation can be corrected at point (b).

At point (b) in Fig. 7, second-order differentiation of measured strain should have a peak. This can be applied to determining cure shrinkage termination point

by smart autoclave processing algorithm. The point when compressive strain increase due to cure shrinkage stops can be determined by searching last peak of second-order differentiation of measured strain after differential strain becomes approximately zero. From equations (9) and (10), the degree of cure at the cure shrinkage termination point is expressed as a function of temperature as follows.

$$\alpha\ (\text{cure shrinkage termination}) = (8.409 \times 10^{-9} \cdot T^3 - 9.871 \times 10^{-6} \cdot T^2 + 0.004519 \cdot T - 0.8714)/(0.003312 \cdot T - 1.613). \quad (11)$$

Thus, degree of cure obtained by integrating cure rate equation can be corrected by equation (11) at cure shrinkage termination point detected by internal strain measurement. By restarting integration of cure rate equation based on corrected degree of cure, cure completion can be determined more precisely. Then, autoclave temperature starts to be decreased when degree of cure shows cure completion. Cure time can be minimized by this procedure.

3. EXPERIMENTAL

To control autoclave with the smart processing procedures described in the previous section, the control system that can continuously change autoclave operating condition according to the result calculated by smart processing program is required. Figure 8 shows the outline of the system the authors used.

Without control by smart processing program, 'autoclave operation program' reads out initial set cure cycle from 'set value data file' to control autoclave and record monitoring data such as temperature, pressure and strain measured by optical fiber sensors on 'recorder data file'. Once smart processing program works, it reads out monitoring data from 'recorder data file' and searches optimum cure cycle. Then, it outputs 'set value' based on the optimum cure cycle to the controller. Thus, the autoclave is operated with the cure cycle optimized by the smart processing program.

The authors try to demonstrate smart autoclave processing by this system. Cure cycle with 2°C/min. ramp rate followed by 183°C isothermal cure for 2 h is set initially. The procedure described in Section 2.1 is demonstrated with 88-ply laminate of MR50K/#982 prepreg (Mitsubishi Rayon Co., Ltd.). The combination of both procedures described in Sections 2.1 and 2.2 is demonstrated with 16-ply laminate of the same prepreg. Outlines of these algorithms are shown in Fig. 9.

4. RESULTS

The result for peak temperature control by Springer's thermochemical model with 88-ply laminate is shown in Fig. 10. This figure includes initial set and actual autoclave temperature, laminate temperature and degree of cure calculated by equation (3).

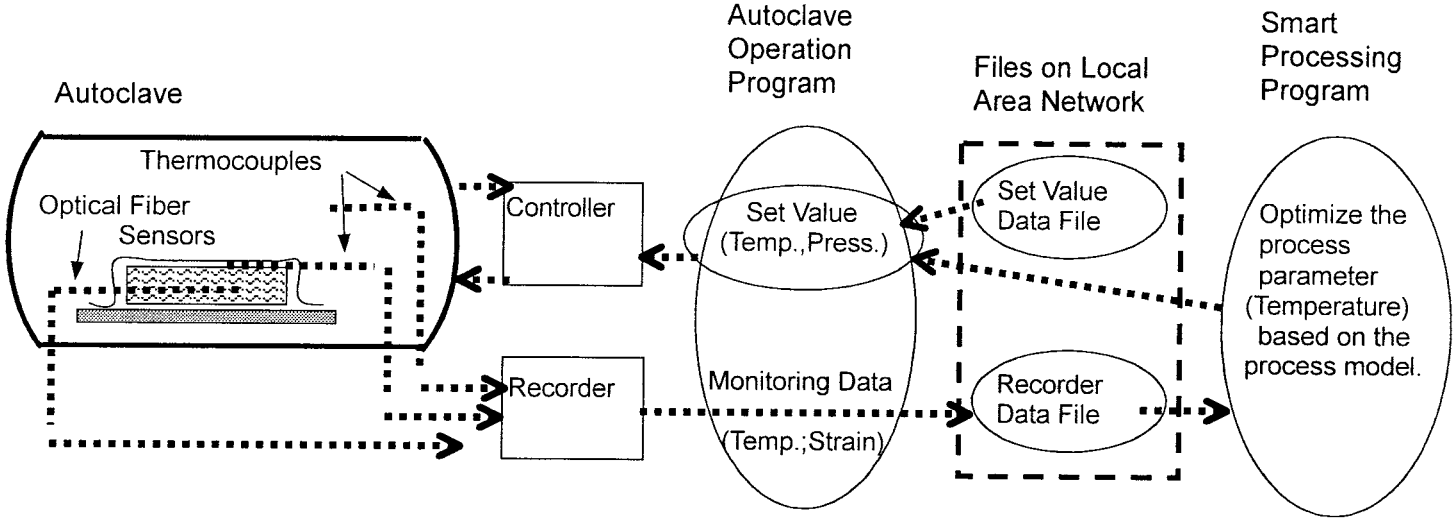


Figure 8. Outline of smart autoclave processing system.

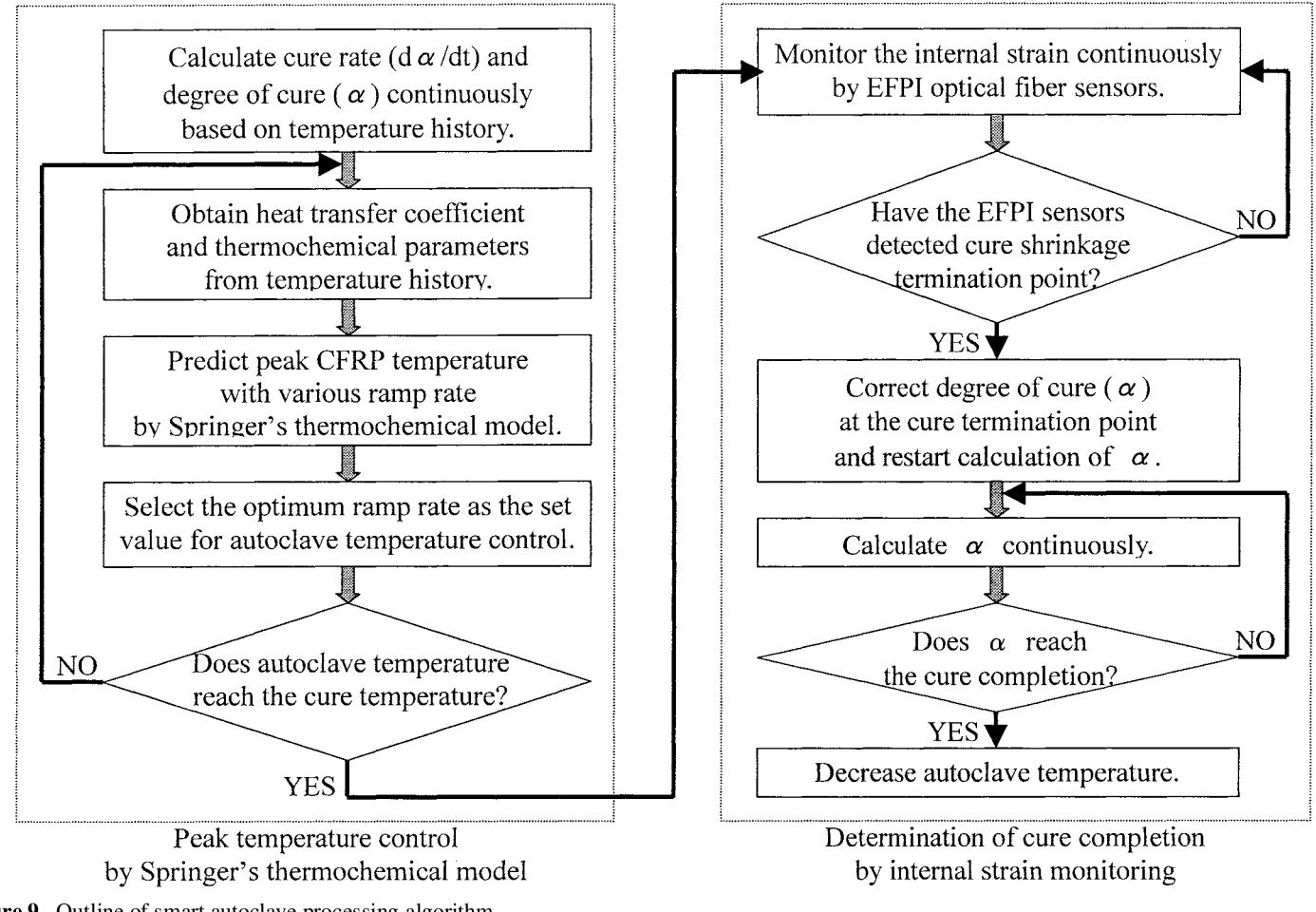


Figure 9. Outline of smart autoclave processing algorithm.

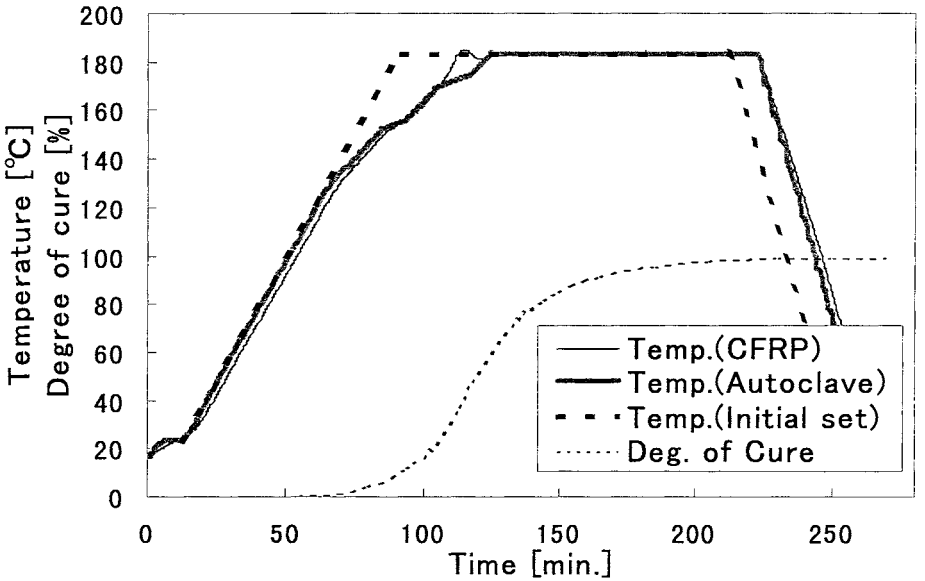


Figure 10. Result of smart autoclave processing. ('Peak temperature control' with 88-ply laminate.)

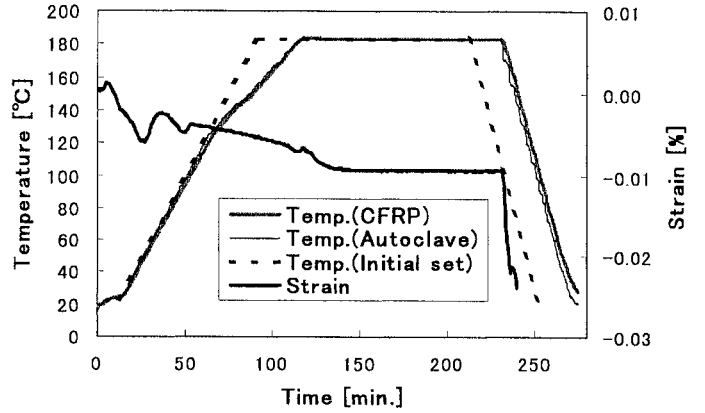
The figure demonstrates that laminate peak temperature is much lower than that in Fig. 2, which shows the result without control by smart processing program. Temperature ramp rate is controlled by the smart processing program after autoclave temperature reaches approximately 120°C. Thus, laminate peak temperature does not exceed initial set cure temperature (183°C) by more than 2°C.

The result for combination of peak temperature control by Springer's thermochemical model and determination of cure completion by internal strain monitoring with 16-ply laminate is shown in Fig. 11. This figure includes initial set and actual autoclave temperature, laminate temperature, internal strain measured by EFPI sensors (denoted by 'S') and its second-order differentiation (d^2S/dt^2), degree of cure calculated by equation (3), resin specific volume calculated by equations (8) to (10), and cure shrinkage termination point determined by the smart processing program.

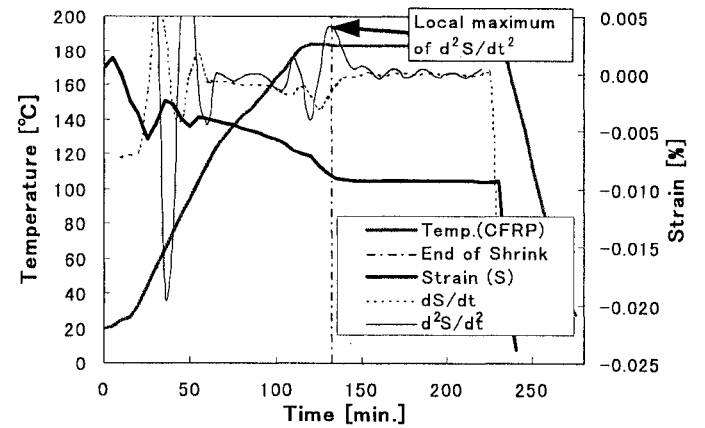
Laminate peak temperature is depressed as well. Besides, the cure shrinkage termination point is precisely detected based on internal strain measurement by EFPI sensors and the cure completion point is determined by degree of cure corrected at the cure shrinkage termination point.

5. CONCLUSIONS

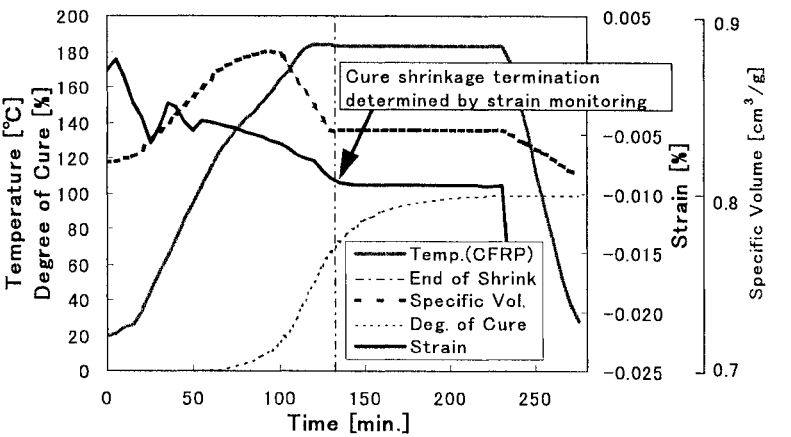
A smart autoclave processing procedure is developed and demonstrated for thick laminate laid up with carbon fiber/epoxy resin prepreg, MR50K/#982, used as aircraft structure material. The procedure includes temperature ramp rate control for depressing peak temperature caused by reaction heat, internal strain monitoring by embedded EFPI optical fiber strain sensors and precise cure completion determi-



(a) Initial set, autoclave and CFRP temperature



(b) Measured stain and its second-order differentiation



(c) Resin specific volume and measured stain

Figure 11. Result of smart autoclave processing. ('Peak temperature control' and 'Determination of cure completion' with 16-ply laminate.)

nation. The cure completion is determined based on degree of cure, which can be calculated by integrating cure rate equation. Monitoring by EFPI sensors provides a tool outlined below for correcting the error in degree of cure calculation. Measurement of the matrix resin specific volume of the prepreg indicates that cure shrinkage terminates when degree of cure reaches certain value before cure completion. On the other hand, internal strain measured by EFPI sensors becomes constant at the same point when cure shrinkage terminates. In other words, EFPI sensors detect cure shrinkage termination point, where degree of cure can be determined. Then, calculated degree of cure is corrected and calculation is restarted at that point. This new approach using EFPI sensors determines cure completion precisely. The procedure described above successfully depresses the peak temperature and determines the cure completion.

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