

Matrix Characterization and Development for the Vacuum Assisted Resin Transfer Molding Process

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ABSTRACT

The curing kinetics and viscosity of an epoxy resin system, SI-ZG-5A, have been characterized for application in the vacuum assisted resin transfer molding (VARTM) process. Impregnation of a typical carbon fiber preform provided the test bed for the characterization. Process simulations were carried out using the process model, COMPRO [8], to examine heat transfer and curing kinetics for a fully impregnated panel, neglecting resin flow. The predicted viscosity profile and final degree of cure were found to be in good agreement with experimental observations.

INTRODUCTION

The VARTM process has been developed over the last ten years for application in both commercial and military, ground-based and marine composite structures [1-3]. The process has advantages over conventional RTM by eliminating the costs associated with matched-metal mold making, volatiles emission, and allowing high injection pressures [4].

VARTM is typically a three-step process including lay-up of a fiber preform, impregnation of the preform with resin, and cure of the impregnated panel. The reinforcement, in the form of woven carbon or glass fabric, is laid onto a rigid tool surface. The matched metal top commonly found in RTM is replaced in the VARTM process by a formable vacuum bag material. The resin is injected through a single or multiple inlet ports depending upon part size and shape. A vacuum port allows the fiber preform to be evacuated prior to injection and provides the mechanism for transfer of the resin into the part. In addition to the pressure

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gradient caused by the vacuum pressure, gravity and capillary flow effects must be considered [5]. The preform infiltration time is a function of the resin viscosity, the preform permeability and the applied pressure gradient. The infiltration time can be greatly reduced by utilizing a distribution medium with a higher permeability than the preform [6,7]. Consequently, the resin flows in the medium first and then the infiltration process continues through the preform thickness.

Work at NASA Langley Research Center has focused on further developing of the VARTM process for fabrication of aircraft-quality composite parts. In order to succeed, it is important to achieve the high mechanical properties and dimensional tolerances required in these applications. The development or selection of the matrix material for application in advanced composite structures cannot be divorced from the manufacturing processes and the specific application geometries. Rather, it is necessary to develop material systems that meet a variety of requirements to ensure successful applications. In addition to the required strength and durability of the polymer matrix, properties that govern the processing characteristics must be considered. Traditionally, development or selection of the matrix for a particular application has been based on a limited number of factors like toughness, glass transition temperature (T_g) and viscosity. Consequently, process difficulties have often been encountered which prevented successful application of the matrix in the structure of interest. The use of process models allows sensitivity analyses that determine the influence of a larger number of polymer properties on final part quality. Material development and characterization efforts can then be focused on the most important parameters for a given application. For example, it was found that the interaction between resin modulus development and cure shrinkage has a profound effect on part dimensional stability [8].

In the present work, the cure kinetics and viscosity of a typical VARTM resin system were characterized. The cure kinetics and viscosity models were validated by processing a carbon fiber composite panel with a typical process cycle. Finally, a processing model was used to study the resin curing behavior for different process cycles and panel thicknesses.

MATRIX CHARACTERIZATION

Accurate prediction of many of the key material properties required in composites process models such as resin viscosity, modulus development and cure shrinkage depend on an accurate knowledge of the cure state of the resin during processing. Furthermore, an understanding of resin viscosity behavior is also required to predict the flow of resin during VARTM infiltration. Cure kinetics and viscosity models are obtained for the resin using a combination of isothermal and dynamic differential scanning calorimeter (DSC) and parallel-plate rheometer scans, respectively. In this work, SI-ZG-5A, a commercially available epoxy blend VARTM resin developed at A.T.A.R.D Laboratories* [9] was selected.

* Use of trade names or manufacturers does not constitute and official endorsement, either expressed or implied, by the National Aeronautics and Space Administration

Cure kinetics model

All tests were performed on a Shimadzu DSC-50 differential scanning calorimeter. The total heat of reaction (H_R) was measured from dynamic scans at 1.1°C/minute from room temperature up to 250°C. The isothermal tests were performed at temperatures ranging from 50°C to 140°C. In these tests, the specimens were heated rapidly to the desired temperature where they were maintained for a total of 2 hours, and then rapidly cooled. The isothermal tests were followed by a dynamic scan at 1.1°C/minute to measure the residual heat of reaction.

Raw data from the DSC experiments consisted of measurements of heat flow and total resin heat of reaction as calculated by the apparatus software. The dynamic runs produced very similar heat flow curves (Figure 1) and the measured H_R was nearly the same in all cases: 350 kJ/kg. From the baseline heat flow ($\dot{q}_{baseline}$) and the total heat flow, the resin cure rate was then determined using:

$$\frac{d\alpha}{dt} = \frac{(\dot{q}_{baseline} - \dot{q}_{in}) / m_{sample}}{H_R / (1 - \alpha_0)} \quad (1)$$

where \dot{q}_{in} is the measured heat flow, m_{sample} is the sample mass and α_0 is the starting resin degree of cure, assumed to be 0.01 in all cases. Resin degree of cure as a function of time was determined by integrating the calculated cure rate.

In this work, the equation chosen for the cure kinetics model is a modified auto-catalytic equation modified to account for a shift from kinetics to diffusion control [10].

$$\frac{d\alpha}{dt} = \frac{K\alpha^m(1-\alpha)^n}{1 + e^{C\{\alpha - (\alpha_{c0} + \alpha_{cr}T)\}}} \quad (2)$$
$$K = Ae^{(-\Delta E / RT)}$$

The significance of the various terms in Equation 2 is presented in Table 1. The first step in calculation of the appropriate model constants is determination of the activation energy, ΔE . This parameter was calculated from the slope of the natural logarithm of the isothermal cure rate, $\ln(d\alpha/dt)$, vs. $1/T$ at a number of different resin degrees of cure. All other model constants were determined using a weighted least-squares analysis, which included data from both isothermal and dynamic DSC measurements. The calculated equation constants are shown in Table 1.

As shown in Figure 2, the model provides an excellent fit to the isothermal cure tests at all temperatures examined. The only discrepancy between the model and the experiments is found at $\alpha > 0.8$ for the 120°C and 140°C case.

Table 1 Parameters used in SIZG-5A kinetics model (Equation 2).

Parameter	Value
Activation energy	$\Delta E = 62 \text{ kJ/gmole}$
Pre-exponential cure rate coefficient	$A = 3.03 \times 10^5 / \text{s}$
First exponential constant	$m = 0.377$
Second exponential constant	$n = 0.295$
Diffusion constant	$C = 16.5$
Critical degree of cure at $T = 0^\circ\text{K}$.	$\alpha_{C0} = 0.65$
Constant accounting for increase in critical resin degree of cure with temperature	$\alpha_{CT} = -1.5 \times 10^{-5} / \text{K}$

Viscosity model

A Rheometric Ares Systems parallel-plate rheometer was used to measure the neat resin viscosity. The viscosity model constants were determined by a series of isothermal cure tests ranging from 50°C to 140°C. A series of dynamic cures at 1.1°C/minute and a typical cure cycle test were conducted to validate the model. The samples were sheared between two 30 mm parallel discs. A dynamic or sinusoidal wave torque signal was applied to the sample. The frequency of the signal was 10 rad/s at a maximum shear strain of 10%. The test was stopped when the resin reached its gel point or after two hours, whichever came first. The room temperature viscosity of the resin was measured at 0.34 Pa·s and no significant curing occurred up to 79 hours at this temperature.

The viscosity model [10] used in this study is as follows:

$$\mu = A_{\mu} \exp(E_{\mu} / RT) \left[\alpha_g / (\alpha_g - \alpha) \right]^{(A+B\alpha)} \quad (3)$$

where A_{μ} , E_{μ} , A and B are experimentally determined parameters, R is the universal gas constant and α_g is the degree of cure at gelation. The slope of a linear regression through the data of $\ln \mu$ versus $1/T$ at low resin degree of cure ($\alpha \approx 0$) yields the value of E_{μ} . The data from the dynamic runs at 1.1°C/minute results was used. The degree of cure remains very low in the initial stages of the cure ($0.01 < \alpha < 0.07$). The gel point degree of cure is evaluated to be 0.6 from the viscosity tests. To evaluate the other constants, a best fit was done by changing the constants A_{μ} , A and B to fit the experimental data from the isothermal and dynamic tests. The best-fit constants are given in [Table 2](#).

The comparison with the dynamic test ([Figure 3](#)) confirms that the model describes the rapid increase in viscosity as the resin reaches the gel point as well as the initial stage of the test. Furthermore, the model prediction is found to agree with results for a typical cure cycle ([Figure 4](#)).

Table 2 Parameters used in SIZG-5A viscosity model (Equation 3).

Parameter	Value
Activation energy	$E_{\mu} = 54803 \text{ J/gmole}$
Pre-exponential coefficient	$A_{\mu} = 9.6 \times 10^{-11} \text{ Pa}\cdot\text{s}$
First exponential constant	$A = 3$
Second exponential constant	$B = 8$
Degree of cure at gel point	$\alpha_g = 0.6$

PANEL MANUFACTURING

A composite panel, having dimensions of 60 cm by 30 cm, was fabricated by the VARTM process using four stacks $[-45,90,45,90,0]_4$ of SAERTEX[®] [11] multi-axial non-crimp carbon fiber fabric and the SI-ZG-5A epoxy resin. Eight hundred grams each of part A and B were mixed by hand stirring. The mixed resin was degassed at room temperature under full vacuum for approximately one hour.

A schematic diagram of the bagging procedure is shown in Figure 5. A 0.32 cm thick stainless steel plate was used as a rigid tool. The preform was cut and placed on the tool so that the 0° rovings were length-wise, or parallel to the direction of resin flow. A layer of Armalon fabric was placed both above and beneath the preform to serve as release film. The distribution media, containing three layers of nylon mesh screen, was laid on top of the preform and release layer. The media was cut to dimensions of 60 cm by 27.4 cm allowing a 1.3 cm gap between the edge of the media and the edge of the preform along the length. The distribution media ended at a distance 2.5 cm before the end of the preform. These gaps prevent race-tracking of the resin as it flows through the media and the fiber. A 5 cm portion of the media was set off of the panel at the inlet side for inlet tube placement. Spiral-wrap tubing was stretched across the width of the panel on top of this section of media providing an even supply of resin to the part. A 0.95 cm inside diameter reinforced-vinyl tube was used to supply resin to the part. Both the vinyl and spiral tubing were also used on the vacuum side of the part. This outlet tubing was connected to a resin trap and vacuum pump. A thermocouple probe was inserted 5 cm into the preform between the second and third stacks of fabric (Figure 5). The bagging procedure was completed when the preform, media and tubing were sealed to the steel tool using a conformable vacuum bag and sealant tape.

The sealed bag and tubing were evacuated under full vacuum and checked for leaks using a vacuum gage and pressure sensor. The free end of the inlet tube was placed in the bucket containing the degassed resin. A tube clamp was released to allow the resin to flow into the spiral tubing, through the distribution media and into the fiber preform. When the preform was fully impregnated, as evidenced through visual inspection, the inlet and then the outlet tube were clamped. The part was then placed in an oven to cure.

The cure cycle utilized for the VARTM panel consisted of a ramp from room temperature to 67°C at 1.1°C/minute and hold for 2.75 hours, followed by a ramp at 1.4°C/minute to 123°C and held for 2.75 hours. The part was then cooled at 1.0°C/minute to room temperature. The part was released from the tool, rebagged, and postcured under full vacuum for six hours at 177°C. The part temperature (Figure 6) followed the oven temperature and no exotherm was observed. The predicted resin degree of cure using Equation 2 is also shown on Figure 6. The final predicted resin degree of cure is 0.96 which is slightly higher than the 0.93 value obtained from the residual heat of reaction measurement for a resin sample cured with the same cure cycle. In Figure 7, the predicted viscosity profile using Equation 3 was compared to the measured viscosity of a resin sample in a rheometer subjected to the same temperature profile measured in the panel (Figure 6). The model captures the magnitude and location of the minimum viscosity point as well as the onset of gelation, around 180 minutes. These results indicate that the cure kinetics and viscosity models developed in this work are adequate for studying the processing of VARTM panels with SI-ZG-5A resin.

CURE SIMULATIONS

A process model was used to simulate the cure of 5 mm and 25 mm thick panels with three different cure cycles with specifications summarized in Table 3. Cycle 1 is the resin manufacturer recommended cycle, cycle 2 is the Seemann Composites Inc. suggested cure cycle and cycle 3 is a cure cycle designed to reduce the resin gel time. The cure simulations were performed using the process model COMPRO [8]. The cure kinetics and viscosity model developed in this work for SI-ZG-5A were used in the simulations. The panel was assumed to be fully saturated with resin at a fiber volume fraction of 0.55. Thermal properties for the resin and the fiber were taken for a typical epoxy and carbon fiber. The panel and a 5 mm thick steel tool were modeled with a one-dimensional column of elements in the thickness direction. A convective heat transfer boundary condition (30 W/m²°C heat transfer coefficient) was assumed on the top and bottom of the tool-part assembly. The heat transfer and resin cure kinetics were solved and resin flow during cure was neglected.

Figures 8-10 present the maximum part temperature and minimum resin viscosity profiles predicted by the model. The two recommended cure cycles for SI-ZG-5A (cycles 1 and 2) produce similar temperature and viscosity profiles. With cycle 1, the 5 mm and 25 mm panels gelled at 255 minutes and 215 minutes, respectively. With cycle 2, the gel point for the 5 mm and 25 mm panels was 220 minutes and 195 minutes, respectively. For cycles 1 and 2, the 5 mm panel exhibited no exotherm while the 25 mm had a 9°C exotherm during the first hold. With cycle 3, the resin gel point was significantly quicker at 95 minutes for the 5 mm panel and 100 minutes for the 25 mm panel. An exotherm of 26°C was observed for the 25mm panel. To reduce curing time, a robust oven control system must be used to reduce the magnitude of the exotherm for thick parts. Another option would be to use the process model and optimize the cure cycle for the part shapes and sizes of interest. Nevertheless, it was found that a resin system like SI-ZG-5A was designed

mainly to insure a long processing window at room temperature and to maximize the infiltration time for VARTM. However its curing behavior can be significantly altered depending on the geometry and cure cycle considered.

Table 3 Cure cycle used in simulations.

Cycle 1	Cycle 2	Cycle 3
Heat to 66°C @ 0.56°C/min	Heat to 66°C @ 1.11°C/min	Heat to 121°C @ 0.83°C/min
Hold 4 hours	Hold 2.5 hours	Hold 2 hours
Heat to 177°C @ 0.56°C/min	Heat to 121°C @ 0.83°C/min	Heat to 177°C @ 0.56°C/min
Hold 6 hours	Hold 2.5 hours	Hold 6 hours
Cool to RT @ 0.56°C/min	Heat to 177°C @ 0.56°C/min	Cool to RT @ 0.56°C/min
	Hold 6 hours	
	Cool to RT @ 0.56°C/min	

CONCLUSIONS

The observed viscosity profile and curing kinetics for a carbon fiber perform fully impregnated with the epoxy resin, SI-ZG-5A were found to be in good agreement with predictions of the process model, COMPRO [8]. Relationships for resin viscosity and degree of cure were shown to accurately model the observed resin characteristics with only modest differences at the extremes of performance variables. The modified auto-catalytic cure kinetics model was shown to provide an accurate representation of the curing phenomenon. The three curing cycles examined showed that time to resin gel and exotherm are strong functions of the cure cycle characteristics and resin properties. Gel times ranged from 95-255 minutes for the panel of 5 mm thickness and 100-215 minutes for the 25 mm panel. Exotherms of 9-26 degrees Celsius were observed for the 25 mm panel.

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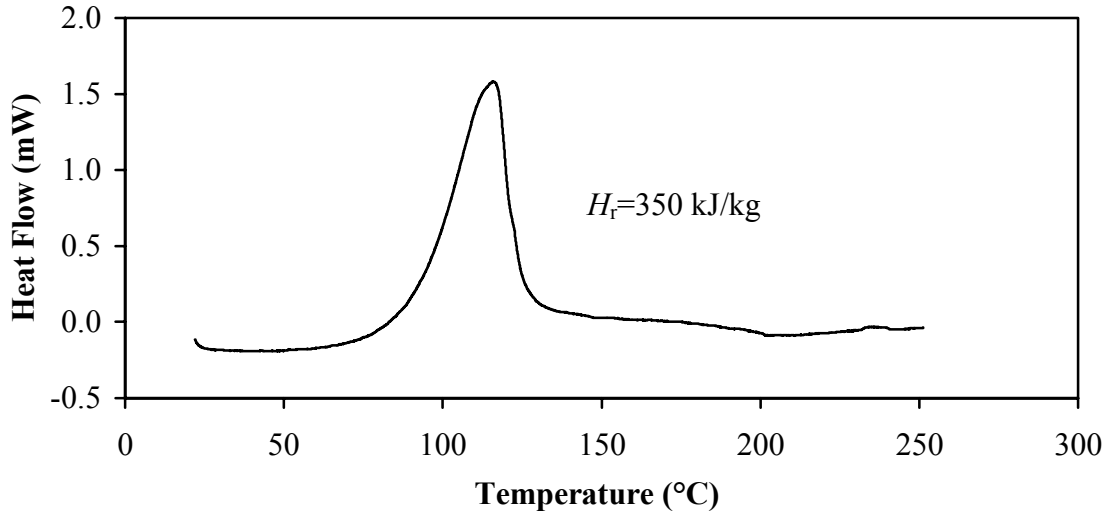


Figure 1 Typical dynamic scan for SI-ZG-5A at 1.1 °C/min. showing a total heat of reaction of 350kJ/kg.

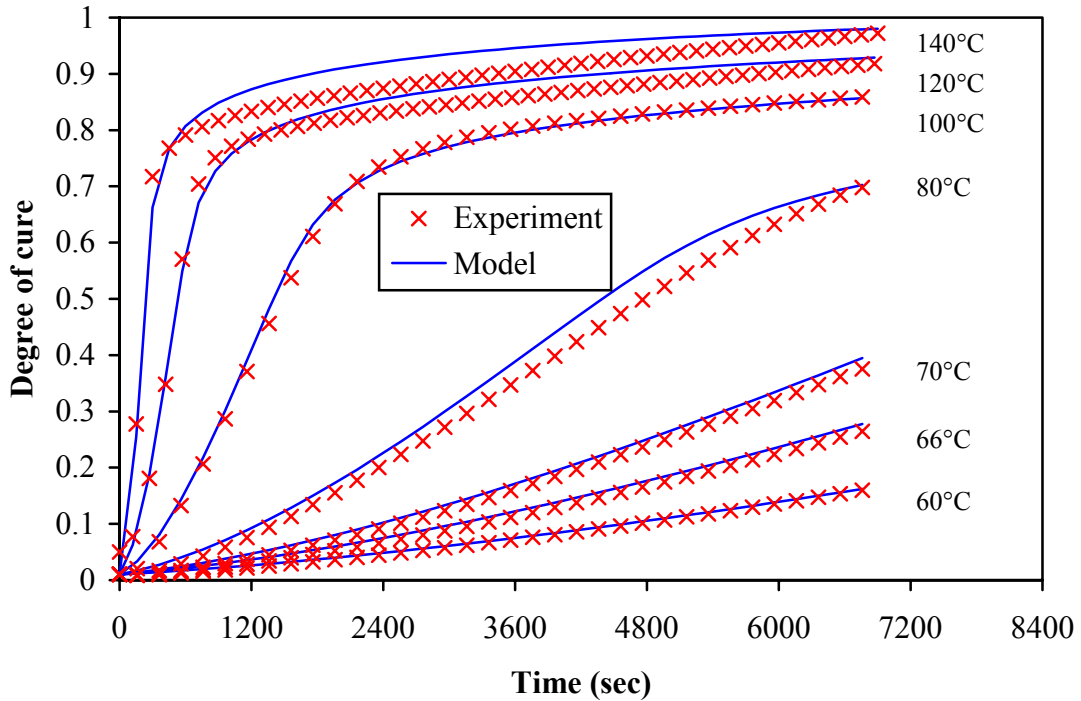


Figure 2 Comparison between measured and predicted SI-ZG-5A resin degree of cure in isothermal curing condition.

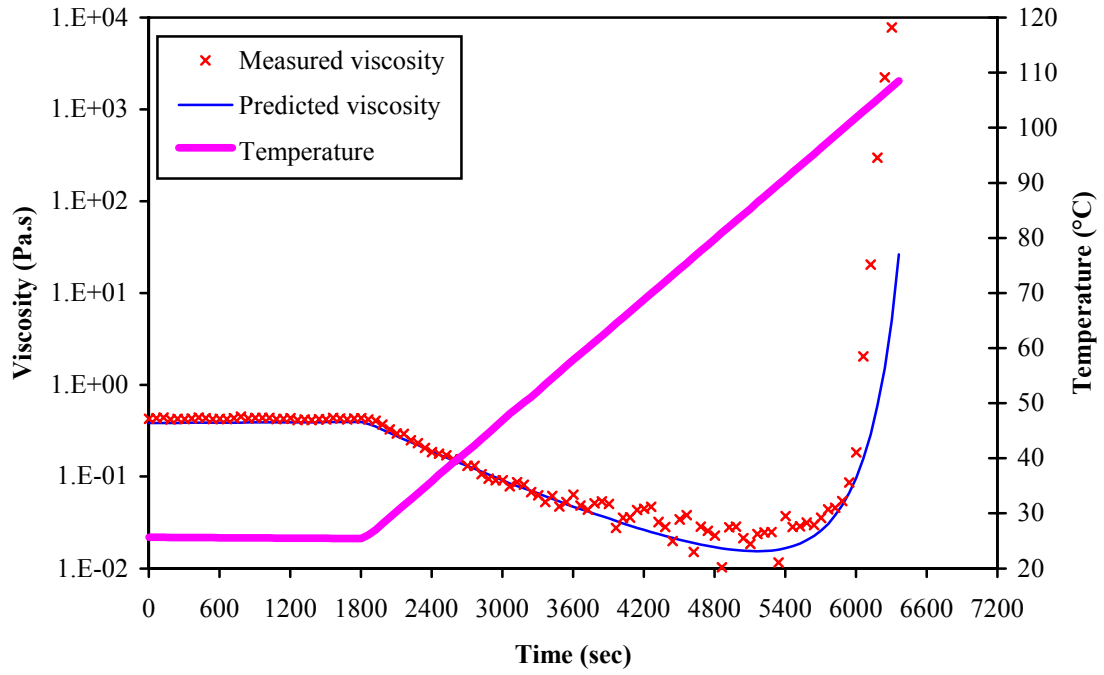


Figure 3 Comparison between measured and predicted viscosity for a dynamic scan at 1.1 °C/min for SI-ZG-5A.

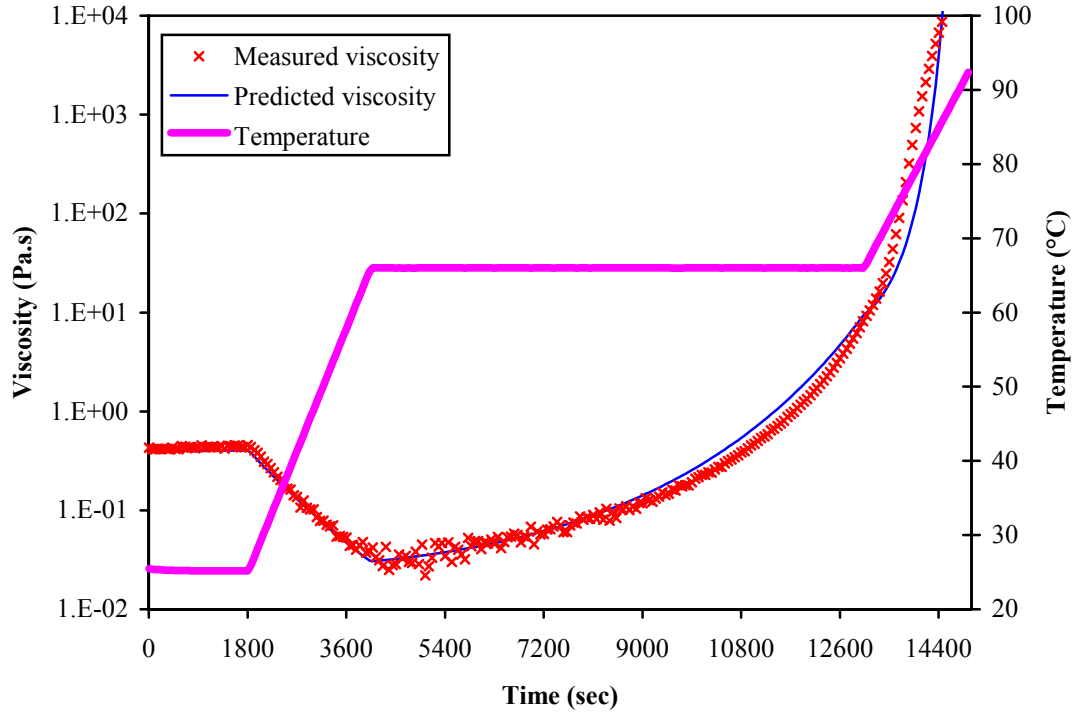


Figure 4 Comparison between measured and predicted viscosity for a typical cure cycle test for SI-ZG-5A.

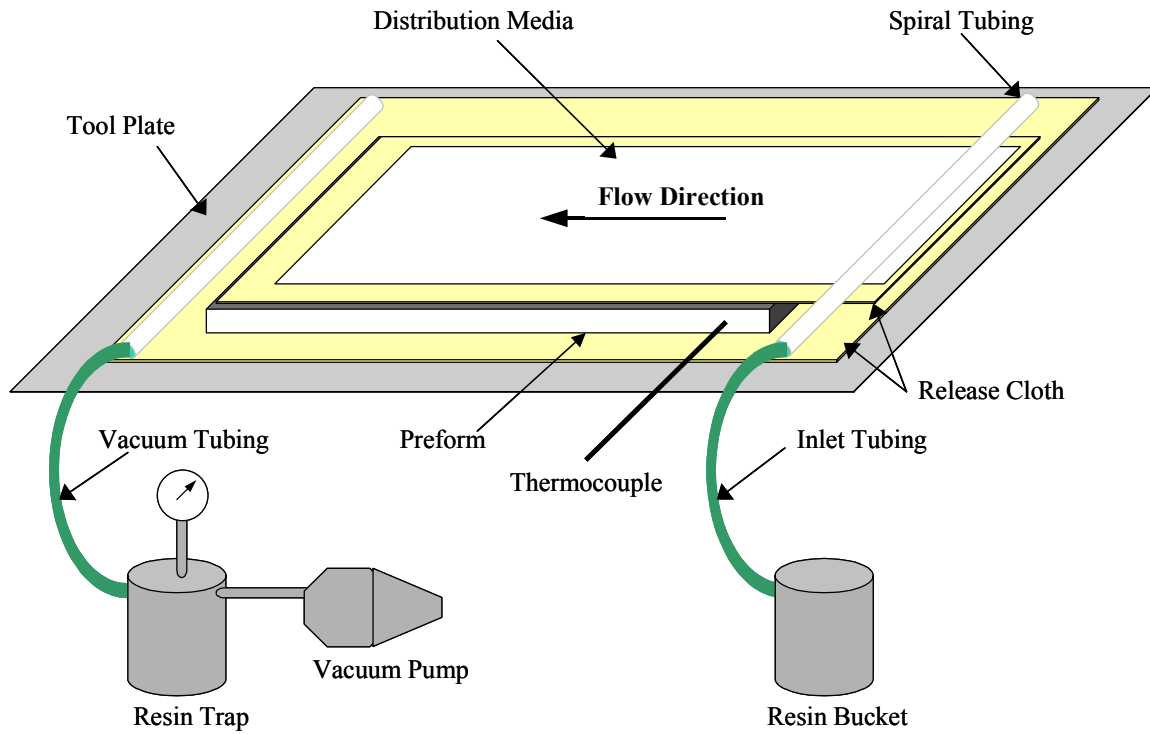


Figure 5 VARTM experimental set-up.

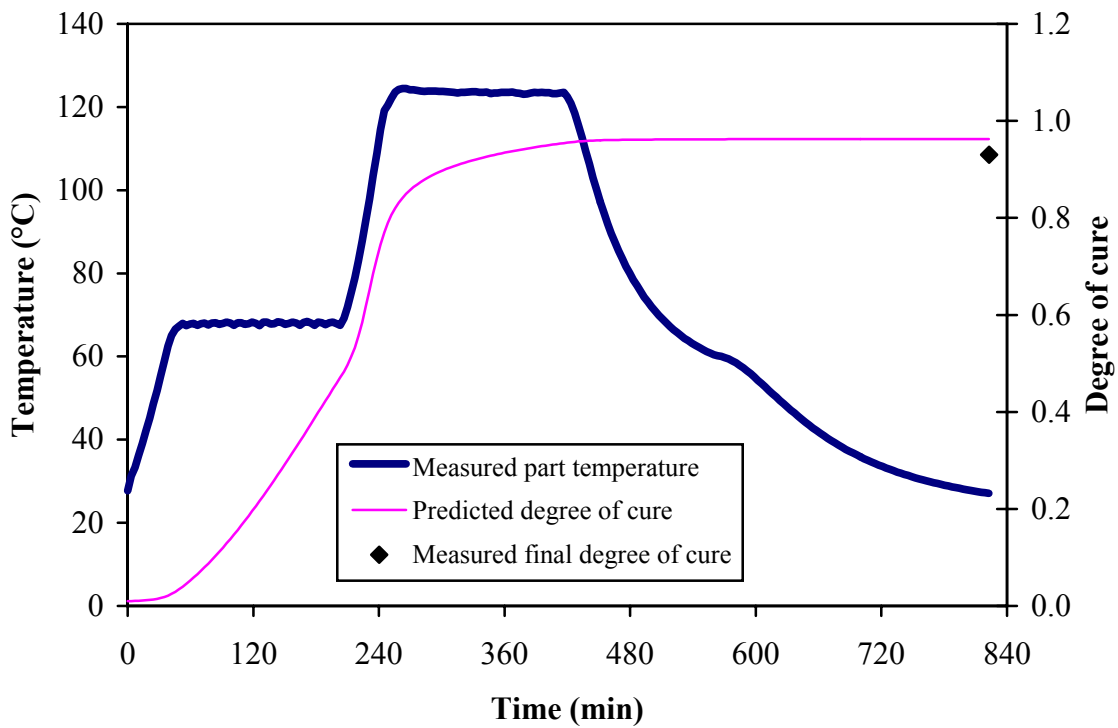


Figure 6 Measured part temperature and predicted resin degree of cure at the center of the SI-ZG-5A VARTM panel. A final resin degree of cure of 0.93 was measured.

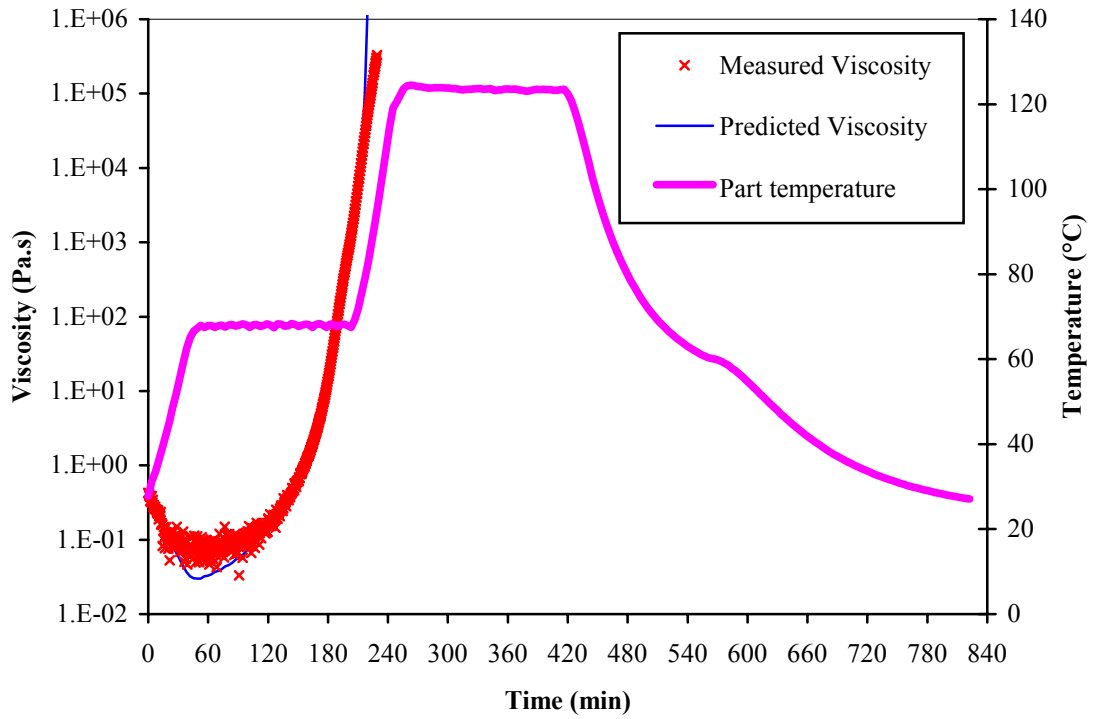


Figure 7 Comparison between resin viscosity predicted and measured at the center of the SI-ZG-5A VARTM panel .

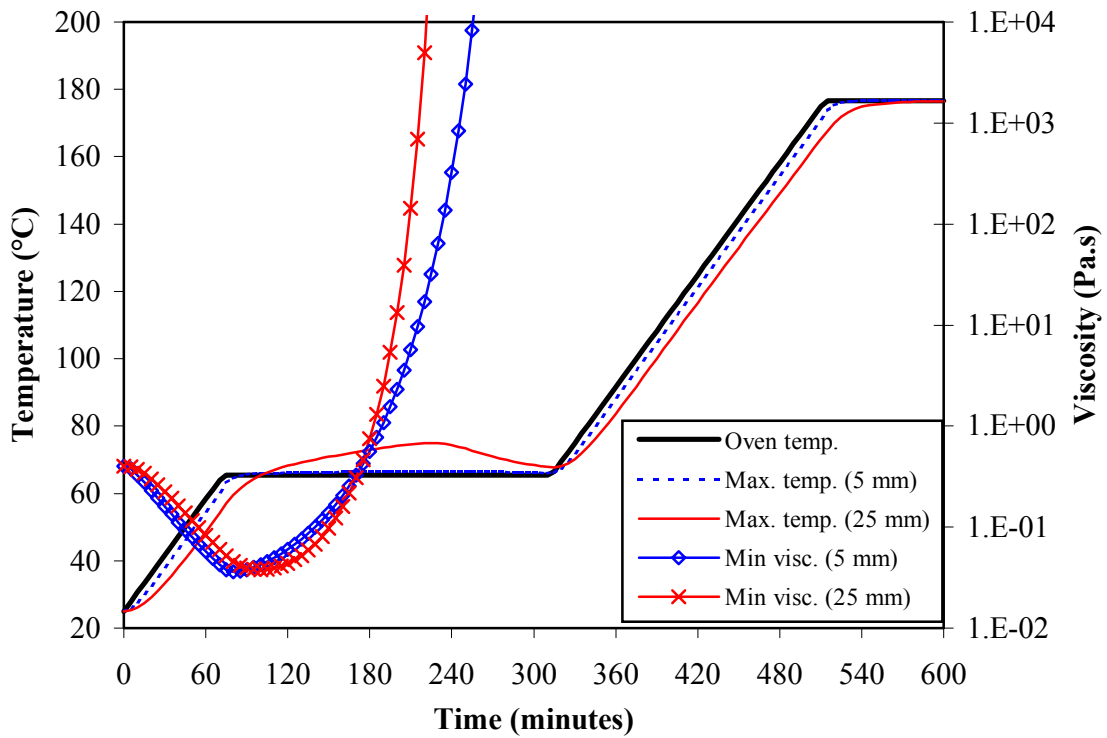


Figure 8 Predicted part maximum part temperature and minimum resin viscosity profile for a 5mm and 25mm thick carbon fiber panel cured following cycle 1 (SI-ZG-5A/Carbon fiber).

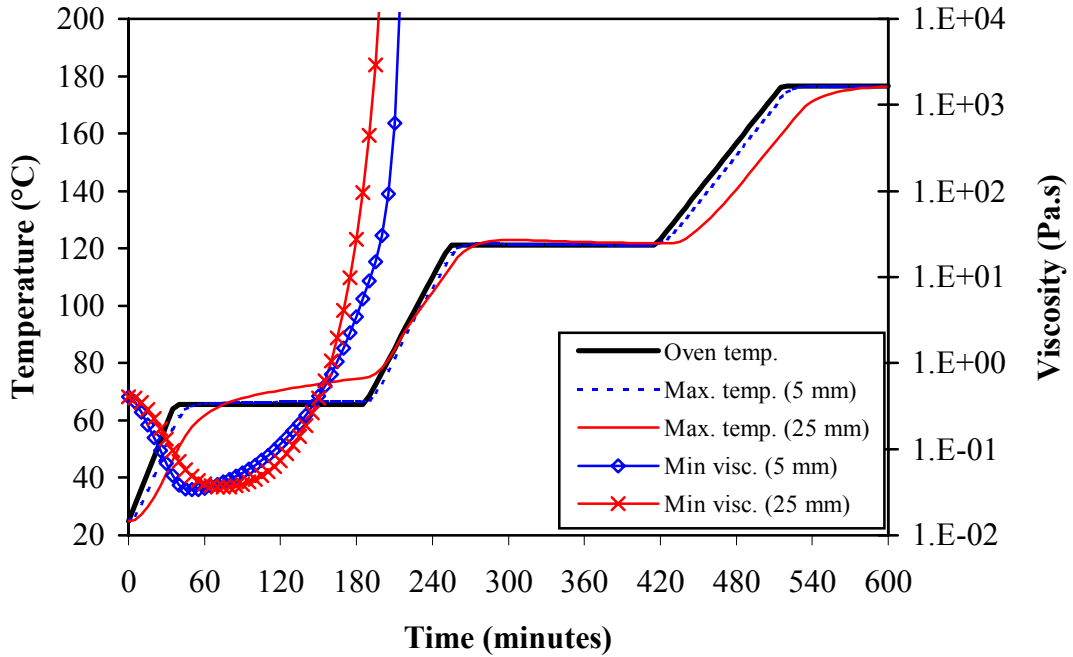


Figure 9 Predicted part maximum part temperature and minimum resin viscosity profile for a 5mm and 25mm thick carbon fiber panel cured following cycle 2 (SI-ZG-5A/Carbon fiber).

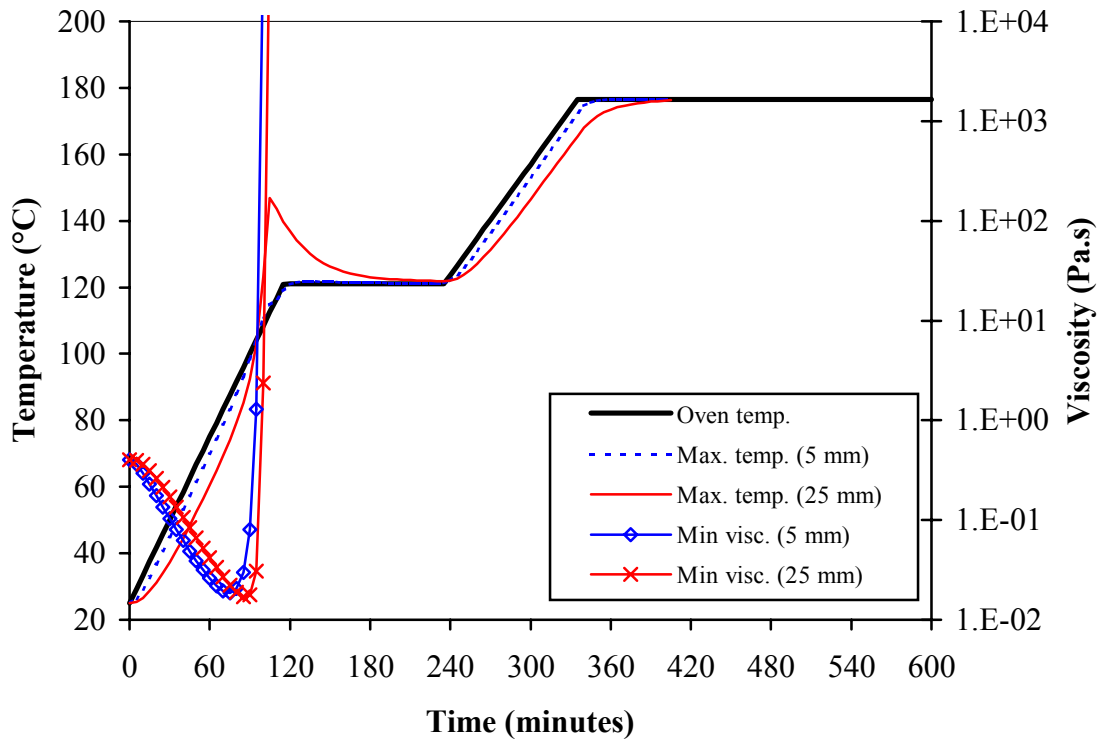


Figure 10 Predicted part maximum part temperature and minimum resin viscosity profile for a 5mm and 25mm thick carbon fiber panel cured following cycle 3 (SI-ZG-5A/Carbon fiber).