Out-time effects on cure kinetics and viscosity for an out-of-autoclave (OOA) prepregs: Modelling and monitoring

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Abstract: The processing and final part quality of out-of-autoclave (OOA) prepreg composites are strongly influenced by the thermo-chemical and thermo-mechanical properties of the resin. These properties are primarily influenced by the out-time, or room temperature exposure time, of the resin prior to cure, and by the chosen cure cycle. However, both these factors can be difficult to control. Therefore, the capacity to track the resin cure state during processing is highly desirable. In this study, neat resin and prepreg samples are aged from 0 to 7 weeks, and the resin cure kinetics and viscosity are measured using differential scanning calorimetry (DSC) and rheometry, respectively, and used to develop accurate predictive models. The dielectric properties of the resin are measured in situ, and correlations to resin cure kinetics and viscosity are developed. The study quantifies the effects of out-time on cure kinetics and viscosity, and shows that both properties can be predicted and monitored in situ with excellent accuracy.

Key words: Dielectric analysis (DEA); B. Curing; C. Modelling; D. Differential scanning calorimetry (DSC); D. Rheology

1. Introduction

Out-of-autoclave (OOA) prepregs allow the manufacturing of low-porosity, high-performance composite structures through flexible, cost-effective vacuum-bag-only (VBO) processing [1] and [2]. In the absence of high consolidation pressure, such as that imparted by an autoclave, voids are suppressed by evacuating entrapped air and vaporized moisture through a partially impregnated microstructure made up of both dry and resin-rich regions. Initially, the dry regions form a permeable vascular network of vacuum channels that allows in-plane gas transfer under vacuum. During processing, they are infiltrated by surrounding resin to form a uniform and ideally void-free microstructure. The rate of infiltration and the quality of OOA laminates are therefore strongly influenced by the cure kinetics and viscosity evolution of the infiltrating resin.

These resin properties are generally assumed to depend on the temperature cycle used during cure, and are commonly described using semi-empirical analytical models [1], [3],[4], [5], [6], [7], [8] and [9]. However, such equations ignore the potential influence of out-time prior to cure. Out-time is unavoidable in industrial settings, as the lay-up and preparation of large structures often takes several days to weeks. Recently, out-time has been shown to cause ambient temperature induced polymerization/cross-linking of the resin, which adversely affects tack and drape and can lead to pervasive and unacceptably high void contents in cured parts [2], [10], [11] and [12]. Furthermore, the chemical reactions taking place during room temperature cure may differ from those at elevated temperatures. Thus, out-time may affect not only the initial degree of cure, but also the evolution of cure kinetics and viscosity during subsequent cure. Altogether, accurate methods for monitoring and predicting the influence of out-time on key resin properties are necessary.

Resin thermo-chemical properties have been previously characterized using differential scanning calorimetry (DSC) [1], [3], [4], [5], [6], [7], [8] and [9] and Fourier transform infrared spectroscopy (FTIR) [6]. In addition, the influence of cure on thermo-mechanical properties has been measured using rheometry [1] and [5] and dynamic mechanical analysis (DMA) [13]. Generally, DSC is the most widely accepted means of characterizing the cure kinetics of thermoset composite matrices, as it is based on the evolution of heat generation as a function of cure time and temperature. Similarly, rheometry is commonly used to define the composite's gel point and measure the viscosity evolution in process conditions. To characterize unknown resins, data is acquired in both dynamic ramp and isothermal dwell temperature conditions, and used to develop various phenomenological models with several fitting parameters [1] and [5]. However, both methods are carried out ex situ, on small-scale samples, and in idealized conditions, rather than on the actual full-scale parts being manufactured.

Recent developments in on-line cure monitoring techniques such as dielectric analysis (DEA) [7], [8], [9], [14] and [15], ultrasonic monitoring [16], Raman infrared spectroscopy[7] and optical fiber methods [17] have been demonstrated. Among them, DEA is the most promising candidate for its non-invasiveness, high sensitivity, and potential wealth of obtainable data. DEA relies on measurement of the mobility of ionic species in the thermoset resin during cure by creating a resistive–capacitive circuit, which can be scrutinized and potentially correlated to properties such as degree of cure, viscosity, gelation time and vitrification. In particular, the evolution of imaginary impedance maximum (Z''_{max}), which directly relates resistivity levels (i.e. dissipative processes) to the amount and mobility of charged species, has been shown to correlate to DSC signals (i.e. heat generation) [8], [9] and [14].

The ambient aging of autoclave prepregs has been studied using DSC [2], micro-CT [2], photoacoustic spectroscopy [11] and infrared spectroscopy [12]. Furthermore, the effect of out-time on the thermochemical properties of an OOA prepreg resin has also been investigated [10]. These studies have identified various phenomena at the resin chemistry level. However, two critical needs have yet to be addressed – models that can accurately predict the degree of cure and viscosity evolution for any cure cycle at any out-time, and experimental methods capable of carrying out real-time, in situ process monitoring on full-scale parts for quality diagnostics and, in extremis, adaptive process control.

The present study seeks to develop accurate methods for predicting and monitoring the effects of out-time on resin properties. To this effect, both traditional and emerging methods are investigated. First, DSC and rheometry measurements obtained from neat resin samples are used to understand and model the evolution of cure kinetics and viscosity for various out-times and cure cycles. In addition, DEA measurements are carried out on prepreg samples, and correlations are developed to allow resin cure to be accurately monitored in situ using dielectric data.

2. Experimental procedure

2.1. Materials

For this study, we selected a commercially available OOA prepreg consisting of a woven eight-harness satin (T650-35 8HS) carbon fiber fabric and a toughened epoxy resin (CYCOM® 5320-1, Cytec Industries Inc.). The manufacturer's stated out-life is 30 days at ambient temperature [18]. Neat resin film was used for cure kinetics and viscosity characterization using DSC and rheometer, and prepreg was used for the same purpose with the DEA system. For both neat resin and prepreg, out-times and freezer times prior to use were consistent and negligible.

2.2. Sample conditioning

Neat resin samples were pre-cut to nominal specifications of 10 mg for DSC tests and 3×3 cm for rheometry tests. Prepreg samples measuring 2.5×2.5 cm were similarly prepared for DEA tests. All samples were stored and aged separately in unsealed containers at stable ambient conditions (21 ± 2 °C, $51 \pm 5\%$ relative humidity).

2.3. Modulated-DSC (MDSC) measurements

MDSC measurements were performed with a rheometer (TA Instruments Q2000) under a constant nitrogen flow of 50 mL/min. For each measurement, 10 ± 2 mg of neat resin was sealed in aluminum hermetic DSC pans (Tzero, TA Instruments). Dynamic ramps were conducted by heating the DSC cell from −60 °C to 280 °C at a constant rate of 1.7 °C/min, and under a temperature modulation of ±0.5 °C/min. The total heat of reaction (ΔH_T) of the resin was determined by integrating the heat flow evolution from these measurements. Isothermal dwell measurements were conducted at three different temperatures spanning the manufacturer's recommended cure range (93 °C, 107 °C and 121 °C). The temperature in the DSC cell was rapidly brought to the isothermal dwell temperature and held constant until negligible heat flow was measured within the sample. After all isothermal tests, the DSC cell was cooled to 20 °C, then heated to 280 °C at a constant heating rate of 1.7 °C/min to measure the residual heat of reaction (ΔH_R). The thermal stability of the resin was investigated by thermogravimetric analysis (TGA). Between 25 °C and 280 °C, the resin weight decreased by less than 0.5%, indicating that no degradation took place and that the measured heat flows were associated with cure.

2.4. Rheometry measurements

Viscosity measurements were performed using 25 mm aluminum parallel plates in a rheometer (TA Instruments AR2000). All tests were conducted under constant oscillatory shear at a frequency of 1 Hz and at a strain of 0.25%, within the linear viscoelastic regime. Pre-cut neat resin samples were sandwiched between aluminum parallel plates and compressed to a gap of 0.5 mm, and excess resin was manually trimmed to prevent boundary effects. Dynamic ramps were conducted by heating at 1.7 °C/min to 260 °C, and isothermal dwells were performed by heating at 10 °C/min to 93 °C, 107 °C and 121 °C and holding until a stopping condition was reached. For both dynamic and isothermal tests, the stopping condition was defined as 90% of the machine-specified maximum torque (200 mN m), to ensure that measurements extended as close to the gel point as feasible. In addition, the same limit was used as an initial condition for high out-times samples, which exhibited higher room temperature viscosity (η) due to extensive cure.

2.5. DEA measurements

DEA measurement was performed using a dielectric monitoring system (DETA SCOPE™, ADVISE E.E., Greece). The system utilizes coplanar electrodes to generate fringing electric field lines that penetrate into the dielectric material and allow non-destructive measurements and one-sided access. Because the penetration depth was up to 100 μm, a glass fiber layer was added to the tool-side surface of the prepreg samples to insulate the sensor from the conductive carbon fibers. DEA tests were performed within an instrumented, integrally heated test cell. First, laminated prepreg samples 30 mm thick (with glass fiber layer) were placed on top of the dielectric sensor, within a thin picture-frame spacer containing a thermocouple. The assembly then was sandwiched between top and bottom sections with embedded heating cartridges, which applied controlled and uniform heating to the sample. Note that while the test cell was used for convenience, the DEA instrument includes

identical sensors that can be embedded at the surface of oven or autoclave tool plates, or within liquid injection molds.

During each experiment, a 10 V excitation voltage was applied and twenty-five frequencies were scanned, logarithmically spaced over a frequency window of 1 Hz to 1 MHz. From the applied voltage and scanned frequency, circuit analysis was used to determine the evolution of the mobility of charged species within the resin as a function of time. Dynamic ramp runs were conducted at 1.7 °C/min up to 220 °C (machine specified maximum temperature) and isothermal dwells were conducted by heating at 10 °C/min to 93 °C, 107 °C and 121 °C, and held constant until no significant change in the signals could be observed.

3. Model framework

3.1. Cure kinetics model development using MDSC measurement

To model cure kinetics, the total heat of reaction (ΔH_T) was first determined from dynamic ramp data from the fresh sample. Assuming that the cure rate is directly proportional to the heat flow measurement, the cure rate is defined as [1], [3], [4], [5], [6], [7], [8],[9] and [14]:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T}\frac{dH}{dt}$$

(1)

where α is the degree of cure, $d\alpha/dt$ is the cure rate and dH/dt is the total heat flow measured from MDSC. Integration of $d\alpha/dt$ versus time then yields α as a function of time ($\alpha(t)$), which ranges from 0 to 1, or fully-uncured to fully-cured.

Phenomenological cure kinetics models are widely used for the generally complex cure reactions of epoxy matrices, where linear polymerization, branching and cross-linking take place concurrently [1], [3], [4], [5], [6] and [7]. Among these, a model was developed by Kratz et al. [1] for

the antecedent of the resin under study. This model accounts for the interplay between kinetics- and diffusion-controlled reactions, and was modified to capture the out-time effects through the following form:

$$\frac{d\alpha}{dt} = \sum_{i=1,3} w_i K_i \alpha^{m_i} (1-\alpha)^{n_i} + \sum_{j=2,4} w_j \frac{K_j \alpha^{m_j} (1-\alpha)^{n_j}}{1 + \exp(D_j(\alpha - (\alpha_{C0,j} + \alpha_{CT,j}T)))}$$

(2)

$$K_n = A_n \exp\left(\frac{-E_{A,n}}{RT}\right) \quad \text{where } n = i, j$$

(3)

where K_n is the Arrhenius temperature dependent term, A_n is the Arrhenius constant, $E_{A,n}$ is the activation energy, m_i and n_i are reaction order-based fitting constants, D_j is the diffusion constant, T is the temperature, α_{C0} is the critical degree of cure at absolute zero, and α_{CT} accounts for the increase in critical degree of cure with temperature. To account for the changes associated with ambient temperature cure, which induces both time- and magnitude shifts in the cure rate profile, the weight factors w_i and w_j, as well as the initial degree of cure α_0 were allowed to vary with out-time. A reference value of $w_i = w_j = 1$ was used as the reference value for the fresh resin samples.

3.2. Viscosity model development using rheometry measurement

To model the viscosity evolution during cure, a phenomenological model used by Khoun et al. [5] was modified to capture the out-time effects. The model includes an additional polynomial term accounting for the viscosity at gelation, shown below:

$$\eta = w_1 \eta_1 + w_2 \eta_2 \left(\frac{\alpha_{gel}}{\alpha_{gel} - \alpha}\right)^{A + B\alpha^d + C\alpha^e}$$

(4)

$$\eta_i = A_{\eta_i} \exp\left(\frac{E_{\eta_i}}{RT}\right), \quad i = 1, 2$$

(5)

where w_1 and w_2 are weight factors that depends on out-time, η_i is the Arrhenius dependent viscosity component, $A_{\eta i}$ is the Arrhenius constant, $E_{\eta i}$ is the viscosity activation energy, α_{gel} is the degree of cure at gelation, and A, B, C, d and e are fitting constants. The model uses a degree-of-cure profile obtained from a MDSC experiment or a cure kinetics model as an input for α. The viscosity evolution is governed by two competing effects: direct thermal effects and cross-linking. Initially, during heat-up, the rate of cure is minimal and the viscosity decreases due to increased molecular mobility. Then, as the rate of cure increases, the effect of cross-linking and increased molecular size begins to dominate, and the viscosity increases. The shift from thermal to cross-linking effects is captured by the d and e terms.

3.3. Cure kinetics and viscosity correlation development using DEA measurement

Skordos and Partridge [8] and Kazilas and Partridge [9] proposed a correlation between degree of cure and dielectric properties that relies on the mobility of charged species in the resin, measured as imaginary impedance (Z'') versus frequency along the cure profile. They reported that the evolution of imaginary impedance maxima $(\log Z''_{max})$ during cure follows the development of α , as obtained from DSC. The correlation relates $\log Z''_{max}$ to α and T by:

$$\log Z''_{max} = (c_{11} + c_{12}T)\alpha + c_2 \tag{6}$$

where c_{11} and c_{12} are fitting constants determined from isothermal dwell measurements; and c_2 is $\log Z''_{max}$ at $\alpha = 0$. Differentiating Eq. (6) with respect to time yields:

$$\frac{d\log Z''_{max}}{dt} = \frac{\partial \log Z''_{max}}{\partial \alpha}\frac{d\alpha}{dt} + \frac{\partial \log Z''_{max}}{\partial T}\frac{dT}{dt} \tag{7}$$

$$\frac{d \log Z''_{max}}{dt} = (c_{11} + c_{12}T)\frac{d\alpha}{dt} + c_{12}\alpha\frac{dT}{dt} \tag{8}$$

where dT/dt is the heating rate term that allows modelling of non-isothermal conditions. A dynamic ramp model can be expressed using the two previously obtained constants (c_{11} and c_{12}). Skordos and Partridge [8] and Kazilas and Partridge [9] reported that the evolution of $\log Z''_{max}$ along the cure profile exhibits competing effects similar to those occurring during the evolution of η. Before the onset of cure, the rate of cure is minimal and $\log Z''_{max}$ decreases due to increased ionic mobility. As the rate of cure increases, the effect of cross-linking and increased molecular size slows ionic mobility, and $\log Z''_{max}$ increases. However, near the end of the cure reaction, the thermal effect returns, and $\log Z''_{max}$ begins to decrease, as little further reaction takes place.

Using modifications similar to those made on cure kinetics and viscosity modelling, Eq.(6) was modified to account for out-time effects, specific to dielectric response, as follows:

$$\log Z''_{max} = (w_1 c_{11} + w_2 c_{12}T)\alpha + c_2 \tag{9}$$

where w_1 and w_2 are weight factors depending on out-time. The $d\alpha/dt$ profile was obtained by differentiating Eq. (9). For this study, fitting constants and weight factors are determined by correlating Eq. (9) with the cure kinetics model developed using MDSC. However, the model is not inherently necessary, as the constants may be obtained by relating DEA data directly to MDSC data. The α profile determined from Eq. (9) was used to predict η by Eq. (4).

4. Results and discussion

4.1. Cure kinetics measurement and modelling using MDSC

Fig. 1 shows cure kinetics measurements and corresponding predictive model results obtained using Eq. (2) (for the same time–temperature cycle). The model parameters determined are provided

in Table 1. Although not shown, isothermal dwell data at 107 °C was also taken into account. As described in Section 3.1, out-time causes both time-based (horizontal) and magnitude (vertical) shifts of the cure kinetics profile, along with α_0 increases. These effects are manifest in Fig. 1, where the top row shows that the shape of the cure rate profile changes from 0 to 49 days of out-time, and the bottom row shows that α_0 increases as a consequence.
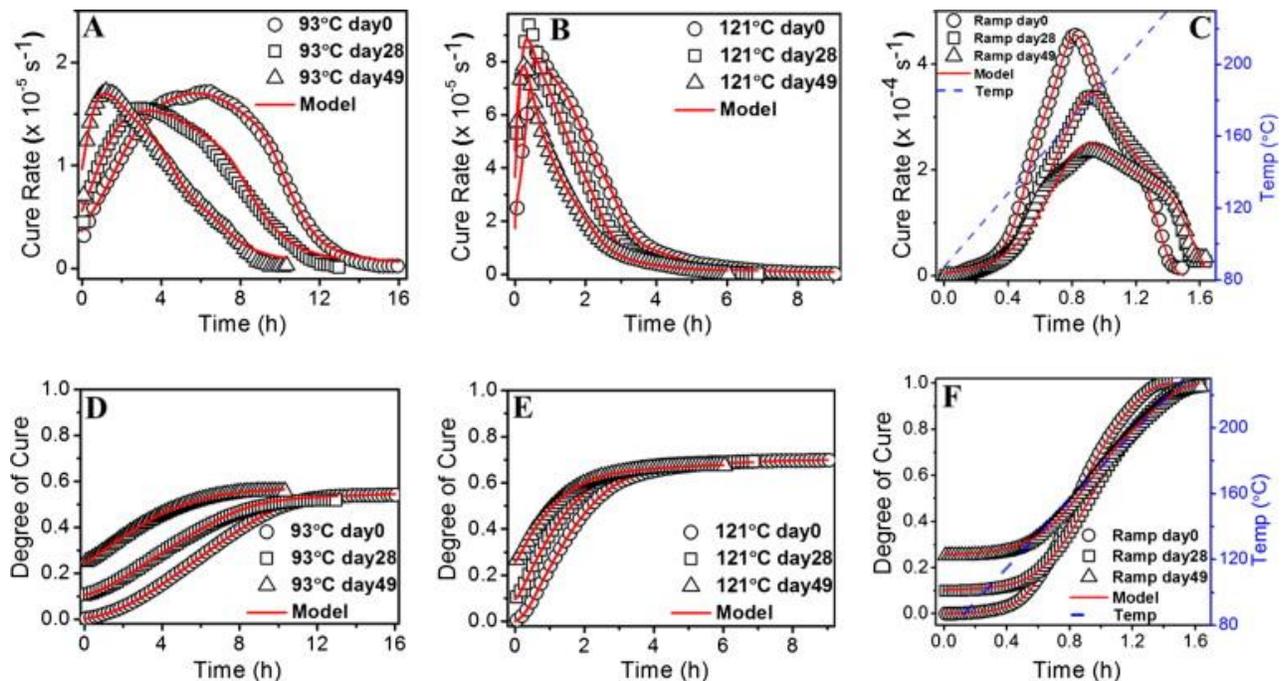

Figure 1*: Cure kinetics measurement and model prediction of dynamic ramp and isothermal dwell at day 0, 28 and 49. Upper row – cure rate versus cure time: (A) isothermal dwell at 93 °C, (B) isothermal dwell at 121 °C, and (C) dynamic ramp. Bottom row – degree of cure versus cure time: (D) isothermal dwell at 93 °C, (E) isothermal dwell at 121 °C, and (F) dynamic ramp.*

***Table 1:** Parameters for cure kinetics models*

Parameter	Value	Parameter	Value
A_1 (s^{-1})	1.48×10^7	A_3 (s^{-1})	6.39×10^7
E_{A1}/R (K)	1.02×10^4	E_{A3}/R (K)	8.94×10^3
m_1	0.17	m_3	1.65
n_1	19.3	n_3	16.6
A_2 (s^{-1})	8.3×10^4	A_4 (s^{-1})	9.8×10^4
E_{A2}/R (K)	8.54×10^3	E_{A4}/R (K)	7.1×10^3
m_2	0.70	m_4	1.66
n_2	0.87	n_4	3.9
D_2	97.4	D_4	63.3
$\alpha_{C0,2}$	-1.6	$\alpha_{C0,4}$	-0.60
$\alpha_{CT,2}$ (K^{-1})	5.7×10^{-3}	$\alpha_{CT,4}$ (K^{-1})	3.0×10^{-3}

Out-time parameters (t = days)
$\alpha_0 = 5.98 \times 10^{-5}t^2 + 2.5 \times 10^{-3}t + 0.005$
$w_1 = -5.34 \times 10^{-3}t^3 + 2.40 \times 10^{-1}t^2 - 2.67\,t + 1$
$w_2 = -2.74 \times 10^{-5}t^3 + 2.24 \times 10^{-3}t^2 - 0.05\,t + 1$
$w_3 = 3.21 \times 10^{-5}t^3 - 1.62 \times 10^{-3}t^2 + 2.74\,t + 1$
$w_4 = 1$

Consistent (and predictable) α_0 increases with out-time are observed for all cure cycles, and can be described by the relation:

$$\alpha_0 = \frac{\Delta H_T(\text{day 0}) - \Delta H_T(\text{out-time})}{\Delta H_T(\text{day 0})}$$

(10)

Out-time induced polymerization/cross-linking causes α_0 to increase. The thermoset resin cure can be perceived as a blend of fast- and slow-occurring reactions, kinetics-driven and diffusion-driven, respectively. The shift from kinetics-driven to diffusion-driven reaction is evident from the vitrification time (t_{vit}), obtained from MDSC data showing the inflection point of the heat capacity (C_p) during cure. The results confirm that t_{vit} decreases with out-time and with higher isothermal

dwell temperatures. A more detailed analysis of the effects of out-time on critical physicochemical transformations is reported in a separate study [19].

Thus, out-time, where the reaction is induced at low temperature, mainly affects kinetically driven reactions. Time-based cure rate shifts are more apparent during low temperature (93 °C) cure than during dynamic ramp conditions. High-temperature (121 °C) cure on the other hand is relatively unaffected, as sufficient heat is provided to overcome the energy barriers associated with slow cure. Because of these complex phenomena, previously developed cure kinetics models [1] and [3] cannot accurately model out-time effects. In contrast, the model developed here incorporates weight factors that provide additional "degrees of freedom" that can capture cure rate shifts, while time-based shifts are accounted for by the α_0 values determined from Eq. (10). Thus, the present cure kinetics models capture out-time effects accurately over the entire range of conditions studied.

4.2. Viscosity measurement and modelling using rheometry

Viscosity measurements and results obtained from the predictive model using Eq. (4) are shown in Fig. 2 for the same time–temperature cycle. The viscosity model parameters are provided in Table 2. The predicted viscosities accurately match the measured values, even for long out-times. The sole notable deviations occur in dynamic conditions, at high out-times and low temperatures (below 90 °C), where the viscosity model underestimates the measured values. In this regime, thermal effects dominate over cross-linking (see Fig. 1C), and the out-time-dependent weight factors used in the equations may not fully capture the influence of ambient exposure. The first weight factor of the modified model remained constant with out-time ($w_1 = 1$), which acts as a baseline for viscosity.
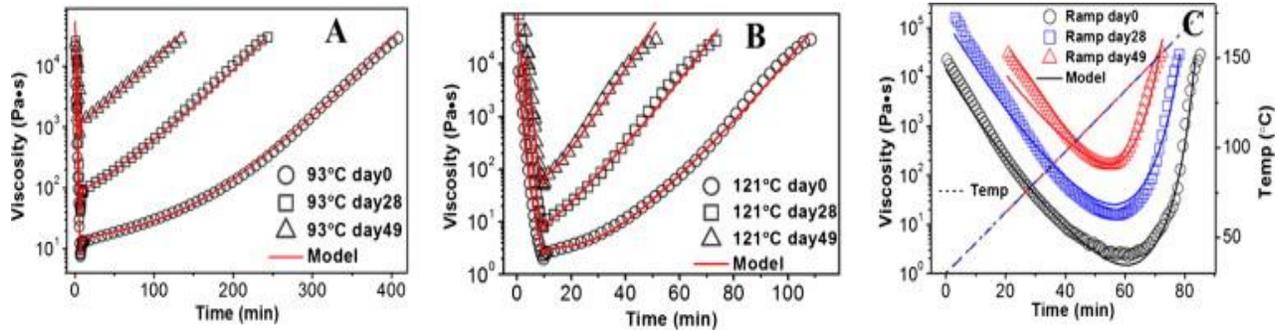
Figure 2: *Viscosity measurement and model prediction of dynamic ramp and isothermal dwell at day 0, 28 and 49 (A) isothermal dwell at 93 °C, (B) isothermal dwell at 121 °C, and (C) dynamic ramp.*

Table 2*: Parameters for viscosity models.*

Parameter	Value	Parameter	Value
$A_{\eta 1}$ (Pa s)	4.52×10^{-9}	A	14.1×10^{-6}
$E_{\eta 1}/R$ (K)	7.59×10^{3}	B	53.7
$A_{\eta 2}$ (Pa s)	1.73×10^{-14}	C	-44.96
$E_{\eta 2}/R$ (K)	1.24×10^{4}	d	-0.13
α_{gel}	0.66	e	-0.11
Out-time parameters (t = days)			
$w_1 = 1$			
$w_2 = 2.9 \times 10^{-5}t^3 - 2.3 \times 10^{-3}t^2 + 2.8 \times 10^{-2}t + 1$			

The second part of the modified model exhibits a complex dependence on out-time. Indeed, w_2 was found to decrease after 14 days, implying that the overall viscosity decreased with out-time. Because the measurements clearly show that viscosity increases due to ambient exposure and cure, we conclude that the agreement between viscosity predictions and measurements can be attributed in part to the interplay with, and accuracy of, the modified cure kinetics model and α input.

The models developed may be used as reference or calibration data for in situ cure kinetics and viscosity measurements using DEA, as demonstrated below. They may also serve as components in process simulations used to develop and optimize cure cycles with minimal experimental cost or that

capture more complex thermomechanical behavior such as consolidation, void formation, and residual stress development.

4.3. Cure kinetics and viscosity measurement and correlation using DEA

As described previously, the nature of the DEA correlation requires that α is first correlated with $\log Z''_{\max}$ from isothermal dwell data and $d\alpha/dt$ is determined from the derivative. Correlation results are plotted in Fig. 3 along with predictions of the cure kinetics model, and the correlation parameters are provided in Table 3. In the correlation data, α first decreases as $\log Z''_{\max}$ decreases due to thermal effects during heating. This non-physical effect can be easily neglected by eliminating the data range during which the rate of cure is negative. When the temperature reaches cure conditions (~90 °C) and the rate of cure increases, the degree of cure begins to increase, as expected. Past this point, the degree of cure correlation closely matches the measured values for all out-times. The calculated $d\alpha/dt$ exhibits small fluctuations due to scatter in the degree of cure measurements. However, the scatter can be reduced by increasing the sampling interval or by data smoothing.
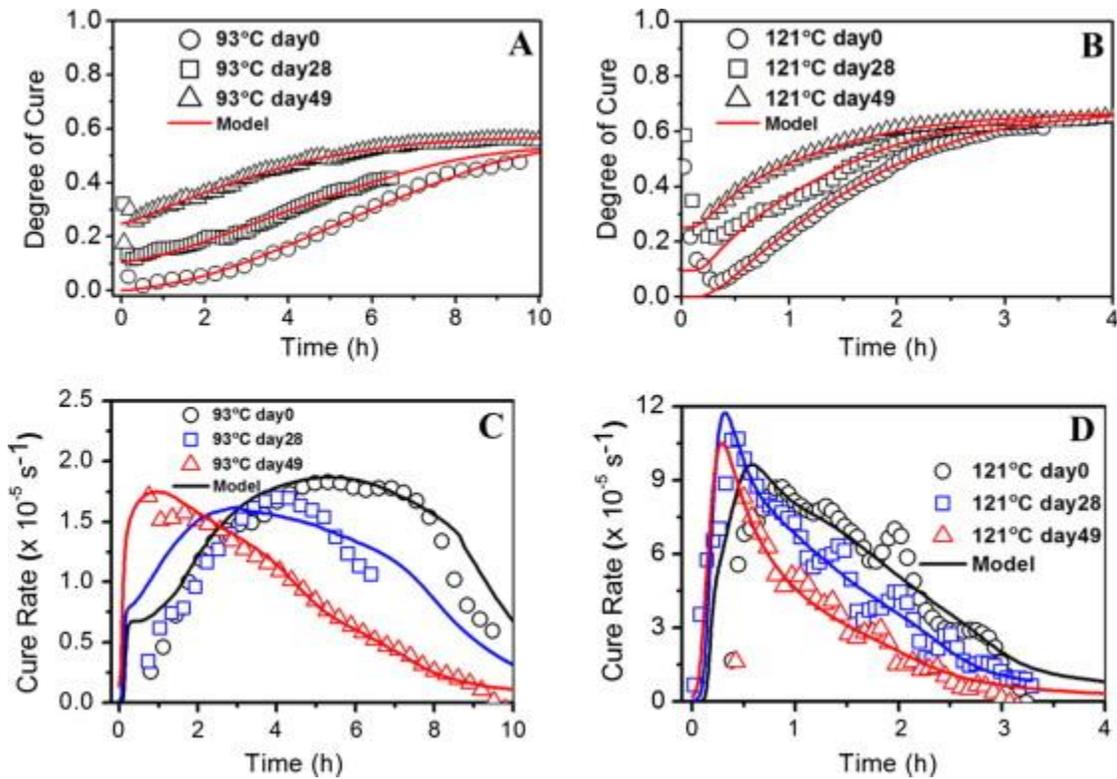
Figure 3: DEA measurement and prediction of isothermal dwell at day 0, 28 and 49. Upper row: degree of cure versus cure time (A) isothermal dwell at 93 °C and (B) isothermal dwell at 121 °C. Bottom row: cure rate versus cure time (C) isothermal dwell at 93 °C and (D) isothermal dwell at 121 °C.

Table 3: Parameters for DEA models.

Parameter	Value
C_{11} (log(Ω))	21.38
C_{12} (log(Ω))	−0.035
C_2 (log(Ω)/K)	6.96
Out-time parameters (t = days)	
$w_1 = 1.8 \times 10^{-4}t^3 - 1.6 \times 10^{-2}t^2 + 3.7 \times 10^{-1}t + 1$	
$w_2 = 2.9 \times 10^{-4}t^3 - 2.6 \times 10^{-2}t^2 + 6.0 \times 10^{-1}t + 1$	

In Fig. 4, data from the dynamic ramp correlations are plotted alongside model predictions. As shown in Fig. 4A, the decrease in α is more pronounced than in the isothermal data. The difference is attributed to the prolonged time required to reach cure conditions (∼90 °C). In such cases, an effective alternate metric for the onset of cure can be defined. During the $\log Z''_{max}$ decrease period,

we assume that $\alpha = \alpha_0$, and cure is assumed to start only after an increase in $\log Z''_{max}$ is observed. When this "thermal adjustment" is implemented, results from the dielectric measurement correlations closely match the predictive model results at all out-times, as shown in Fig. 4.
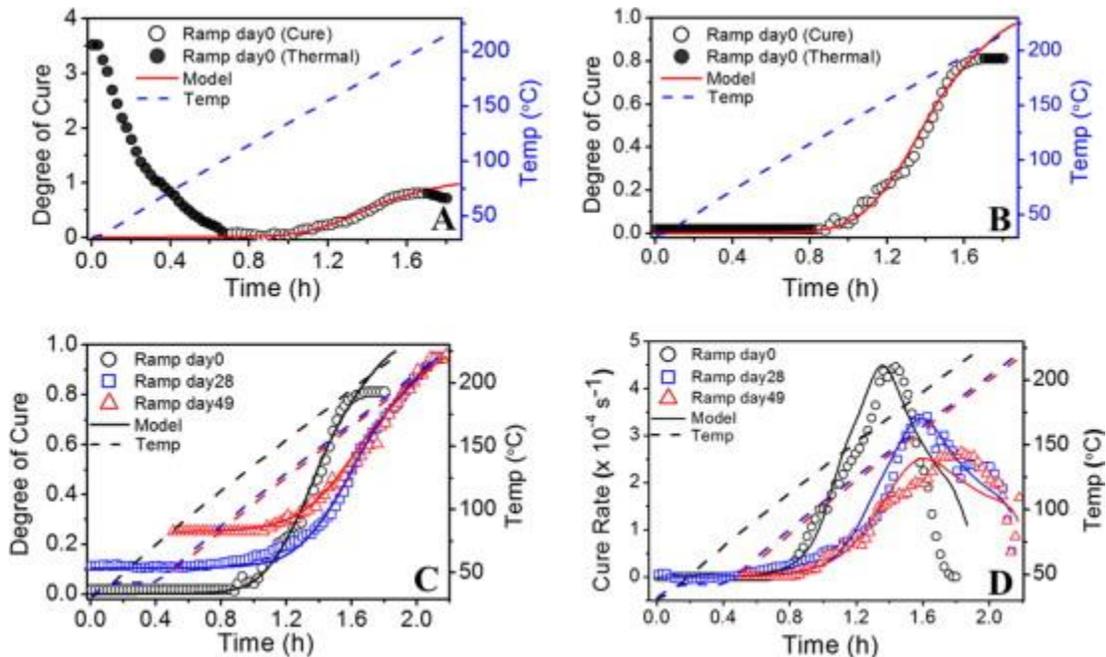

Figure 4: DEA measurement and prediction of dynamic ramp: (A) day 0 sample without thermal adjustment, (B) day 0 sample with thermal adjustment, (C) degree of cure versus cure time at day 0, 28 and 49, and (D) cure rate versus cure time at day 0, 28 and 49.

The α values obtained from the $\log Z''_{max}$ correlation were substituted directly into Eq. (4)to obtain viscosity data. The results are plotted in Fig. 5 along with predictive model data obtained using the cure kinetics model as input. The upper row plots show isothermal dwell measurements, where the viscosity correlation generates values several orders of magnitude greater than those obtained from rheometry. This discrepancy can be attributed to the nature of dielectric measurement, wherein ionic mobility is monitored instead of the actual mechanical response.
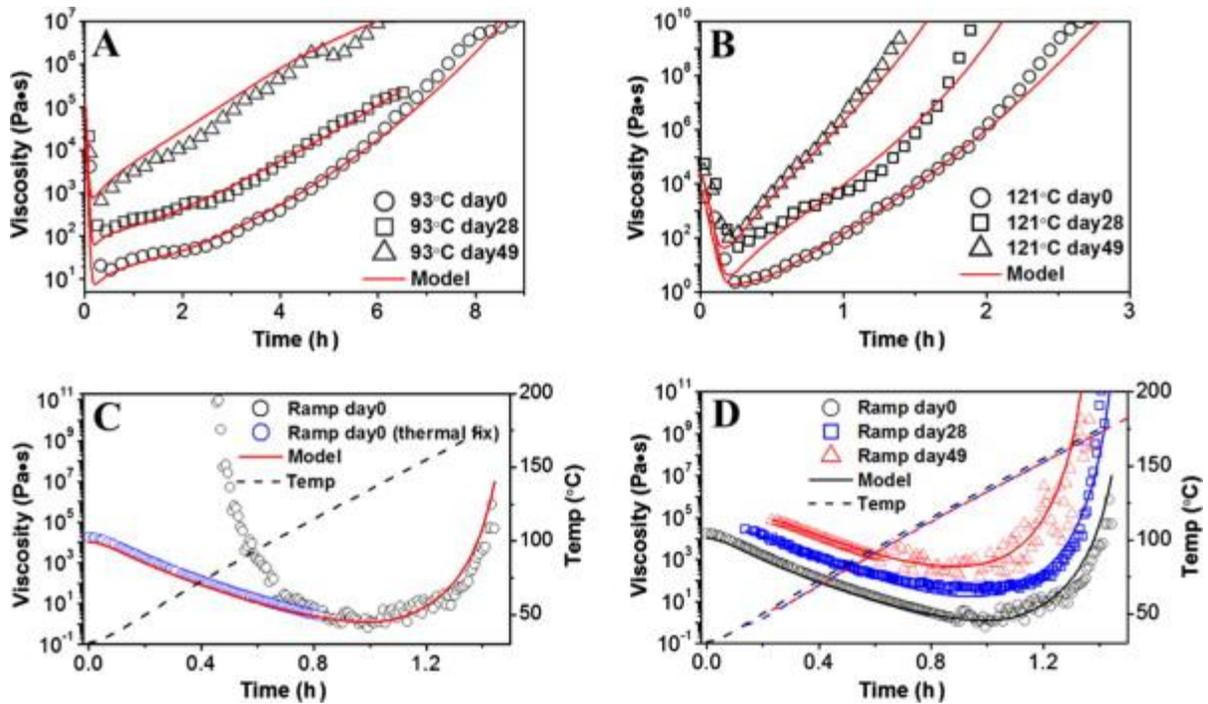
Figure 5: DEA measurement and viscosity correlation. Upper Row – isothermal dwell at day 0, 28 and 49: (a) viscosity versus cure time at 93 °C and (b) viscosity versus cure time at 121 °C. Bottom Row – dynamic ramp: (c) viscosity versus cure time at day 0 with thermal adjustment demonstration and (d) viscosity versus cure time at day 0, 28 and 49.

The importance of the thermal adjustment is specifically highlighted in the bottom row plots of Fig. 5. Without thermal adjustment, prediction from dielectric measurement over-predicts viscosity during periods where thermal effects dominate. The difference is not as significant under isothermal conditions, where the heating ramps (10 °C/min) to dwell temperatures are relatively short. With thermal adjustment, however, the viscosity evolution is accurately predicted from dielectric measurement.

5. Conclusions

In the present work, we investigated feasible, effective methods for quantifying the effects of out-time on an OOA prepreg resin. First, a representative OOA resin was characterized using conventional MDSC and rheometry methods, and predictive models that comprehensively captured

out-time effects on cure kinetics and viscosity in process conditions were developed. Polymerization at ambient temperatures altered the initial degree of cure of the resin as well as the evolution of cure rate and viscosity at elevated temperatures. Subsequently, in situ dielectric monitoring experiments were used to determine the evolution of key dielectric properties during the same temperature and out-time conditions, and effective correlations were developed to obtain degree of cure and viscosity from these properties. Together, these methods constitute complementary methods for predicting and monitoring in situ the "instantaneous" degree of cure, cure rate, and viscosity evolution of composite prepregs. Used together, the methods offer a means to improve process effectiveness and efficiency in composite manufacturing.

Note that the rich dataset obtained from dielectric monitoring offers additional opportunities for detecting and identifying key resin properties and transitions, and for further evaluating the effect of out-time. These issues are discussed elsewhere [19].

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