



Modelling and monitoring of out-time and moisture absorption effects on cure kinetics and viscosity for an out-of-autoclave (OoA) prepreg

Daniel Kim^{a,*}, Timotei Centea^b, and Steven R. Nutt^a

^a Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, CA, 90089-0241, USA

^b Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA, 90089-1453, USA

* E-mail: kim344@usc.edu

Abstract: Out-time and moisture absorption during out-of-autoclave (OoA) prepreg preparation are generally unavoidable. The resulting cross-linking and increase in resin viscosity can prevent sufficient flow into the fiber tows during processing and cause porosity. In this study, efficient modelling and in situ methods to monitor cure kinetics and viscosity were developed to account for the effects of out-time and absorbed moisture. First, a commercial OoA prepreg was conditioned to specific levels of out-time and relative humidity (RH). Property data were obtained from differential scanning calorimetry (DSC) and rheometry and used to develop cure kinetics and viscosity models for a wide range of process conditions, initial out-times, and humidity conditions. The dielectric signals were correlated to the measured data and used to demonstrate real-time monitoring of resin state during cure. The predictive models were then used to understand the influence of out-time and absorbed moisture on resin viscosity during consolidation of OoA prepreg.

Key words: dielectric analysis (DEA), curing, thermomechanical properties, differential scanning calorimetry (DSC), Rheology.



1. INTRODUCTION

Over the past decade, increasing use of composites has created a demand for manufacturing methods with lower costs and improved processing efficiency. As a result, OoA prepreg processing has been introduced and implemented in industrial settings [1]. In the absence of high consolidation pressure, voids are suppressed by evacuating entrapped air and vaporized moisture through a partially impregnated microstructure consisting of both dry and resin-rich regions. Initially, the dry regions form a permeable vascular network of vacuum channels that allow in-plane gas transport. During processing, these channels are infiltrated with the goal of forming a fully saturated, defect-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.

The manufacture of high quality, defect-free parts by OoA processes requires the development of defect mitigation strategies and technologies, including in situ process monitoring [2-5]. The accurate determination of the resin state prior to and during cure is particularly important, as resin properties govern in-process phenomena and have a substantial impact on final part quality and performance for all OoA processes. During pre-cure operations, the resin state can be affected by environmental factors such as out-time and ambient humidity. Extended out-time can advance the degree of cure and viscosity of the resin and potentially prevent full infiltration of the fiber bed during cure [4-6]. Exposure to ambient humidity generally leads to the rapid absorption of moisture. The dissolved water can then evolve during cure, causing the nucleation and growth of voids with internal pressures that exceed that which is imparted to the resin by vacuum bag-only processing [6]. Moreover, moisture absorption has also been shown to affect process-relevant properties, such as degree of cure and viscosity, by acting as both catalyst and solvent for the amine-epoxy reaction

[7,8] and accelerating cross-linking. Water absorption can also disrupt hydrogen bonds among
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segments of the polymers and cause swelling of the polymer, thus increasing the diffusion coefficient of water within the polymer and reducing the glass transition temperature [7]. In addition, water can act as a catalyst, facilitating epoxy-amine and etherification reactions [8]. Therefore, the combination of out-time and moisture absorption can lead to permanent changes in the resin state prior to cure which affect cure kinetics and viscosity evolution during cure.

The specific objectives of this study were to develop:

1. A methodology for tracking the resin degree of cure prior to cure of prepreg subjected to humidity as well as out-time using in situ, real-time dielectric monitoring.
2. Efficient models for cure kinetics and viscosity that capture out-time and moisture absorption effects during consolidation.
3. A novel method for monitoring cure kinetics and viscosity capable of accounting for both out-time and moisture absorption.

Finally, to demonstrate the utility of these methods, predictive models for resin properties were used to understand the influence of out-time on resin viscosity evolution during consolidation, prior to gelation, when resin flow takes place. For OoA prepreg with exposure time exceeding the manufacturer's specified out-life, two viscosity controlled (or flow-enhanced) cure cycles were proposed to limit flow-induced defects using adaptive heating and the model. The non-standard cure cycles were shown to increase 'flow-time' spent at targeted viscosity levels.

2. EXPERIMENTAL PROCEDURE

The detailed protocols associated with sample preparation as well as thermochemical, thermomechanical and dielectric measurement methods have been described elsewhere [4,5], and are briefly described below. In this study, we investigated the additional nature and effects of

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humidity conditioning on the properties of an OoA prepreg resin, and developed efficient cure kinetics and viscosity modelling and monitoring methods.

2.1. Sample conditioning: humidity & out-time control

An OoA prepreg consisting of eight-harness satin (8HS) carbon fiber fabric and a toughened epoxy resin (CYCOM[®] 5320-1, Cytec Industries, USA) was used for analysis [9]. The initial outtime of all material was 0 days, and samples were stored frozen prior to testing. Two types of samples were prepared: prepreg laminates were used for DEA, and neat resin was used for DSC, rheometry, and TGA. All samples were stored in humidity chambers created with saturated salt solutions, where accurate control of equilibrium vapor pressure is possible [10], with RH levels of 30 and 90% for 0e5 weeks and of 60% for 0e7 weeks, and tested weekly.

2.2. Modulated dynamic scanning calorimetry (MDSC)

Dynamic and isothermal measurements were performed on a differential scanning calorimeter (TA Instruments Q2000). For each dynamic measurement, a constant temperature ramp from -60 °C to 280 °C at a rate of 1.7 °C/min was applied. For isothermal measurements, dwells were performed at 93, 107, and 121 °C for an RH level of 60% to build accurate cure kinetics models, and at 121 °C for RH levels of 30 and 90% to quantify effect of moisture absorption on cure. Both dynamic and isothermal dwells were subjected to temperature modulation of ± 0.5 °C/min.

2.3. Rheometry



The same dynamic and isothermal dwell tests were performed on a parallel-plate rheometer (TA Instruments AR2000ex). The termination condition consisted of 90% of the machine-specified maximum torque (200 mN·m).

2.4. Dielectric Analysis (DEA)

Dielectric signals were collected using a (DETA SCOPE™, ADVISE E.E., Greece). Prepreg samples were placed in a test cell consisting of the dielectric sensor, resistive heaters, and a monitoring and control system. Measurements were carried out under the isothermal and ramp conditions described above by applying a sinusoidal voltage of 10 V, scanning twenty-five selected frequencies (f) ranging from 1 Hz to 1 MHz. The measured signals were automatically converted to a useful immitance function—complex permittivity (ϵ^*)—which was subsequently converted to ionic conductivity (σ). Studies [3, 11] have shown that σ exhibits strong correlation to viscosity (η), yet no accurate modelling has yet been published.

3. MODEL FRAMEWORK

In a previous study, we developed models for cure kinetics and viscosity (for this resin system) capable of accounting for the cure cycle temperature profile as well as for prepreg out-time using ‘weight factors’ [4,5]. In this study, we develop efficient cure kinetics and viscosity models to support analysis of flow phenomena before resin gelation during material processing while accounting for absorbed moisture and out-time effects. Specifically, we focus on modelling up to 150 °C to separate the amine-epoxy reaction from the etherification reaction (i.e., post cure) [13]. In



addition, we develop a cure monitoring method using ionic conductivity as a metric to correlate to the resin viscosity and cure kinetics (from the conversion using equation (3)).

3.1. Cure kinetics ($d\alpha/dt$) model development

To model cure kinetics, the total heat of reaction at day 0 (ΔH_0) was first determined from dynamic ramp data for the fresh sample. Assuming that the cure rate ($d\alpha/dt$) is directly proportional to the heat flow (dH/dt) measurement, the cure rate is defined as the measured dH/dt divided by ΔH_0 . 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. Then, a semi-empirical model developed by Kratz et al. [12] accounting for the interplay between kinetics- and diffusion-controlled reactions was adapted and modified to capture out-time and moisture absorption effects:

$$\frac{d\alpha}{dt} = K_1 \alpha^{m_1} (1 - \alpha)^{n_1} + \frac{K_2 \alpha^{m_2} (1 - \alpha)^{n_2}}{1 + \exp^{(D(\alpha - (\alpha_{c0} + \alpha_{CT} T)))}} \quad (1)$$

$$K_i = A_i \exp \left[\frac{-E_{A,i}}{RT} \right]_{i=1,2} \quad (2)$$

where K_i is the Arrhenius temperature dependent term, A_i is the Arrhenius constant, $E_{A,i}$ is the activation energy, m_i and n_i are reaction order-based fitting constants, D 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. The first term from equation (1) describes an Arrhenius type autocatalytic reaction, while the second adds a diffusion factor to account for the shift from kinetics to a diffusion-controlled reaction as α increases. To account for the changes associated with ambient temperature cure and moisture absorption, which induce both time and



magnitude shifts in the cure rate profile, the initial degree of cure (α_0) and the variables A_i , m_i , n_i , D , α_{C0} , and α_{CT} were defined as the general form $f(r, t_o) = g(r)t_o^2 + h(r)t_o + i(r)$, where $g(r)$, $h(r)$ and $i(r)$ are second-order polynomials, r is RH, and t_o is out-time. The model parameters determined are provided in Table 1.

$\alpha_0 = (-5.6r^2 + 9.3r + 0.9) \times 10^{-3} t_o + (4.06r^2 - 2.52r - 0.3) \times 10^{-2}$	
$A_1 (x10^6 s^{-1}) = (-2.1r^2 + 2.1r + 2.7)t_o + (-62.5r^2 + 81.6r - 14.2)$	
$A_2 (x10^4 s^{-1}) = (-5.0r^2 + 4.9r + 3.3)t_o + (-17.9r^2 + 22.2r - 9.8)$	
$m_1 = (2.1 \times 10^{-3})t_o^2 + (-1.6 \times 10^{-2}r^2 + 1.7 \times 10^{-2}r + 9.1 \times 10^{-3})t_o + (-7.6 \times 10^{-2}r^2 + 0.1r + 0.9)$	
$m_2 = (1.1r^2 + 1.7r + 3.0) \times 10^{-3} t_o^2 + (0.53r^2 + 0.81r + 0.25)t_o + (8.6 \times 10^{-2}r^2 + 0.16r + 2.02)$	
$n_1 = (2.2 \times 10^{-3})t_o^2 + (0.2r^2 - 0.22r - 7.5 \times 10^{-2})t_o + (0.54r^2 - 0.65r + 10.6)$	
$n_2 = (2.2 \times 10^{-3})t_o^2 + (4.8r^2 - 5.4 \times 10^{-2}r - 4.2 \times 10^{-2})t_o + (-0.13r^2 + 0.21r + 3.74)$	
$D = (0.17r^2 - 0.18r - 0.03)t_o^2 + (1.64r^2 - 1.82r + 2.84)t_o + (-5.0r^2 + 1.05r + 43.1)$	
$\alpha_{C0} = (-1.1 \times 10^{-3})t_o^2 + (3.33 \times 10^{-2}r^2 - 4.7 \times 10^{-2}r + 3.66 \times 10^{-2})t_o + (-4.61 \times 10^{-2}r^2 + 0.11r - 1.42)$	
$\alpha_{CT} (x10^{-3} K^{-1}) = (2.87 \times 10^{-3})t_o^2 + (-2.17 \times 10^{-2}r^2 - 4.22 \times 10^{-2}r + 7.18 \times 10^{-2})t_o + (-0.16r^2 + 0.05r + 5.20)$	
$E_{A1}/R (K) = 9.01 \times 10^3$	$E_{A2}/R (K) = 7.54 \times 10^3$

Table 1: Parameters for cure kinetics models (where r = RH in fraction and t_o = out-time in days)



3.2. Viscosity (η) model development

The viscosity of curing epoxy resin is affected by two competing effects. Heating the resin increases molecular mobility, thereby decreasing viscosity, but also eventually increases molecular size, increasing viscosity. To capture these phenomena, a phenomenological model developed by Khoun et al. [14] was adapted and modified to capture out-time and moisture absorption effects:

$$\eta = \eta_1 + \eta_2 \left(\frac{\alpha_1}{\alpha_1 - \alpha} \right)^{A+B\alpha^d+C\alpha^e} \quad (3)$$

$$\eta_i = A_{\eta_i} \exp \left(\frac{E_{\eta_i}}{RT} \right)_{i=1,2} \quad (4)$$

where η_i is the Arrhenius dependent viscosity component, A_{η_i} is the Arrhenius constant, E_{η_i} is the viscosity activation energy, α_1 is the degree of cure at gelation, and A , B , C , d and e are fitting constants. The first term from equation (3) takes an Arrhenius type form, and the second term is added to account for the rapid viscosity increase near gelation point. Here, the variables A_{η_i} , E_{η_i} , α_1 , B , and d were defined as $f(r, t_o) = g(r)t_o^2 + h(r)t_o + i(r)$ to account for changes associated with ambient temperature cure as well as moisture absorption. In addition, the current model focuses on viscosity before gelation, at which point deviations from Newtonian behavior are expected (gelation can be taken as $\eta \sim 10$ kPa·s [4, 13] or σ inflection point [4, 5]) and flow drastically reduces. The model parameters are provided in Table 2.

$A_{\eta 1} (\times 10^{-3} \text{Pa} \cdot \text{s}) = (5.11r^2 - 4.12r + 2.23)t_o + (20.04r^2 - 25.17r + 8.46)$
$A_{\eta 2} (\times 10^{-14} \text{Pa} \cdot \text{s}) = (7.67 \times 10^{-4})t_o^2 - (3.84 \times 10^{-2})t_o + (-4.78 \times 10^{-2}r^2 - 2.73 \times 10^{-2}r + 0.5)$



$E_{\eta 1}/R \text{ (x10}^3\text{K)} = (9.4r^2-9.8r+4.1)\text{x10}^{-3}t_o^2+(-0.21r^2+0.2r-0.14)t_o+(-2.65r^2+3.12r+1.97)$		
$E_{\eta 2}/R \text{ (x10}^4\text{K)} = (1.2r^2-1.4r+0.2)\text{x10}^{-3}t_o^2+(-2.61r^2+2.85r-0.23)\text{x10}^{-2}t_o+(8.3\text{x10}^{-3}r^2+8.5\text{x10}^{-3}r+1.26)$		
$\alpha_1 = (5.0\text{x10}^{-3})t_o^2-(3.5\text{x10}^{-2}r-1.67\text{x10}^{-2})t_o+(-8.93\text{x10}^{-2}r+0.71)$		
$B = (4.57\text{x10}^{-2}r-8.9\text{x10}^{-3})t_o^2+(-0.36r+0.29)t_o+(-1.38r+11.66)$		
$d = (3.0\text{x10}^{-3})t_o^2+(2.7r-6.7)\text{x10}^{-3}t_o+(-3\text{x10}^{-3}r+0.11)$		
$A = 12.37$	$C = -0.43$	$e = -1.9\text{x10}^{-3}$
$L_1 \text{ (x10}^{-4}\text{S/m)} = (-8.0r^2+16.0r-6.0)\text{x10}^{-4}t_o^2+(4.11r^2-6.3r+2.19)\text{x10}^{-2}t_o+6.22\text{x10}^{-2}$		
$L_2 = (5.0r^2-5.5r+1.1)\text{x10}^{-3}t_o^2+(-0.15r^2+0.15r-2.97\text{x10}^{-2})t_o-0.79$		
$L_3 = (-7.3r^2+8.2r-1.4)\text{x10}^{-3}t_o^2+(2.24r^2-2.22r+0.37)\text{x10}^{-1}t_o+0.68$		
$L_4 \text{ (x10}^6\text{S/m)} = (-0.6r^2+1.2r+1.9)\text{x10}^{-3}t_o^2+(0.5r^2-2.35r+12.24)\text{x10}^{-2}t_o+1.83$		
$L_5 \text{ (x10}^3\text{K)} = (-1.67r^2+1.2r+0.13)\text{x10}^{-2}t_o^2+(0.85r^2-0.65r+0.14)t_o+1.71$		

Table 2: Parameters for viscosity & conductivity models (where $r = RH$ in fraction and $t_o =$ out-time in days)

3.3. Ionic conductivity (σ) model development

There are multiple ways to monitor cure using DEA. In previous work [4, 5], we proposed using imaginary impedance maxima, which measures ionic mobility and concentration of charges, to monitor cure kinetics and viscosity evolution during cure. Another approach consists of using dipolar



contribution to dielectric loss to track the evolution of the bulk relaxation time of the resin during cure. Both of these methods, however, require significant analytical efforts. The evolution of ionic conductivity (σ) during cure, however, provides rich information, including change in viscosity (η), minimum η (η_{min}) or maximum flow point, gelation time (t_{gel}), and reaction end point (Figure 5) without extensive analysis [2]. In particular, σ correlates closely with η , where increases in σ reflect increased ionic mobility and thus decreased viscosity, and vice versa. Thus, accurate modelling of σ up to the gelation point, where resin flow abruptly decreases, is useful. We selected a mathematical form for σ based on the inverse relationship to η to describe the evolution during cure:

$$\sigma_{mix} = L_1 \eta^{(L_2 + L_3 \alpha)} + L_4 \exp\left(\frac{L_5}{T}\right) \quad (5)$$

where L_i , $i = 1$ to 5 are fitting variables defined as functions of out-time and RH (Table 2), and σ_{mix} represents the viscosity of a resin and water mixture. The model was developed specifically to monitor viscosity evolution until gelation. Note that σ can be used as a separate metric to model and monitor cure (section 4.4), but for the purpose of demonstrating the correlation to viscosity, equation (5) was developed. Also, σ can be converted to α by taking a reverse route from equation (5) to equation (3), thereby providing complete cure monitoring capability.

4. RESULTS AND DISCUSSION



4.1. Out-time characterization

Previous studies have shown that the primary volatile in OoA prepreg resins is absorbed water, and that voids grow via diffusion of water from the surrounding resin [6]. To verify this, thermogravimetric analysis (TGA) was used to monitor mass stability during heating, and results were compared to resin moisture contents measured by Coulometric Fischer titration, during which prepreg samples were heated, and released moisture was quantified using titration. Within the margin of error (<5%), the weight percent values of water contents measured by titration were equal to the values for total sample weight loss determined by TGA. Fig. 1(a) shows that the amount of water absorbed increased with RH. At equilibrium, roughly 0.9 wt% water was absorbed for a RH of 90%, while only 0.3 wt% was absorbed for a RH of 30%. Thus, at a molecular level, we expect that samples conditioned at higher humidity levels will exhibit greater changes associated with the catalytic/solvent effect.

The effects of absorbed moisture on the total heat of reaction (ΔH) and the B-stage glass transition temperature ($T_{g,0}$) during out-time were measured from MDSC data and are displayed in Fig. 1 (b) and (c). The results show that DH, which represents the exothermic heat release during resin cure, decreases with out-time in a predictable manner. Resin conditioned at higher RH exhibited a sharper decrease in DH, as absorbed water facilitated cross-linking at the ambient temperature. This consistency allows prediction of the initial degree of cure (α_0), defined as a function of ΔH_0 (the total heat of reaction at day 0) and ΔH (the total heat released at various out-times and RH levels conditioned, Table 1), resulting in a difference in α_0 of up to 6% from RH of 30%-90%.

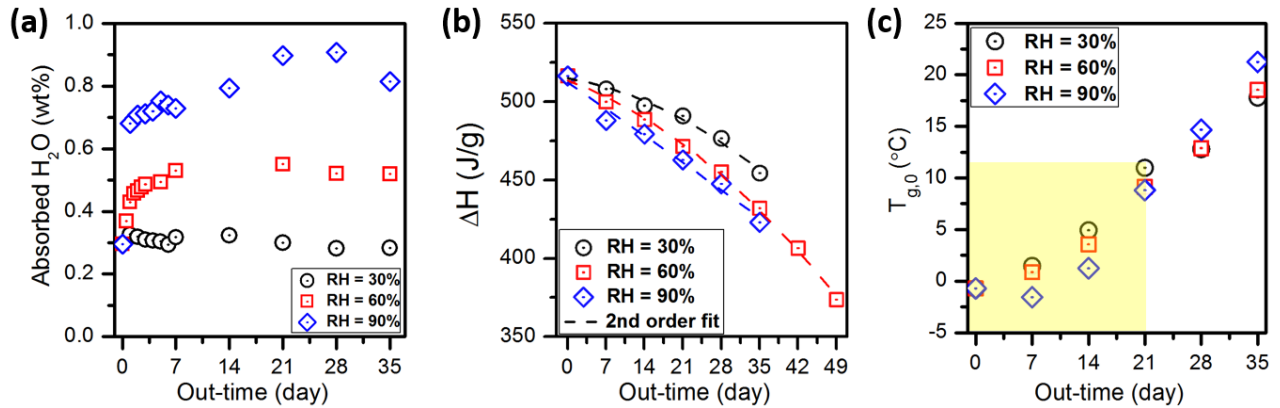


Figure 1: (a) Weight percent of absorbed water (H₂O) versus out-time at different humidity conditions (b) Total heat of reaction (ΔH) and (c) B-stage glass transition temperature ($T_{g,0}$) and on out-time

The initial glass transition temperature $T_{g,0}$ exhibits RH-dependent changes with out-time. Resin aged at 90% RH exhibited a decrease in $T_{g,0}$ at day 7 and had lower $T_{g,0}$ than the resin samples aged at 30% and 60% RH until day 21 (highlighted portion in Fig. 1(c)), despite the progression towards a higher a . This difference is attributed to the solvent effect dominating over the catalytic effect of water. Thus, tracking evolution of $T_{g,0}$ may not be a reliable way to track a_0 for resin exposed to variable environmental conditions. Overall, the combination of out-time and moisture absorption led to permanent changes in the resin state prior to cure (i.e. increasing a_0), which is expected to affect the course of cure kinetics and viscosity evolution during cure.

Fig. 2 (a) shows dielectric analysis (DEA) data expressed as logarithmic ionic conductivity ($\log(\sigma_{mix})$) as a function of out-time at 30 °C. The subscript “mix” is used to denote the mixture of water and resin. As DEA measures the direct physical state of the prepreg, we assumed that the measured conductivity can be expressed as:

$$\sigma_{mix} = w_r \sigma_r + w_w \sigma_w \quad (6)$$

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where w_r and w_w are weight fraction of resin and water respectively, and σ_r and σ_w are ionic conductivities of resin and water respectively ($\sigma_w = 2 \times 10^{-5}$ S/m at 30 °C). The reasoning for describing conductivity as a weighted sum of resin and water was that (1) a weighted sum is a simple, direct method for describing the properties of a composite, and (2) the low moisture absorption level suggests that the nature of the resin has not been changed. With this assumption and the known weight fraction of water in each sample (from TGA), σ_{mix} and σ_r were plotted against α_0 (Figure 2(b)). Although σ_w is four to five orders of magnitude greater than σ_r at 30 °C, its effect on the measured σ is limited by the low levels of absorbed moisture in the resin. Therefore, the measurement of $(\log(\sigma_{mix}))$ remains an effective method of monitoring α_0 (Figure 2(c)), despite the substantial effect of water on α_0 during out-time. This result indicates that accurate monitoring of out-time, even in challenging environments, is possible due to the low moisture absorption of this OoA prepreg. However, this finding also implies that the conductivity measured using dielectric analysis cannot be used to easily determine the moisture content at a given out-time. For the case presented here, the relation between $(\log(\sigma_{mix}))$ and α_0 is:

$$\log(\sigma_{mix}) = A\alpha_0 + B \quad (7)$$

where A is -11.31 S/m and B is -8.79 S/m.

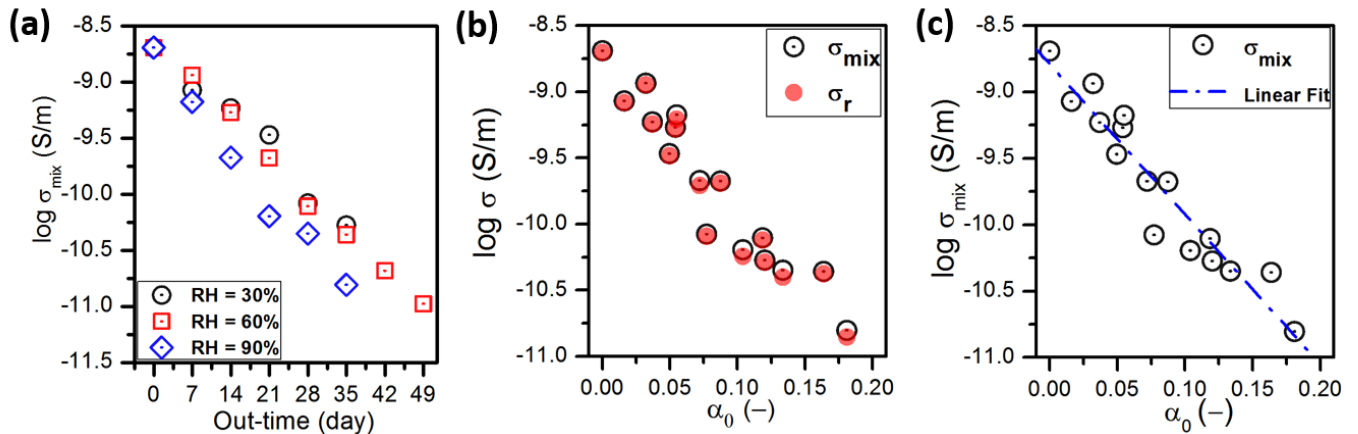


Figure 2: (a) σ_{mix} versus out-time; (b) σ_{mix} and resin conductivity (σ_r) versus initial degree of cure (α_0); and (c) σ_{mix} versus α_0

4.2. Cure kinetics modelling

Fig. 3 shows representative cure kinetics measurements and corresponding results of the predictive model obtained using equation (2). The cure kinetics model was first developed using isothermal dwell data at 93, 107 and 121 °C and dynamic ramp data with resin samples conditioned at RH = 60% from 0 to 49 days. Subsequently, isothermal dwells at 121 °C and dynamic ramps were conducted on resins conditioned at RH = 30 and 90% from 0 to 35 days to determine the effect of moisture absorption during cure and determine parameters in the cure kinetics equation. Confining the parameters to predictable patterns as functions of out-time and RH (sec 3.1), the present cure kinetics model captured out-time and humidity effects accurately over the entire range of conditions studied.

Out-time induced cross-linking causes α_0 to increase, and absorbed moisture can further catalyse this reaction. Fig. 3 shows that although the resin conditioned at higher RH attained higher



α_0 , the reaction end time was not affected as much. The result can be understood by considering the reaction chemistry: the primary amine-to-epoxy reaction occurs more rapidly than the secondary amine-to-epoxy reaction [14], as the former must occur first in order for the latter reaction to take place, in addition to it having higher steric hindrance. Thus, out-time and moisture absorption mainly affect the primary amine-to-epoxy reaction, producing only small differences in reaction end time.

Conversely, from the standpoint of flow, a higher α_0 and a shorter gel time [5], which occurs prior to reaction end time, implies less time available for flow and full resin impregnation during OoA processing. Therefore, the current work focuses on developing an accurate model for $\alpha = f(\alpha_0, RH, t_o, t, T)$, as it will be used as an input to the η model. However, accurate a modelling also allows accurate prediction of cure rate (da/dt).

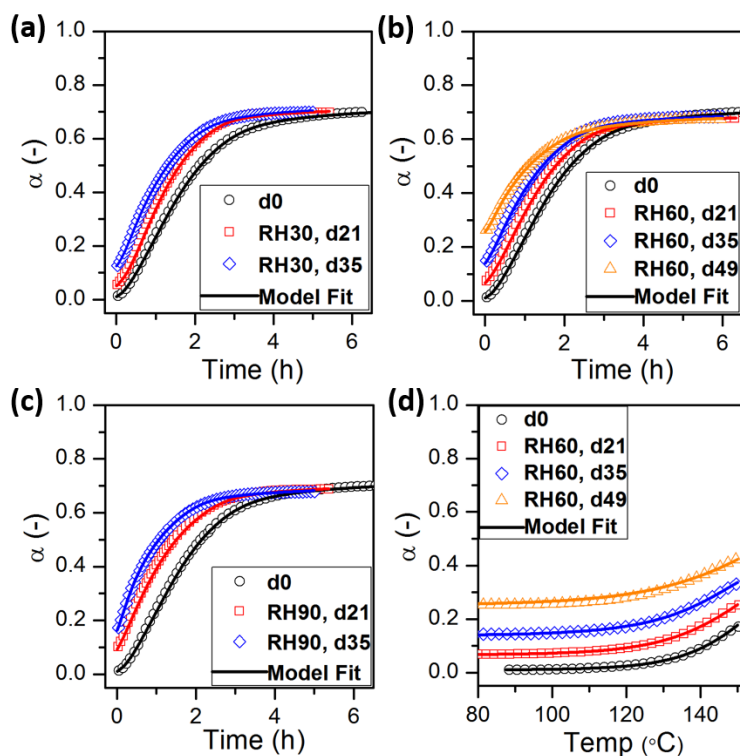




Fig. 3. Cure kinetics measurement. a versus cure time under isothermal dwell at 121 °C for resins conditioned at: (a) RH = 30% for day 0, 21 and 35, (b) RH = 60% for day 0, 21, 35 and 49, and (c) RH = 90% for day 0, 21 and 35. (d) a versus cure temperature under dynamic ramp for resins conditioned at RH = 60% for day 0, 21, 35 and 49.

4.3. Viscosity modelling

Fig. 4 shows representative viscosity measurements and corresponding results of the predictive model obtained using equation (3). As with the development of the cure kinetics model, resin samples conditioned at RH = 60% were used to develop a benchmark viscosity model, and resin samples conditioned at RH = 30 and 90% were modeled to capture the effects of moisture absorption during cure and on viscosity equation parameters. Fig. 4 shows that the viscosity model captured out-time and humidity effects accurately over the entire range of conditions studied.

Generally, viscosity evolution for a cure cycle is governed by the competing effects of cure (which increases viscosity) and heating (which decreases viscosity). Initially, as the temperature increases and the resin degree of cure is low, the thermal effect is predominant, and the viscosity decreases. As the degree of cure begins to accelerate and the temperature approaches the isothermal dwell, the process becomes cure-driven, and the viscosity increases at an increasing rate until gelation occurs. Such an effect is apparent in Fig. 4. In addition, the viscosity increases with ambient exposure, moisture absorption, and cure. The result is especially important as viscosity directly affects resin flow, and the deviation from Newtonian behaviour is expected near the gel point ($\eta \sim 10 \text{ kPa}\cdot\text{s}$ [4,13]), or the flow stop point. In other words, the viscosity levels and resin



flow times required to completely wet fiber tows during processing are progressively limited by ambient temperature, moisture absorption, and cure.

Therefore, the increase in viscosity due to ambient exposure and moisture absorption is most likely the primary factor that determines the manufacturer's stated out-life. In Section 5, the models developed for $\eta = f(\alpha, RH, t, T)$ will be used to propose viscosity controlled (or flow enhanced) cure cycles that can in principle extend the manufacturer's stated out-life.

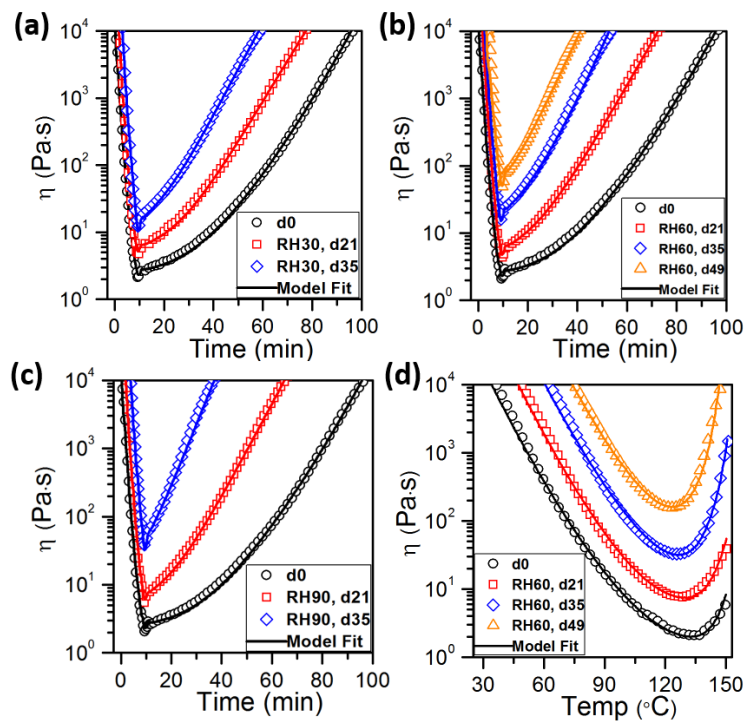


Fig. 4. Viscosity (η) measurement. η versus cure time under isothermal dwell at 121 °C for resins conditioned at: (a) RH = 30% for day 0, 21 and 35, (b) RH = 60% for day 0, 21, 35 and 49, and (c) RH = 90% for day 0, 21 and 35. (d) η versus cure temperature under dynamic ramp for resins conditioned at RH = 60% for day 0, 21, 35 and 49.



4.4. Conductivity modelling - viscosity monitoring

Fig. 5 (b) shows representative conductivity measurements and corresponding results of the predictive model obtained using equation (5). Resins were conditioned at RH = 60% and used to develop a benchmark conductivity model, and resins conditioned at RH = 30 and 90% were modeled to elucidate the effect of moisture absorption during cure and the viscosity equation parameters. The model was developed using data up to the gelation point (rheologically, $\eta \sim 10$ kPa·s), which is defined as the inflection point in the plot of $\log(\sigma)$ versus cure time. This point corresponds to the maximum rate of σ change, which corresponds to the maximum decrease in ionic mobility during cure [4]. The resulting model captured out-time and humidity effects accurately over the entire range of conditions studied.

Fig. 5(a) depicts the maximum flow point or maximum conductivity (σ_{max}), gelation time (t_{gel}), and reaction end point detection by monitoring conductivity evolution during cure. In Fig. 5(c), closed and open symbols correspond to traditional rheological and DEA measurements, respectively. The t_{gel} comparison shows close correlation between the two methods with a high degree of accuracy for a quadratic relation of the form: $t_{gel} = f(t_o, RH, T)$. Overall, the results demonstrate that DEA is an effective and robust method for assessing material out-time prior to cure and for monitoring the evolution of key resin properties at elevated temperatures. Furthermore, the model and methods presented here eliminate post-processing of measured dielectric data [4,5] and allow direct and efficient correlation of the measured conductivity to viscosity accounting for out-time and moisture absorption.

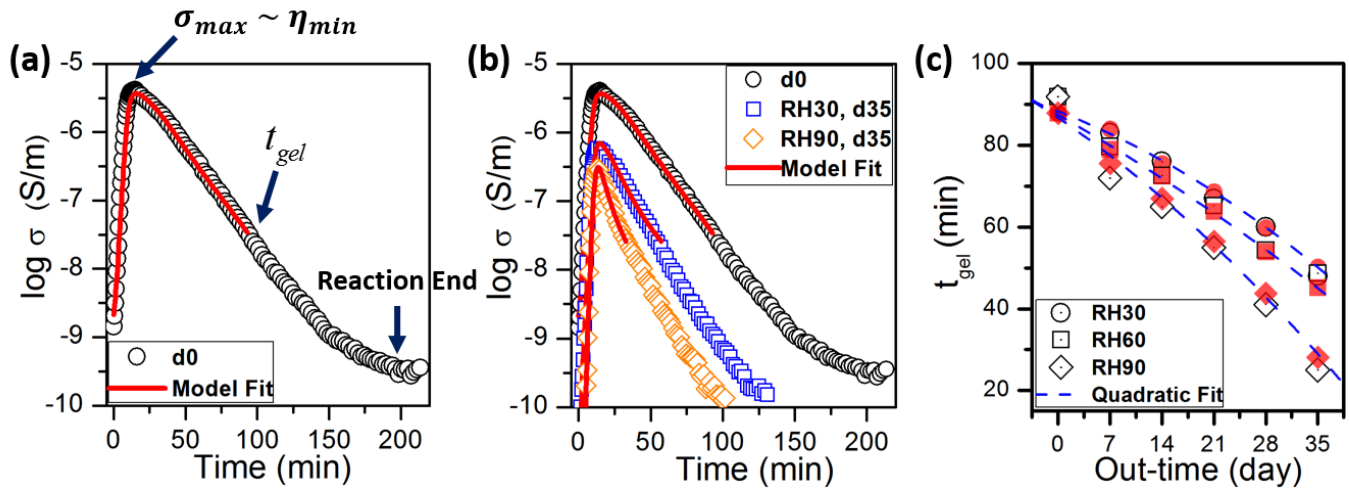


Figure 5: (a) critical signal detection demonstration using σ evolution (b) σ versus cure and (c) t_{gel} versus out-time (closed symbol: rheometry and open symbol: DEA)

4.5. Viscosity controlled cure cycle development

The predictive models developed here show that the influence of out-time and absorbed moisture on the resin viscosity can be significant. Studies have shown that these undesired factors can lead to incomplete impregnation of the fiber bed [15]. To avoid these issues, manufacturers specify an out-time limit (or an out-life) on material exposure. With the accurate model for viscosity or conductivity developed in this study, it is possible to develop a viscosity-controlled (or flow-enhanced) cure cycle that can potentially extend out-life and limit flow-induced defects while minimizing cycle time.

The key assumption of this methodology is that as heat and time induce cure, a fast ramp to a target viscosity is desirable, thus minimizing cure during the heat-up ramp [13]. Once the target viscosity level is attained, there is a competition between the cure effect, which increases viscosity,



and the thermal effect, which decreases viscosity, so a temperature profile that maximizes the thermal effect can be specified. Fig. 6 demonstrates two methods for maximizing the thermal effect (and flow) for resin conditioned at RH = 60%. The viscosity evolution at day 28 (~out-life) was used as a benchmark that allows manufacturing of quality parts (void content < 2% [15]), with one of the manufacturer's recommended cure cycles [10] (2.8 °C/min to 121 °C with a 3 h dwell). From this data, one can determine a viscosity level and flow duration (defined here as time spent at or below the target viscosity level) required for successful production.

The first flow-enhanced method (Path 1 in Fig. 6) targets a viscosity level of 500 Pa·s, which is below the gelation point ($\eta = 10$ kPa·s or s inflection point) and thus maximizes the flow duration at this level. A demonstration of this approach using resin conditioned at RH ¼ 60% at out-time of 49 days, is shown. The method features a fast ramp (~10 —————C/min) to 500 Pa·s, followed by a slow ramp (~0.9 °C/min) to maximize flow duration at viscosity level of 500 Pa·s or below. The method is developed by calculating the flow time as a function of cure cycle using equation (3) and employing a simple gradient-based solver to minimize the difference between the calculated flow time and a specified target (e.g., flow duration at viscosity level of 500 Pa·s or below for ~47 min under the manufacturer's recommended cure cycle at the out-life). The results show that for an arbitrary target viscosity and dwell time (strictly optimizing dwell time for viscosity at or below the target level), the viscosity evolution of material with excessive out-time (49 days) can be rendered comparable to that of the stated out-life.

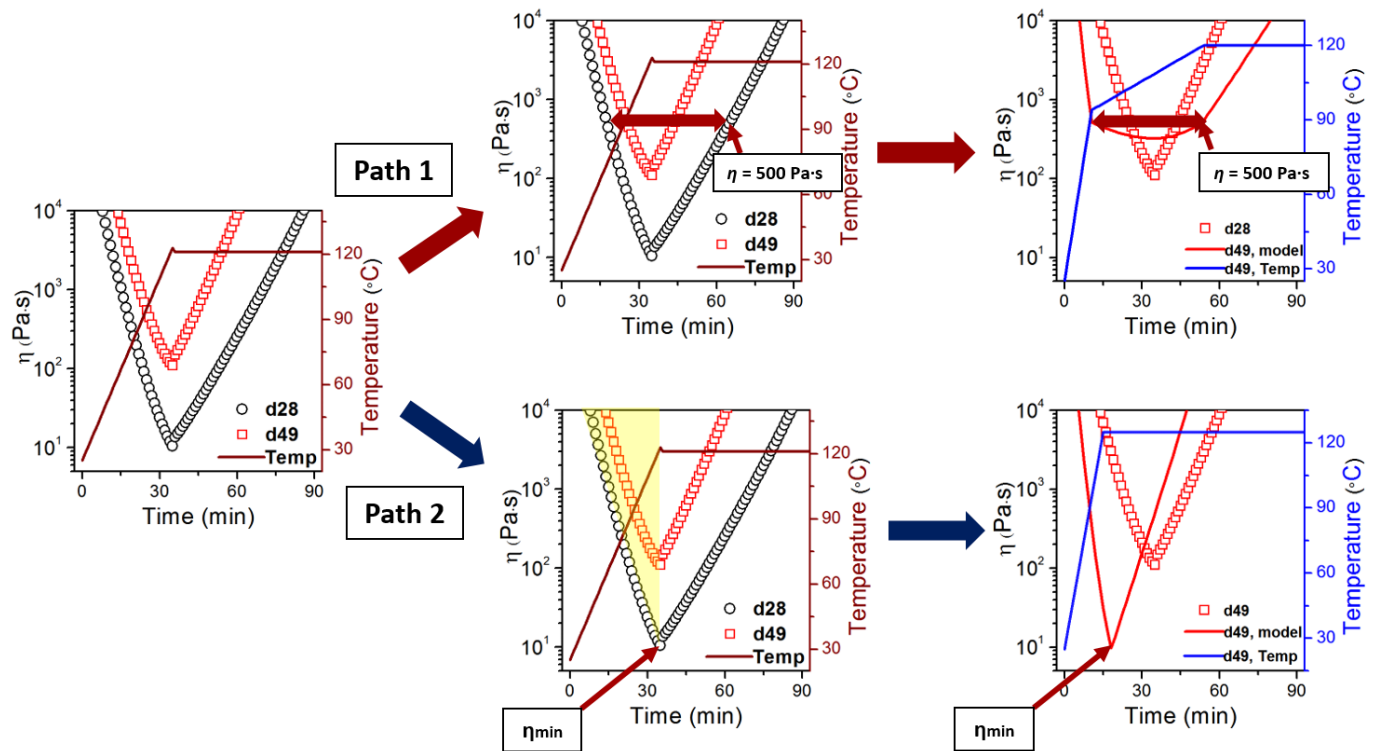


Figure 6: Schematic of flow enhanced cure cycle development method: Path 1. Target η (ex. 500 Pa·s); and Path 2. Target minimum viscosity (η_{\min})

The second flow-enhanced method (Path 2 in Fig. 6) seeks to achieve a target minimum viscosity level using a fast ramp ($\sim 10 \text{ }^{\circ}\text{C}/\text{min}$ in this example) and subsequent isothermal dwell (at $121 \text{ }^{\circ}\text{C}$). This method was developed in an attempt to maximize the period of Newtonian flow.

The effective out-life of prepreg materials is reported to be determined by flow-induced porosity caused by elevated viscosity [6,15]. The case studies discussed above, while simple, indicate that non-traditional cure cycles can counteract the effects of out-time and thereby extend the effective out-life of aged material by leveraging the thermal effect and lowering the viscosity profile during cure.

The ramp rates required for these cure cycles are not typically achievable during autoclave or

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oven cure. However, OoA materials can be processed in a variety of curing environments, including heating blankets and heated tools, which can significantly expand the thermal envelope available for processing. Finally, note that the optimization process highlighted above does not yet account for cure cycle time. However, models such as those developed in this work can be used within multi-objective optimization algorithms that identify optimal solution fronts. Future efforts will combine modeling with experiments within a parametric study targeting the two methods, to better understand OoA prepreg consolidation phenomena and develop flow-enhanced cure cycles.

5. CONCLUSIONS

We have developed accurate process models that comprehensively capture out-time and humidity effects on cure kinetics and viscosity in process conditions, and further developed a method for accurate process monitoring using DEA. First, conventional ex-situ methods (MDSC and rheometry) were used to collect benchmark data. Subsequently, in-situ dielectric analysis was conducted to gain a more detailed understanding of the physical phenomena involved, and to verify which phenomena can be detected in real-time. The results indicate that out-time and moisture absorption primarily affect the initial degree of cure and consequently influence the course of cure kinetics and viscosity evolution during cure. Tangibly, these changes decrease flow time, gelation time, and reaction end time, and potentially complicate manufacturing. The production of high-quality parts using OoA prepreg therefore requires out-time and humidity control and/or appropriate thermal control to ensure adequate flow time and to fully impregnate the prepreg during processing. In addition, we demonstrated that DEA allows accurate monitoring of initial degree of cure, gel-time, and reaction-end time for the entire range of relative humidity studied in this paper, confirming the robustness of the previously proposed methodology. The study resulted in practical insights, including (1) T_g



measurements using DSC can be problematic for out-time monitoring, since they can be affected by moisture absorption; (2) DEA is insensitive to moisture absorption, rendering it effective for out-time measurements but unsuitable for determining moisture contents; and (3) ΔH is a reliable/robust metric for both out-time and moisture.

Viscosity measurements showed that out-time mainly increases resin viscosity and limits resin flow during cure. Using the predictive model, we proposed non-standard cure cycles that can potentially limit flow-induced defects by optimizing the viscosity profiles of aged samples, effectively extending out-life. Validation studies on such flow-enhanced cure cycles are in progress. Furthermore, while the models presented here were calibrated for a specific resin system, the proposed equations and methods are applicable to many other typical aerospace-grade epoxy resins with similar chemical formulations.

Overall, this work provides foundational knowledge for understanding and optimizing consolidation phenomena as well as methods that can be used to predict material properties or monitor them within advanced curing environments. Combined, they allow the fabrication of low-defect parts under non-ideal material and process conditions.

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