



In Situ Cure Monitoring of an Out-of-Autoclave Prepreg: Effects of out-time on viscosity, gelation and vitrification

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Abstract: The cutting, lay-up and bagging of out-of-autoclave (OOA) prepregs for composite part fabrication can take from several days to weeks, depending on the desired part size. This period of ambient temperature “out-time” induces resin polymerization/cross-linking, and affects critical physicochemical phenomena such as minimum viscosity, gelation, and vitrification. Therefore, the capability to monitor out-time at ambient conditions and to understand its influence on key resin properties is valuable to minimize waste and increase efficiency. In this study, the dielectric properties of out-of-autoclave (OOA) carbon/epoxy prepreg aged from 0 to 7 weeks are investigated. The measured dielectric data is used to develop an in-situ out-time monitoring method at ambient condition. Furthermore, the effects of out-time and out-life on critical physicochemical parameters are identified.

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

1. Introduction

Recent studies have shown out-of-autoclave (OOA) prepreg processing via vacuum-bag-only (VBO) consolidation to be a viable and potentially cost-effective alternative to autoclave cure [1], [2] and [3]. OOA prepregs are cured under a much lower maximum compaction pressure “In Situ Cure Monitoring of an Out-of-Autoclave Prepreg: Effects of Out-Time on Viscosity, Gelation, and Vitrification” D. Kim, T. Centea, and S.R. Nutt, *Compos. Sci. & Tech.* 102 132-138 (2014)
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of 101,325 Pa (1 atm), and voids are suppressed by evacuating entrapped air and volatiles through a microstructure that is initially only partially impregnated (by design), and that is infiltrated by surrounding resin during cure [1]. The physicochemical properties of the resin thus govern the rate at which this microstructure evolves, and must be understood and appropriately controlled to ensure successful part manufacture. Therefore, the adverse effects that derive from prolonged out-time, or room temperature exposure time before cure are arguably even more critical in OOA processes than in autoclave processing.

1.1. Background

Out-time causes polymerization/cross-linking of the resin at ambient temperature, adversely affecting tack and drape and potentially leading to unacceptable porosity levels in cured parts due to inhibited flow [3], [4], [5] and [6]. For OOA prepregs, out-time was shown to cause pervasive porosity once the out-life was exceeded [4]. Therefore, accurate methods to monitor out-time and to predict the effects of out-time on the key resin properties are necessary. Investigators have measured out-time of prepregs using differential scanning calorimetry (DSC) [3] and analyzed the resin's physicochemical parameters (minimum viscosity, gelation, and vitrification) using DSC [7], rheometry [8] and [9] and dynamic mechanical analysis (DMA) [10]. Among these, DSC and rheometry techniques have been particularly useful. However, DSC measurements are mass-specific, and the exact amount of resin within a prepreg sample is difficult to quantify. Similarly, rheometry requires neat resin film for viscosity data. In addition, both tests are conducted ex-situ, on small samples, in idealized conditions.

Dielectric analysis is both non-invasive and highly sensitive to degree of polymerization, and is thus appealing [9], [11], [12] and [13]. Recent studies have shown that dielectric analysis can be used to identify physicochemical transformations in prepregs during cure, highlighting the possibility of "In Situ Cure Monitoring of an Out-of-Autoclave Prepreg: Effects of Out-Time on Viscosity, Gelation, and Vitrification" D. Kim, T. Centea, and S.R. Nutt, *Compos. Sci. & Tech.* 102 132-138 (2014)
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distinguishing both micro- and macroscopic information using appropriate signal processing. The minimum viscosity and gelation state of the resin were identified as a maximum and an inflection in ionic conductivity, respectively, during isothermal cure. Furthermore, vitrification can be detected by tracking α -relaxation time from the dipolar contribution of the dielectric loss at a frequency of 0.1 Hz. These correlations can be used to understand specific changes in the physicochemical parameters and process-critical moments associated with out-time. However, such systematic studies have not yet been reported.

In a recent study, we investigated the effects of out-time on the rate of cure and viscosity evolution of an OOA prepreg and developed accurate predictive models from DSC and rheometer data [14]. Furthermore, we proposed accurate correlations between dielectric behavior and resin cure kinetics and viscosity, thus demonstrating the potential for an in-situ process diagnostic to dynamically monitor cure. In the present study, we analyze a large thermochemical, thermomechanical and dielectric dataset to specifically determine the effects of out-time on several resin properties of interest to composites processing. The two key objectives of the study are: (1) to establish correlations between dielectric properties and the key processing transitions of minimum viscosity, gelation and vitrification; and (2) to investigate the effects of out-time and out-life on these moments.

2. Experimental procedure

This experimental procedure was previously described in [14], but the current study considers a second, previously undiscussed set of data.



2.1 Materials

We selected an OOA prepreg consisting of eight-harness satin (8HS) carbon fiber fabric and a toughened epoxy resin (CYCOM® 5320-1, Cytec Engineered Materials Inc.). The resin content of the 5320-1/8HS is 36% by weight, and the fabric areal weight is 375 g/m². Prepreg was used for dielectric analysis, while neat resin film was used for modulated DSC (MDSC) and rheometry. The specified out-life at ambient temperature was 30 days [16], and samples were stored below -12 °C before use. The samples were then conditioned at 21 ± 2 °C and 51 ± 5% relative humidity for 7 weeks.

2.2. Modulated Dynamic Scanning Calorimetry (MDSC)

MDSC was conducted under a nitrogen purge (TA Instruments Q2000). Applying sinusoidal temperature modulation on top of the linear temperature ramp allows signal separation of the total heat flow into reversing and non-reversing components. The reversing component of heat flow depends on heat capacity and heating rate, while the non-reversing kinetic component directly indicates the cure exotherm [3] and [7]. For each dynamic measurement, a constant temperature ramp from -60 °C to 280 °C at a rate of 1.7 °C/min with a temperature modulation of ±0.5 °C/min was applied. For isothermal measurements, dwells were performed at 93 °C, 107 °C and 121 °C, and a temperature modulation of ±0.5 °C/min was applied over the dwell period.

2.3 Rheometry

Rheological measurements were performed (TA Instruments AR2000) using 25 mm aluminum parallel plates at a gap setting of 0.5 mm. All tests were conducted under constant oscillatory shear



at frequency of 1 Hz and at strain of 0.25%, within the Newtonian plateau regime. Isothermal dwells were performed by heating at 10 °C/min to 93 °C, 107 °C and 121 °C and holding until 90% of the machine-specified maximum torque (200 mN·m) was required for shear displacement.

2.4 Dielectric analysis

Dielectric measurements were conducted with a dielectric monitoring system (DETA SCOPE™, ADVISE E.E., Greece). Coplanar electrodes were used as the sensor, which generated fringing electric field lines (~100 μm) penetrating into the dielectric material (the epoxy resin in the prepreg), thus enabling non-invasive measurements. To insulate the sensor from the conductive carbon fiber bed, thin (10 μm) glass fiber layers were first placed over the sensor. Laminated prepreg samples 3 mm thick were placed within a thin picture-frame spacer containing a thermocouple. Finally, top and bottom plates with embedded heating cartridges were used to uniformly heat the sample. A sinusoidal voltage of 10 V and a frequency scan over the range from 1 Hz to 1 MHz were used for each measurement. The comparison of the input and the return signals was automatically carried out in real-time within the system software. The isothermal dwell heating profile was the same as that used for rheometry measurements, with heating at 10 °C/min to 93 °C, 107 °C and 121 °C.

3. Principles of dielectric analysis

The electrical response of a thermoset resin during cure is better understood in terms of the two major immittance functions: complex impedance (Z^*) and complex permittivity (ϵ^*). The complex impedance, Z^* , relates directly to electric circuitry, and correlates well with cure kinetics and viscosity evolution during cure [14] and [15]. Permittivity, ϵ^* , on the other hand, permits detailed analysis of the physicochemical changes during cure through complex analysis [9], [11] and [12]:



$$\varepsilon^* = \varepsilon' + \varepsilon''$$



(1)

where ε' is a real part and ε'' is an imaginary part of ε^* . ε'' can be further divided into two parts for the thermoset resins as [9], [11] and [12]:

$$\varepsilon'' = \varepsilon_i'' + \varepsilon_d''$$

(2)

where ε_i'' is the ionic conductivity contribution and ε_d'' is the dipolar contribution. The former term, ε_i'' , dominates at low frequencies through a linear drop. Subtraction of ε_i'' from ε'' yields ε_d'' , and allows analysis of the dipolar relaxation of the thermoset resin.

Ionic conductivity (σ) is also related to ε_i'' by [9], [11] and [12]:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon_i''$$

(3)

where ε_0 is the free space permittivity of 9.85 pF/m [13]. The motion of ionic species reflects macroscopic viscosity.

4. Determination of physicochemical parameters

4.1. Out-time monitoring

Ex-situ methods for monitoring out-time were investigated by tracking changes to the B-stage glass transition temperature ($T_{g,0}$) and the total heat of reaction (ΔH_{rxn}), as measured by MDSC. Glass transition manifests as an inflection point in the change in specific heat within the reversing heat flow, while the heat of reaction is directly obtained by integrating the non-reversing heat flow [3].



The method developed in this study for monitoring out-time *in-situ* involves measurements of the conductivity σ at ambient temperature (chosen here as 30 °C for stability) via dielectric analysis. The thermoset resin contains significant amounts of ionic impurities introduced during resin preparation. Thus, the resin transformation from liquid-like states toward solid-like states during out-time will cause a decrease in measurable σ , even at ambient temperature. In contrast to rheological measurements, dielectric analysis involves measurement of ionic species motion, thus avoiding the limitations associated with material viscosity/stiffness near gelation.

4.2. Minimum viscosity and gelation point

The minimum viscosity, η_{min} , of a resin during cure is critical due to its influence on resin infiltration, part impregnation and void minimization. Using the isothermal cure profile, the η_{min} measured from rheometry was associated with the maximum ionic conductivity (σ_{max}), the highest ionic mobility point during cure, from dielectric analysis.

Gelation refers to the moment when an “infinitely large” cross-linked network of resin molecules is formed during cure. For epoxies, gelation is often defined as the moment when viscosity (η) reaches 10 kPa·s after passing minimum viscosity (η_{min}) [9] and [12]. In this range, η increases quickly as cure effects dominate over thermal effects, and rheometric measurements are constrained by the limits of machine torque. For dielectric measurements, gelation was 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 [12].

4.3. Vitrification point



Vitrification is defined as the point at which the polymer chains become closely packed, cooperative motion cannot occur due to insufficient volume, and the rate of cure drastically decreases [12]. Therefore, vitrification is a good guideline to define the minimum duration of the isothermal portion of a cure cycle. Using MDSC, studies have shown that the inflection point of the heat capacity (C_p) during the isothermal dwell period corresponds to the vitrification point [7].

Dielectric analysis, on the other hand, tracks α -relaxation of the resin during cure. The α -relaxation process is interpreted as a dipolar loss peak ($\epsilon_{d,max}''$) along the frequency-time scale. That is, assuming that insignificant change occurs during each frequency scan, $\epsilon_{d,max}''$ and the corresponding frequency (f_{max}) is tracked and extrapolated to 0.1 Hz, which closely matches the vitrification point determined from MDSC [11] and [12]. While this empirical finding may differ for specific resin systems, it allows one to track the evolution of bulk relaxation time (τ_b) of the resin during cure, defined as follows [17]:

$$\tau_b = (2\pi f_{max})^{-1} \quad (4)$$

5. Results and discussion

5.1. Out-time monitoring (ex-situ versus in-situ)

The total heat of reaction (ΔH_{rxn}) and the B-stage glass transition temperature ($T_{g,0}$) measured from MDSC are displayed in Fig. 1A and B. A quadratic fit captures both data series accurately, where:

$$\Delta H_{rxn} = -A_1 t^2 - B_1 t + C_1 \quad (5)$$

$$T_{g,0} = A_2 t^2 + B_2 t - C_2 \quad (6)$$



where t is the out-time in days, and the values of constants are as follows: $A_1 = 0.03 \text{ J/g day}^2$, $B_1 = 1.28 \text{ J/g day}$, $C_1 = 513.64 \text{ J/g}$, $A_2 = 0.01 \text{ }^\circ\text{C/day}^2$, $B_2 = 0.34 \text{ }^\circ\text{C/day}$, $C_2 = 1.31 \text{ }^\circ\text{C}$. ΔH_{rxn} measures the exothermic heat release during resin cure. Thus, the decrease in ΔH_{rxn} with out-time in a quadratic manner indicates that the polymerization/cross-linking at ambient temperature accelerates with out-time. The trend is explained by the autocatalytic nature of the epoxy cure reaction. The change in $T_{g,0}$ with out-time reportedly exhibits a linear dependence until the resin cure temperature is exceeded, at which point vitrification occurs [3]. However, in the current study, $T_{g,0}$ increased in a quadratic manner with respect to the out-time. Note that $T_{g,0}$ is a function of the amount of unreacted end-groups. Thus, a decrease in the amount of unreacted end-groups due to out-time increases $T_{g,0}$ and decreases segmental mobility. Furthermore, a quadratic dependence of ΔH_{rxn} on out-time leads to the same expected trend in $T_{g,0}$.

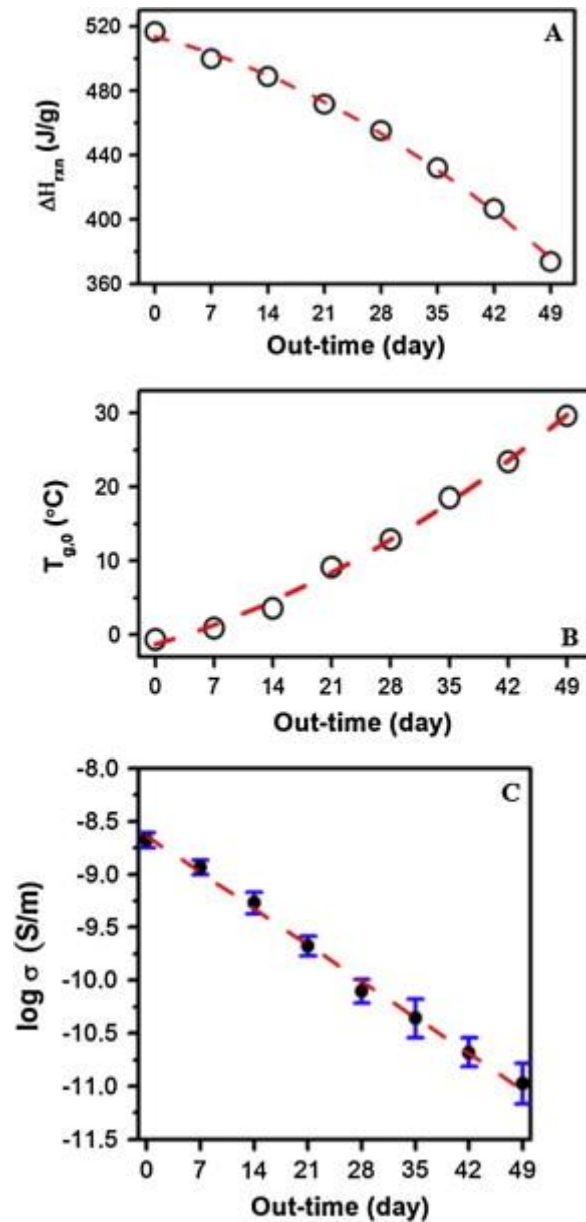


Figure 1: (A) Total heat of reaction (ΔH_T) and quadratic fit (dotted line) on out-time, (B) B-stage glass transition temperature ($T_{g,0}$) and quadratic fit (dotted line) on out-time and (C) conductivity ($\log(\sigma)$) versus out-time.

From dielectric analysis, logarithmic ionic conductivity ($\log(\sigma)$) as a function of out-time at 30 $^{\circ}\text{C}$ is displayed in Fig. 1C. The measurements are averaged over 100 repetitions and the resulting error bars are drawn on each data point. As described in Section 3, $\log(\sigma)$ is a strong function of the resin η , where the resin transformation from a liquid-like to a solid-like state during out-time restricts the “In Situ Cure Monitoring of an Out-of-Autoclave Prepreg: Effects of Out-Time on Viscosity, Gelation, and Vitrification” D. Kim, T. Centea, and S.R. Nutt, *Compos. Sci. & Tech.* 102 132-138 (2014)
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mobility of ionic species and thus results in a σ decrease (i.e., σ is inversely proportional to η). $\log(\sigma)$ can be related to out-time as

$$\log(\sigma) = -B_3 t - C_3 \quad (7)$$

where t is time in days and the constants are $B_3 = 0.05$ S/m·day, $C_3 = 8.64$ S/m. This relation can be used as a convenient method of predicting and monitoring out-time directly from a dielectric signal.

5.2. Minimum viscosity and gelation point (ex-situ versus in-situ)

The minimum viscosity point is identified as η_{min} and σ_{max} during isothermal cures, as both η_{min} and σ_{max} occurred simultaneously, regardless of out-time, for the same isothermal dwell temperature. Normalized viscosity ($\eta_r = \eta_{min}(t)/\eta_{min}(day0)$) and normalized conductivity ($\sigma_r = \sigma_{max}(t)/\sigma_{max}(day0)$) versus out-time are plotted in Fig. 2A and B. Both η_r and σ_r increase quadratically with out-time and more rapidly with increasing dwell temperature. The fit parameters are shown in Table 1. Because η_{min} or σ_{max} is associated with the highest resin flow rate (all other factors being equal), the results demonstrate that dielectric analysis can be used to determine the potential moment of maximum infiltration flow rate, and to obtain microstructural information.

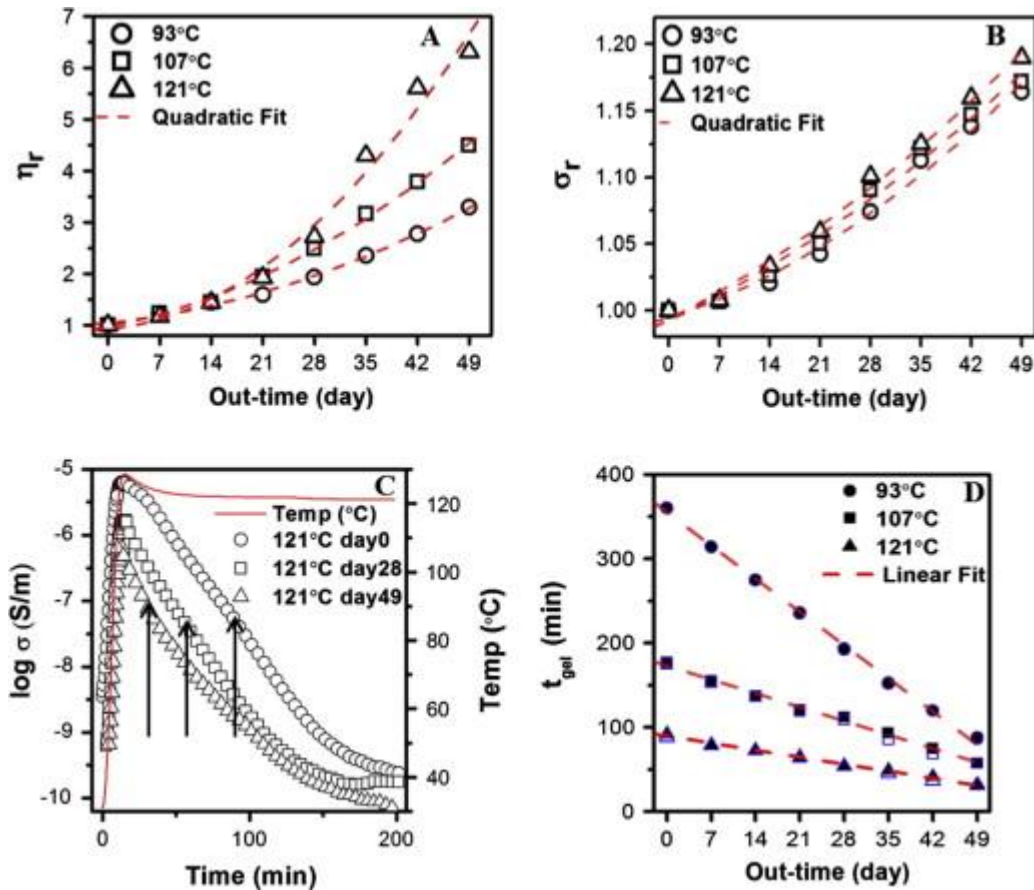


Figure 2: Isothermal dwell at 93 °C, 107 °C, and 121 °C: (A) reduced viscosity (η_r) versus out-time, (B) reduced conductivity (σ_r) versus out-time, (C) conductivity ($\log(\sigma)$) versus cure time on isothermal dwell at 121 °C on day 0, 28 and 49 (corresponding t_{gel} points are drawn in arrow) and (D) gelation time (t_{gel}) versus out-time on isothermal dwell at 93 °C, 107 °C, and 121 °C (closed symbol: dielectric analysis and open symbol: rheometry).



<i>Equation (t = days)</i>				
$\log(\eta_r) = b_1 t^2 + b_2 t + 1$				
$\log(\sigma_r) = c_1 t^2 + c_2 t + 1$				
<i>Parameters</i>				
<i>Temp (°C)</i>	b_1 (day^{-2})	b_2 (day^{-1})	c_1 (day^{-2})	c_2 (day^{-1})
93	5.64×10^{-4}	0.019	4.45×10^{-5}	1.33×10^{-3}
107	9.56×10^{-4}	0.026	3.47×10^{-5}	1.97×10^{-3}
121	2.22×10^{-3}	0.007	3.47×10^{-5}	2.28×10^{-3}

Table 1: Parameters for η_r and σ_r during isothermal cure ($\log(\eta)$ on day 0 = 0.88, 0.48, and 0.27 Pa s at 93 °C, 107 °C, and 121 °C respectively and $\log(\sigma)$ on day 0 = -5.93, -5.53, and -5.20 S/m at 93 °C, 107 °C, and 121 °C respectively).

A representative plot of σ evolution during isothermal dwell is shown in Fig. 2C, where $\log(\sigma)$ versus cure time is displayed for an isothermal dwell at 121 °C on days 0, 28 and 49. The $\log(\sigma)$ increases during heat-up, when thermal effects dominate over cure effects, and the mobility of ionic species increases relative to the initial condition. After reaching the cure temperature, cure effects begin to dominate over thermal effects, and $\log(\sigma)$ decreases. The magnitude of $\log(\sigma)$ decreases throughout cure for increasing out-times, showing, as expected, an inverse trend to the η evolution. The gelation time (t_{gel}), starting from cure onset, is taken to be the inflection point, calculated by taking the second derivative of the curve for dielectric measurements, and 10 kPa s for rheological measurements.

The t_{gel} versus out-time plot is shown in Fig. 2D for isothermal dwells at 93 °C, 107 °C, and 121 °C (where closed symbols indicate dielectric measurements and open symbols denote rheological measurements). The comparison shows close correlation between the two methods, and a high degree of accuracy for a linear relation of the form: $t_{gel} = f(t, T)$ where t is out-time and T is isothermal dwell temperature. Parameters for the correlation is provided in Appendix A.1.

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5.3. Vitrification point (ex-situ versus in-situ)

Fig. 3A shows representative dipolar contributions to dielectric loss ($\log(\epsilon_d'')$) as functions of logarithmic frequency ($\log(f)$) and cure time at various out-times during isothermal dwell at 121 °C. Typically, the maximum dipolar loss peak ($\epsilon_{d,max}''$) occurs earlier with increasing out-time. The frequencies ($\log(f_{max})$) corresponding to $\log(\epsilon_{d,max}''$) are plotted versus cure time during isothermal dwell at 121 °C from day 0 to 49 (Fig. 3B). Linear fits corresponding to each out-time point indicate that the slope remains the same regardless of out-time, but the intercept changes. Intercepts and slopes from different isothermal dwell measurements are shown in Table 2. The trend shows that for a given out-time, both the intercept and the absolute value of the slope increase with isothermal dwell temperature. The behavior can be interpreted in light of the evolution of the polymer chain relaxation during cure. Eq. (4), which expresses the inverse relationship of f_{max} and bulk relaxation time (τ_b), suggests that the value of τ_b at which vitrification occurs (t_{vit}) will be shorter for higher isothermal dwell temperatures.

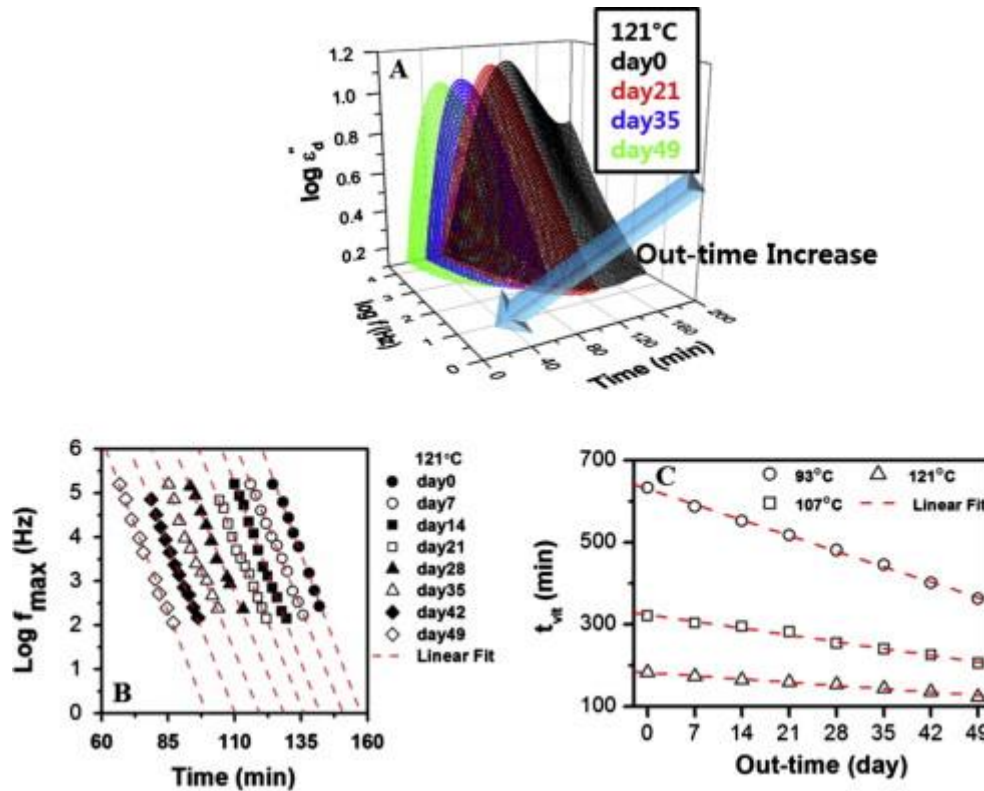


Figure 3: (A) Dipolar contribution (ϵ_d'') of dielectric loss (ϵ'') as function of frequency (f) and out-time on isothermal dwell at 121 °C on day 0, 21, 35, and 49, (B) frequency ($\log(f_{max})$) corresponding to dipolar loss peak ($\epsilon_{d,max}''$) during isothermal dwell at 121 °C on day 0, 7, 14, 21, 28, 35, 42, and 49 and (C) MDSC results on vitrification time (t_{vit}) versus out-time on isothermal dwell at 93 °C, 107 °C, and 121 °C.

Table 2: Parameters for α -relaxation analysis during isothermal cure at 93 °C, 107 °C, and 121 °C on out-time.

	Intercept ($t = \text{days}$)	Slope	$\log(f_{max})$ at t_{vit}	τ_{vit} (s)
93 °C	$-0.23t + 21.83$	-0.05 ± 0.001	-7.02 ± 0.12	1.74×10^6
107 °C	$-0.21t + 23.19$	-0.08 ± 0.002	-4.39 ± 0.22	4.42×10^3
121 °C	$-0.18t + 24.20$	-0.15 ± 0.004	-3.64 ± 0.28	8.17×10^2

The vitrification time (t_{vit}) versus out-time obtained from MDSC is shown in Fig. 3C for isothermal dwell measurements. The plots confirm that t_{vit} decreases with out-time and with higher isothermal dwell temperatures. In the present case, t_{vit} is related to temperature and out-time in the form: $t_{vit} = f(t, T)$. Parameters for the correlation are provided in Appendix A.2. The values

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of t_{vit} decrease more rapidly at lower cure temperatures. As expected, because out-time affects the initial degree of cure in a quadratic manner, the time required for fresh resin to reach the initial degree of cure induced by out-time is more sensitive at lower isothermal dwell temperatures.

Previous studies [9], [12] and [13] have identified the point of vitrification by determining the cure time at which $\varepsilon_{d,max}$ occurs and recording the corresponding f_{max} . The value of f_{max} was then related to t_{vit} determined from MDSC. In those studies, t_{vit} was closely related to the f_{max} value of 0.1 Hz ($\tau_b \sim 1.59$ s using Eq. (4)), regardless of the isothermal dwell temperature. However, for the present system, f_{max} at t_{vit} increased markedly with dwell temperature (and consequently, τ_b decreased). Also, while out-time decreased t_{vit}, τ_b was largely unaffected. This result supports the assertion that by determining τ_b at $t_{vit}(\tau_{vit})$ as a function of temperature, one can determine the effective end of cure cycle on-line, regardless of out-time. In the present case, τ_{vit} is related to temperature as the form: $\tau_{vit} = f(t, T)$. Parameters for the correlation are provided in Appendix A.3. The relationship is resin-specific, as expected from the results of other studies [9], [12] and [13].

5.4. Effect of out-time (and out-life) on resin state

A clear trend in the evolution of the uncured state parameters ($T_{g,0}$ and $\log(\sigma)$) during and beyond the specified out-life for the material was observed. Furthermore, η_{min} exhibited a quadratic dependence on out-time, and t_{gel} and t_{vit} continued to decrease linearly with out-time well beyond the out-life specified for the prepreg. These results show that the manufacturer-specified out-life does not consist of a sudden change in properties, or correspond to a unique or additional physicochemical change in the resin. Rather, the resin undergoes chemical transformations (polymerization/cross-linking) as soon as it is exposed to ambient temperature. Therefore, the out-life can be conceived as the point at which the resin properties no longer enable one to produce a

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part with acceptable microstructural quality. For VBO prepregs, previous work has shown that, once the prepreg out-life is exceeded, high resin viscosities no longer permit sufficient resin infiltration into the tows during cure, under the recommended cure cycle [4]. The present study shows that, while the onset of porosity may be sudden, the deviation of resin properties is gradual. The following section examines the manufacturing implications of this resin property shift.

5.5. Manufacturing considerations

The primary manufacturing consideration associated with out-time is part quality. By considering the gradual effects of out-time on viscosity and gelation before and after the stated out-life, situation-appropriate cure cycles can be developed. Fig. 4A and B show maps of η_{min} as a function of out-time and ramp rate for 93 °C and 121 °C dwell temperatures, respectively. As expected, higher temperatures yield lower viscosities. However, other dependencies also exist. At 93 °C (A), the η_{min} increases continuously with out-time, and this behavior is relatively insensitive to ramp rate. However, at 121 °C, at high ramp rates, the same property exhibits a low viscosity plateau between 10 days and 30 days. This difference allows low viscosities to be achieved at high out-times. For 30 days of out-time, a 3 °C/min ramp to 121 °C enables 13 Pa s to be achieved, compared to, remarkably, the same 13 Pa·s at 10 days. In contrast, a 3 °C/min ramp to 93 °C leads to a 30 day minimum viscosity of only 119 Pa·s, versus 41 Pa·s for the same cure cycle and 10 days. Thus, for this resin, prepreg subjected to long out-times should be rapidly heated to high temperatures to counteract the influence of out-time.

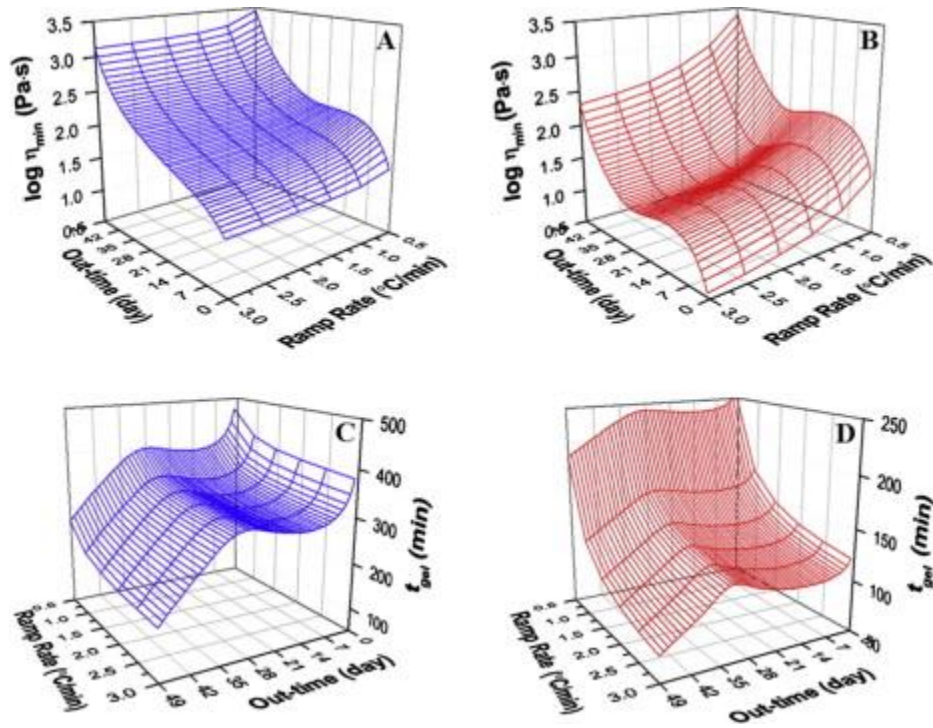


Figure 4: Minimum viscosity (η_{min}) as function of ramp rate and out-time on isothermal dwell at (A) 93 °C, and (B) 121 °C. Gelation time (t_{gel}) as function of ramp rate and out-time on isothermal dwell at (C) 93 °C, and (D) 121 °C.

Fig. 4C and D show the gel time as a function of out-time and ramp rate for 93 °C and 121 °C dwells, respectively. The former is associated with long t_{gel} values due to low cure rates, but is weakly dependent on ramp rate: at 30 days and 0.5 °C/min, the t_{gel} is only 25% longer than at 3 °C/min. Conversely, the latter dwell temperature produces faster gelation but shows strong ramp rate dependence: the 30-day t_{gel} is twice as long at 0.5 °C/min compared to 3 °C/min. Furthermore, at 121 °C, the t_{gel} is also less sensitive to increasing out-time. For all cure cycles, faster gelation allows faster cure. For a given part, reducing elevated temperature processing time by one (or a few) hours may be negligible, given that out-time is measured in weeks. However, in situations where the curing vessel availability is rate-limiting, faster cure may allow one to manufacture more parts per day.

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6. Conclusions

In this study, we investigated effective methods (1) for monitoring out-time under ambient conditions, and (2) for identifying critical physicochemical events (minimum viscosity, gelation, and vitrification) and their dependence on out-time (and out-life) for an OOA prepreg resin during cure. 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 develop a means for detecting such phenomena in real-time. We discovered that while the out-life may correspond to the onset of pervasive porosity (as shown in previous studies), it does not constitute a fundamental shift in resin properties. Rather, the results show that the processing-critical resin transitions (minimum viscosity, gelation and vitrification) gradually but significantly change during the out-life specified for the material.

In previous work, we presented a method to predict and monitor the instantaneous degree of cure, cure rate, and viscosity evolution of composite prepregs by dielectric cure monitoring in-situ [14]. The results of the present study demonstrate that dielectric analysis can be used as a stand-alone technique to monitor both the extent of out-time at ambient temperature as well as the major effects of out-time during cure. Ultimately, this information can be used to design efficient cure cycles that ensure that the part has been fully cured at any level of out-time, and ultimately to control cure in real-time. Therefore, dielectric monitoring methods and the insight they provide offer a means to improve process effectiveness and efficiency in composite manufacturing.

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Appendix A

A.1. Gelation time (t_{gel}) as a function of out-time (t) and isothermal dwell temperature (T)

$$t_{gel} = (a_1 - a_2 T)t + (a_3 - a_4 T)$$

where the constants are $a_1 = 0.16$ min/day, $a_2 = 19.86$ min/day °C, $a_3 = 1222$ min, and $a_4 = 9.51$ min/°C and T is temperature in °C.

A.2. Vitrification time determined from MDSC (t_{vit}) as a function of out-time (t) and isothermal dwell temperature (T)

$$t_{vit} = (-d_1 + d_2 T - d_3 T^2)t + (e_1 - e_2 T + e_3 T^2)$$

where T is in °C, t is in days, and the constants are $d_1 = 0.01$ min/day, $d_2 = 1.15$ min/day °C, $d_3 = 72.13$ min/day·°C², $e_1 = 0.42$ min, $e_2 = 106.38$ min/day·°C, and $e_3 = 6869.9$ min/day·°C².

A.3. Vitrification time determined from dielectric analysis (τ_{vit}) as a function of out-time (t) and isothermal dwell temperature (T)

$$\tau_{vit} = k_1 \exp(-k_2 T)$$

where τ_{vit} is in s, $k_1 = 9.56 \times 10^{16}$ s, $k_2 = 0.27$ /°C and T is in °C.

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