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In situ resin age assessment using dielectric analysis and resin cure map for efficient vacuum infusion

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ABSTRACT

The physical state of epoxy resin designed for vacuum infusion was assessed *in situ* by immersing a dielectric sensor into the resin pot. The measured ion viscosity of aged resin was directly converted to a degree-of-cure metric using a resin cure map constructed by correlating cure kinetics and dielectric analysis data. Next, an age-adjusted infusion process map was employed to define a nominal infusion window and to identify key process metrics. Finally, process simulations and flow contour maps were used to validate and refine the process map and to guide adjustment of infusion process parameters based on resin age and part size/geometry. The study describes a pathway to more efficient use of aged resin using *in situ* process diagnostics, cure map design, and process simulation. The methodology employed to evaluate resin age and to adjust process parameters accordingly can be extended to other composite manufacturing processes, including conventional prepreg processing.



KEYWORDS

Cure behavior; process simulation; process monitoring; vacuum infusion

1. Introduction

In this work, we evaluate the physical state (age or life) of resin *in situ* using dielectric analysis (DEA) in conjunction with a resin cure map. Based on the assessed resin age, we use process simulations and flow contour maps to adjust process parameters for vacuum infusion (VI). The study is motivated by a need to increase VI process efficiency. High-performance thermoset resins designed for VI have relatively short shelf-lives and out-lives, and require multiple protracted steps to pre-condition and pre-heat prior to infusion. In general, excess resin is prepared for each infusion trial to ensure uninterrupted and complete saturation of dry preforms, inevitably leaving unused aged resin as waste. The use of aged resin must be accompanied by accurate and meticulous tracking of resin working time and thermal history, which is often difficult in practice. Otherwise,

additional thermal analysis must be conducted to assess resin life prior to each infusion trial, and thus excess or expired resin is often discarded for convenience.

VI can be a cost-effective alternative to the conventional autoclave prepreg process, especially for the manufacture of large and complex unitized composite structures [1–8]. In VI, a dry fiber preform is placed on a one-sided rigid mold and sealed with a flexible vacuum bag, and resin is infused into the preform under vacuum pressure, then heated and cured [6–12]. Interest in VI has grown rapidly in recent years, particularly in the aerospace industry, which seeks to reduce the manufacturing costs associated with prepreg processing. However, because vacuum pressure alone is applied during infusion, VI involves much slower infusion rates and thus longer fill times relative to resin transfer molding (RTM), in which resin is injected under positive

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pressure [1, 6]. Inserting a high-permeability flow distribution medium on top of the preform (e.g. SCRIMP, Seemann Composites Resin Infusion Molding Process) can enhance resin flow and reduce fill times, but also can induce unacceptable void contents, particularly for large parts with complex geometries [1, 6]. To mitigate this issue, resin is often heated during filling, although doing so increases resin degree of cure and viscosity with flow time and distance [1, 13]. Thus, the process parameters for heated filling during VI must be selected carefully; even for SCRIMP, the problem of evolving resin state can persist, particularly as part size increases.

Aerospace-grade thermoset resins designed for VI processes (e.g. Hexcel HexFlow® RTM6) have relatively short shelf-lives (months) and out-lives (weeks or days) and require protracted pre-processing and pre-heating [14-16]. In general, a VI resin must be pre-conditioned at room temperature (from cold storage), then pre-heated to reduce viscosity for transfer to an infusion pot. The resin is maintained at the pre-heating temperature until degassing and infusion steps are completed. Depending on the size and geometry of the part being infused, resin will age (i.e. resin degree of cure will advance) throughout the protracted pre-conditioning and pre-heating steps, reducing resin life. Furthermore, each infusion run generates waste resin, because excess resin generally is prepared to ensure uninterrupted infusion of preforms. Unused resin cannot be reused unless the thermal history-including shelf-life, out-life, and working time-of the material has been tracked rigorously [17]. Even for previously unused resin, accurate evaluation of resin life can be challenging, as resin ages even during freezer storage, albeit slowly. Hence, expired resin is generally discarded without further material assessment, resulting in economic loss and environmental hazards [17].

Previous studies have explored the use of in situ process diagnostics in liquid molding for on-line monitoring of resin state, and investigated the effects of curing dependent viscosity on heated infusion processes. For example, Pantelelis and Bistekos developed a DC-based process monitoring system to track the electrical resistance of resin during cure, and modeled resin viscosity as a function of resistance using an empirical power law [17]. The same work also identified the common manufacturing problem of aged resin exhibiting greater initial viscosity and more rapid viscosity increase during infusion (compared to fresh resin). However, no remedies were offered to guide process adjustments to mitigate the problem aside from mixing aged resin with fresh resin at an arbitrary ratio [17, 18]. For dielectric cure monitoring (DCM) of epoxy

resin (RTM6), Karkanas related the dielectric response of the resin to chemical and physical changes (e.g. gel point and vitrification) using a principle specific to selected resin systems (autocatalytic resins including RTM6) [19]. Kazilas conducted impedance curve modeling and temperature modulated dielectric analysis on the same resin (RTM6) [20]. Finally, Grujicic [21] and Wu [22] developed mold-filling models to account for cure-state-dependent viscosity and performed heated filling simulations to minimize filling time for non-isothermal VI.

In this work, we demonstrate a new method to more accurately assess the physical state of resin, using in situ process diagnostics coupled with cure modeling. To accurately monitor and analyze the resin state, we develop a new resin cure map by correlating a cure kinetics model to DEA ion viscosity measurements. We then plot degree-of-cure isolines across different temperatures using an ion viscosity model. The straightforward linear relationships between the ion viscosity model parameters and the resin degree of cure lead to accurate predictions of ion viscosity across a wide span of resin age and temperature. Such predictions minimize the need for extensive material characterization generally required for DEA modeling. Using these tools, we can convert the ion viscosity data for an aged resin directly into a metric for resin life. We demonstrate how to use this metric to guide process adjustments "on-the-fly" to compensate for resin age. In addition, we conduct heated infusion simulations to determine the effects of process temperature and resin age on the maximum resin flow distance and to develop flow contour maps. The flow maps are intended to guide selection of resin-age-adjusted process parameters (infusion temperature or number/placement of resin inlets).

The work described outlines a pathway to reduce the waste of aged resin, a widespread problem in VI, and to efficiently adjust heated infusion process parameters based on resin age and part geometry. First, the cure kinetics, rheology, and aging behavior of epoxy resin are examined using differential scanning calorimetry (DSC), rheometry, and DEA. Next, a resin cure map is constructed and deployed in conjunction with an on-line DCM system to assess the life of aged resin in situ. The nominal infusion window and key process metrics are determined using an age-adjusted infusion process map, while heated filling VI simulations demonstrate how resin age and infusion temperature (combined) can affect the maximum resin flow distance. Finally, we conduct a parametric filling simulation study and develop flow contour maps to guide the selection of infusion parameters. The methods allow more

efficient use of aged resin and informed process adjustments. Overall, the methodology employed in this work provides a blueprint to implement VI process diagnostics and to guide adjustments that will reduce material waste for VI, as well as for other composite manufacturing processes.

2. Experimental

2.1. Materials

An aerospace qualified epoxy resin was selected and acquired (HexFlow[®] RTM6, Hexcel). The mono-component epoxy resin system (with curing agent pre-mixed) was developed for liquid composite molding processes and featured a shelf-life of 9 months (at -18 °C) and an out-life of 15 days (at ambient conditions) [14]. After freezer storage, the resin must be pre-conditioned at room temperature for 24 h, followed by pre-heating to 60–80 °C for infusion pot transfer. In the pot, the resin is maintained at 80 °C throughout degassing and infusion. The manufacturer-recommended infusion temperature is 120–140 °C.

2.2. Cure kinetics and rheology

2.2.1. Modulated differential scanning calorimetry (MDSC)

Resin cure kinetics was characterized using DSC (TA Instruments, Q2000) under a nitrogen purge $(50 \text{ cm}^3/$ min). Resin samples (8-10 mg) were first exposed to a dynamic ramp at four heating rates (5, 10, 15, and 20 $^{\circ}$ C/min) from –50 to 340 $^{\circ}$ C to determine the total heat of reaction. Isothermal dwell measurements were conducted at four temperatures (120, 140, 160, and 180 °C) to analyze the cure kinetics, followed by a ramp to 300 °C at 5 °C/min to measure the residual heat of cure. During the subsequent ramp, the samples exhibited an endothermic annealing peak near the residual cure exotherm because of physical aging of the resin [23]. To eliminate the annealing peak, the specimens were quenched rapidly at the endotherm spike to -50 °C and reheated during re-scan. During the ramp, a sinusoidal temperature modulation of ±0.5 °C/min was applied to distinguish reversing and non-reversing heat flow signals. Reversing heat flow is associated with heat capacity and rate of temperature change, while non-reversing heat flow is dependent on kinetic component of reaction [24, 25]. Glass transition can be examined from the reversing heat flow signal, while the curing reaction appears in the nonreversing signal.

2.2.2. Rheometry

Viscosity evolution during cure was measured using a rheometer (TA Instruments, AR2000ex). Resin

samples were subjected to an isothermal dwell at four temperatures (120–180 °C), analogous to MDSC isothermal dwell measurements. A disposable parallel-plate geometry fixture (diameter 25 mm) was used to measure the evolving viscosity throughout the cure cycle. Cell temperature was raised from the pre-heating temperature (80 °C) to the dwell temperature at approximately 30 °C/min (the maximum ramp rate of the rheometer) and held constant for prescribed durations, under oscillatory shear at 1 Hz frequency and 5% strain (within the linear viscoelastic region).

2.2.3. Dielectric analysis (DEA)

A dielectric cure monitoring (DCM) system (Netzsch, DEA 288 Epsilon) was used to perform DEA measurements in frequency intervals from 1 Hz to 1 kHz at four temperatures (120, 140, 160, and 180 °C). An interdigitated electrode sensor (Netzsch, Mini-IDEX 100/35) with 33 mm² sensing area and $100\,\mu\text{m}$ electrode spacing was mounted on a rheometer Peltier plate, along with a thermocouple. A resin sample was placed on the sensor, and cell temperature was increased from 80 °C to the dwell temperature at $\sim 30^{\circ}$ C/min, then held constant until completion of cure. Once a sinusoidal excitation voltage is applied, dipoles and charge carriers within resin align with the applied electric field and move toward electrodes of opposite charge. The resulting sinusoidal current and phase shift response yields dielectric properties, including complex permittivity (ε^*) and ionic conductivity (σ). The reciprocal of σ is the ion viscosity and exhibits a strong correlation to mechanical dynamic viscosity (η) [26–28].

2.3. Resin aging

Resin samples were aged by storing at room temperature (25 °C) for 1, 2, 4, 7, 10 days and 2, 3, 4, 5, 6 weeks (two samples tested for each out-time period). Once aging was complete, each sample was placed in the DSC and heated to 340 °C at 5 °C/min to determine the degree of cure (α) accrued during aging. All samples were weighed before and after aging to confirm that no weight loss had occurred. The purpose of this task was to monitor how fast the resin aged at ambient condition, and thus to enable prediction of α advancement with respect to out-time.

2.4. Filling simulation

Simulations of VI heated filling were conducted using commercial software (PAM-RTM, ESI Group). The simulations assumed a preform comprised of 20



Figure 1. (a) MDSC data showing heat flow profiles measured during isothermal dwell tests, and (b) experimental (solid line) and cure kinetics model-predicted (dotted line) degree of cure profiles for the isothermal dwell tests.

plies of plain weave carbon fiber fabric (areal weight of 193 g/m² and 3000 fiber/tow count, part #1530, Fibre Glast). The in-plane permeability of the fabric was measured previously $(2.5 \times 10^{-11} \text{ m}^2, \text{ isotropic})$ using an unsaturated radial flow configuration [29]. Three VI cases were simulated, each with different infusion length: 530 mm (Case A), 600 mm (Case B), and 670 mm (Case C). The width of the preform was constant (200 mm) in all cases. In each case, aged resin with an initial degree of cure (α_0) of 0.10 was infused, and three different initial mold temperatures were employed (120, 130, and 140 °C). The process pressures were specified across the linear width boundaries: atmospheric pressure $(1.01 \times 10^5 \text{ Pa})$ was applied at the resin inlet boundary on one end, while vacuum (0 Pa) was applied at the vent boundary on the opposite end. For each simulation run, a total of 9558 elements were meshed (triangle type and linear order). The objective of the filling simulation was to validate and refine the infusion process map and to inform subsequent adjustment of process parameters. A second purpose was to demonstrate

 Table 1. Values of the cure kinetics model parameters for RTM6 epoxy resin.

| Parameter | Value | Parameter | Value |
|-------------------------------|---------------------|----------------------------------|----------------------|
| $A_1 [s^{-1}]$ | $1.70 	imes 10^{6}$ | $A_2 [s^{-1}]$ | $1.63 	imes 10^4$ |
| <i>E_{A1}</i> [J/mol] | $8.22 	imes 10^4$ | <i>E_{A2}</i> [J/mol] | $5.72 	imes 10^4$ |
| m_1 | 0.27 | m_2 | 1.15 |
| n1 | 10.65 | <i>n</i> ₂ | 1.22 |
| D | 43.34 | α _{co} | -0.11 |
| | | α_{CT} [K ⁻¹] | $2.23 	imes 10^{-3}$ |

the need to adjust the infusion process parameters not only for part size and geometry, but particularly for resin age.

3. Results and discussion

3.1. Cure kinetics, rheology, and dielectric analysis

3.1.1. Cure kinetics

The total heat of cure reaction $(H_{r,total})$ measured was 430 J/g, similar to a previous report (436 J/g [23]). Figure 1(a) shows the MDSC heat flow data measured via isothermal dwell tests. The heat flow curves evolved more rapidly as the cure temperature increased, with shorter reaction induction periods. Assuming that the rate of cure reaction was proportional to the rate of heat flow, the heat flow data was converted to cure rate data using the equation [30,31]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{H_{r,\,total}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) \tag{1}$$

where α is the resin degree of cure, *t* is time, and *H* is the heat flow measured from the MDSC. The resin degree of cure can be calculated by integrating Equation (1). The final degree of cure (α_{f}) values for samples reacted at 120, 140, 160, and 180 °C were 0.83, 0.88, 0.93, and 0.97, respectively.

The MDSC data for resin cure were fit to a phenomenological cure kinetics model developed by Kratz et al. [30], which accounts for transitioning from kinetics-controlled to diffusion-controlled cure reaction as α exceeds α_{gel} (α at resin gelation), and a rapid rate of cure present at low- α ($\alpha < 0.1$):

$$\frac{d\alpha}{dt} = K_1 \alpha^{m_1} (1 - \alpha)^{n_1} + \frac{K_2 \alpha^{m_2} (1 - \alpha)^{n_2}}{1 + \exp(D(\alpha - (\alpha_{C0} + \alpha_{CT}T)))}$$
(2)

$$K_i = A_i \cdot \exp\left(-\frac{E_{Ai}}{RT}\right)$$
 where $i = 1, 2$ (3)

where K_i is the Arrhenius temperature dependent term, m_1 , m_2 , n_1 , and n_2 are the reaction order-based fitting constants, D is the diffusion constant, α_{C0} is the critical α at absolute zero, α_{CT} accounts for the increase in critical α with temperature, A_i is the preexponential factor, E_{Ai} is the activation energy, R is the universal gas constant, and T is the temperature.



Figure 2. (a) Rheology data showing experimental (dotted) and viscosity model-predicted (solid line) mechanical viscosity profiles for isothermal dwell tests, and (b) storage and loss modulus profiles measured at 160 °C.

The measured (solid line) and predicted (dotted line) degree of cure profiles for isothermal reactions are shown in Figure 1(b). The results demonstrate that the model accurately predicted degree of cure at all four cure temperatures. The values of the cure kinetics parameters are shown in Table 1.

3.1.2. Rheology

Viscosity profile data were acquired from isothermal scans conducted at temperatures between 120 and 180 °C. A phenomenological viscosity model developed by Khoun et al. was used to fit rheology data [31]:

$$\eta = \eta_1 + \eta_2 \left(\frac{\alpha_{gel}}{\alpha_{gel} - \alpha}\right)^{A + B\alpha + C\alpha^2} \tag{4}$$

$$\eta_i = A_{\eta i} \cdot \exp\left(-\frac{E_{\eta i}}{RT}\right) \quad \text{where } i = 1, 2 \quad (5)$$

where η is the viscosity, η_1 and η_2 are the Arrhenius dependent viscosity components, α_{gel} is the degree of cure at gelation, *A*, *B*, and *C* are the fitting constants, $A_{\eta i}$ is the Arrhenius constant, and $E_{\eta i}$ is the viscosity activation energy. Figure 2(a) shows the measured data (dotted) and model fitting results (solid line) for resin viscosity evolution during cure. Parameter values for the viscosity model are shown in Table 2. The viscosity profile exhibited a sigmoidal shape after a brief induction period, much like the degree of cure profiles shown in Figure 1(b). Values measured below 0.1 Pa·s exhibited greater variance because of the rheometer geometry constraints. However, the initial resin viscosity values for different temperatures were accurately predicted by the model, yielding values similar to those reported in the material datasheet [14].

Figure 2(b) shows representative storage modulus (G') and loss modulus (G") profiles measured during cure at 160 °C. The gelation point (G' = G"), which marks the phase transition from liquid state (G" > G') to rubbery state (G' > G") [32], was determined to be roughly $\eta = 10^3$ Pa·s and $\alpha_{gel} = 0.63$. Gelation time is an important process metric, because flow ceases at gelation, thus arresting impregnation [27]. The gel times of the resin at different cure temperatures were measured three times at each cure temperature and are summarized in Table 3, and range from 20 to 270 min.

3.1.3. DEA and resin cure map

Figure 3(a) shows DEA data measured during the isothermal dwell tests at 120, 140, 160, and 180 °C. The sigmoidal shape of the ion viscosity curves resembles the profiles for degree of cure and mechanical viscosity, indicating that the three properties are correlated. As the state of cure advances and mechanical viscosity increases, the degrees of both ion mobility and dipole rotation subside, leading to an increase in ion viscosity [33]. Like mechanical viscosity, ion viscosity (*IV*) depends strongly on temperature, and can be expressed using the equation [34]:

$$\log(IV) = \log\left(\frac{k}{q^2 n D_0}\right) + \log(T) + \frac{Q}{kT \ln(10)}$$
(6)

where k is Boltzmann's constant, q is the magnitude of electronic charge, n is the free ion concentration, D_0 is the pre-exponential factor for the diffusion coefficient, and Q is the activation energy for diffusion. In Equation (6), all parameters on the right side are independent of temperature, and the equation can be re-written as:

$$\log(IV) = A + \log(T) + \frac{B}{T}$$
(7)

where both coefficients *A* and *B* depend on α and thus η , because D_0 and *Q* vary with degree of cure [34]. Of the two temperature terms, $\log(T)$ and 1/T, the latter term dominates the temperature dependence of ion viscosity, and ion viscosity decreases as temperature increases.

Based on the correlations described, a resin cure map was constructed (for RTM6) by plotting ion viscosity for α isolines (lines that connect the same

|--|

| $\overline{A_{\eta 1}}$ [Pa·s] | <i>E</i> _{η1} [J/mol] | $A_{\eta 2}$ [Pa·s] | $E_{\eta 2}$ [J/mol] | α _{gel} [-] | A [-] | B [-] | C [-] |
|--------------------------------|---|---------------------|----------------------|----------------------|-------|---------------------|-------|
| 1.54×10^{-5} | $\textbf{3.10}\times\textbf{10}^{\textbf{3}}$ | 1.02×10^{-8} | 4.90×10^4 | 0.63 | 3.72 | 5.69×10^{-3} | 0.03 |

 Table 3. Gelation times of RTM6 epoxy resin at different reaction temperatures.

| | | , | | |
|---------------------|--------------|--------------|-------------|-------------|
| Temperature [°C] | 120 | 140 | 160 | 180 |
| Gelation time [min] | 270.6 (±1.9) | 101.5 (±0.6) | 47.1 (±1.3) | 21.5 (±0.3) |
| | | | | |



Figure 3. (a) DEA data showing ion viscosity profiles during isothermal dwell tests, (b) resin cure map, in which filled squares (connected by solid isoline) and unfilled circles (connected by dashed isoline) represent experimental and model-predicted data points respectively, (c) ion viscosity model parameters plotted against resin degree of cure, exhibiting a linear relationship, and (d) model-predicted and experimental ion viscosity values at the resin pre-heating temperature of 80 °C.

| | Table 4. | Values of th | ie ion viscosit | y model | parameters | for | RTM6 | epoxy | resi |
|--|----------|--------------|-----------------|---------|------------|-----|------|-------|------|
|--|----------|--------------|-----------------|---------|------------|-----|------|-------|------|

| Tuble 1 | | iscosity model paral | neters for fitting epo, | iy resin | | |
|---------|-------------------|----------------------|-------------------------|-------------------|-------------------|----------------------|
| α | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 |
| A | -1.10 | -2.32 | -3.51 | -4.96 | -6.09 | -6.95 |
| В | $2.48 	imes 10^3$ | $3.10 	imes 10^3$ | $3.73 	imes 10^3$ | $4.48 	imes 10^3$ | $5.13 	imes 10^3$ | 5.69×10^{3} |

level of α) as a function of cure temperature (Figure 3(b)). The filled squares (from 393 to 453 K in the α range between 0.1 and 0.6) were plotted by comparing cure kinetics data to DEA measurements, and the α isolines (solid curves) were mapped by fitting the data points to the ion viscosity model (Equation

(7)). The values of the *IV* model parameters are shown in Table 4. Both parameters *A* and *B* exhibited a linear dependence on resin degree of cure (Figure 3(c)), indicating that the α isolines can be constructed for any α values of interest (e.g. $\alpha = 0.01$ and 0.05 isolines drawn in Figure 3(b)).



Figure 4. (a) Degree of cure accrued during aging (α_{aged}) plotted against room temperature out-time, and (b) degree of cure profile at 80 °C, predicted by the cure kinetics model.

Using the *IV* model, the α isolines were extended to a pre-heating temperature of 80 °C (unfilled circle points along 353 K), which was deemed the most practical temperature at which resin life can be monitored in situ using a DCM system. At 80°C, the ion viscosity values were measured at different levels of α and were compared against the modelpredicted values (Figure 3(d)). The comparison showed that the measured and predicted values differed by only 0.08 on average (below 1.0%), demonstrating the accuracy of the ion viscosity model. Overall, the DCM system enabled in situ measurement of resin ion viscosity, while the resin cure map and ion viscosity model were deployed to convert the measured ion viscosity straight into a metric that reflected resin life. Using these tools, we can develop a program that yields resin degree of cure at the specified temperature and ion viscosity, or one that predicts resin ion viscosity evolution during a process cycle.

3.2. Resin aging

Resin samples were aged at ambient conditions for up to 6 weeks. The degree of cure accrued

during aging (α_{aged}) was calculated using the equation:

 α_{aged} (fraction of aged resin)

$$=\frac{H_{r,total}(J/g)-H_{r,aged}(J/g)}{H_{r,total}(J/g)}$$
(8)

where $H_{r,total}$ is the total heat of cure reaction (430 J/g) and $H_{r,aged}$ is the heat of reaction of the aged resin. The underlying assumption was that the degree of cure increased as a function of aging time. The data from the aging study, shown in Figure 4(a), demonstrated that α_{aged} increased linearly with out-time ($R^2 = 0.98$). According to the material datasheet [14], the resin shelf-life at room temperature was 15 days. The linear regression line (Figure 4(a)) yielded α_{aged} of 0.05 for resin aged 15 days. After 30 days of out-time (twice the manufacturer's out-time specification), α_{aged} reached 0.10.

Figure 4(b) shows the predicted degree of cure profile for a pre-heating temperature of 80 °C, obtained using the cure kinetics model. At this temperature, α is expected to reach 0.05 and 0.10 after 16 and 21 h of dwell, respectively. The manufacturer's processing guideline [15] states that the maximum available working time of the resin is 12 h at 80 °C. Combining this specification with results from the thermal analysis, the resin will be suitable for infusion, provided α remains below ~0.05. The purpose of the aging study was to monitor and predict resin aging at ambient and pre-heating conditions and to determine the degree of cure (α) considered suitable for infusion without requiring further material assessment.

3.3. Infusion process map

The age-adjusted nominal infusion process window, and key process metrics for infusion of aged resin at different temperatures, can be determined by constructing an infusion process map. In principle, infusion must be completed before the resin gels, because resin flow ceases at gelation ($\alpha_{gel} = 0.63$) [27]. In practice, however, resin viscosity continuously rises with increasing degree of cure, and once η exceeds a threshold value, resin velocity becomes impractically low for further impregnation of dry preforms. This critical η value ($\eta_{critical}$), which can vary with the reinforcement type and resin system used, can be readily adjusted as needed. In this work, a value of 1 Pa·s for $\eta_{critical}$ was applied, which is widely regarded as the maximum resin viscosity suitable for infusion [35-37]. The degree of cure at the threshold $(\alpha_{critical})$ changes with process temperature because resin viscosity exhibits an Arrhenius temperature dependence.



Figure 5. (a) Infusion process map for aged resin with α_0 of 0.05, infused at 120 °C, and (b) more comprehensive process map for infusion temperatures of 120, 130, and 140 °C, using aged resin with α_0 of 0.10.

Figure 5(a) shows an example of a process map for infusion with aged resin (initial degree of cure (α_0) = 0.05). At an infusion temperature of 120 °C, $\alpha_{critical}$ (α at $\eta_{critical}$ of 1 Pa·s) is 0.38. The cure kinetics model predicts that for previously unused fresh resin, the degree of cure becomes α_0 (0.05) and $\alpha_{critical}$ (0.38) after 85 and 210 min at 120 °C, resulting in a nominal infusion window of 125 min (210 less 85) for aged resin, depicted in the red shaded region. A more comprehensive infusion map and its application are illustrated in Figure 5(b). In this case, α_0 is increased to 0.10, the value for resin corresponding to 30 days of out-time (twice the manufacturer-specified room temperature shelf-life). With increasing infusion temperature (indicated by red, green, and blue curves in Figure 5(b)), the initial resin viscosity (η_0 or η at α_0) decreases, while $\alpha_{critical}$ increases slightly because of the Arrhenius temperature dependence of resin viscosity. For resin with $\alpha_0 = 0.10$, the nominal infusion windows, indicated by red, green, and blue shaded areas in Figure 5(b), are 89, 61, and 42 min at 120, 130, and 140 °C, respectively.



Figure 6. Time required for aged resins ($\alpha_0 = 0.01$, short dashed; 0.05, dashed; 0.10, solid line) to reach different levels of viscosity, plotted against viscosity at infusion temperatures of (a) 120 and 130 °C, and (b) 120 and 140 °C.

The competing effects of temperature on resin viscosity are depicted in Figure 6(a,b), which show the time required for aged resin ($\alpha_0 = 0.01$, short dashed; 0.05, dashed; 0.10, solid line) to reach different viscosity levels (η) at different temperatures. As infusion temperature is increased, η_0 (x-intercept) decreases, expediting infusion flow. Yet, higher temperature also accelerates the evolution of viscosity, and consequently resin impregnation decelerates more rapidly. For example, when $\alpha_0 = 0.10$, the initial viscosity values of the aged resin are 0.06, 0.04, and 0.03 Pa·s at 120, 130, and 140 °C, respectively. However, after 28 and 22 min at the dwell temperature, the resin viscosity at 130 (0.10 Pa·s) and 140 °C $(0.09 \text{ Pa} \cdot \text{s})$ eventually exceeds the resin viscosity at 120 °C.

Beyond these η cross-over points, the benefits of higher infusion temperature vanish, because higher temperature causes η to increase more rapidly, decelerating the infusion process. For an infusion process predicted to saturate before or shortly after reaching $t_{cross-over}$ (time required to reach the η cross-over point), infusing at higher temperatures would expedite infusion. Otherwise, infusing at lower temperatures would help prevent premature resin gelation before infusion completion. Also, with increasing resin age (α_0), $t_{cross-over}$ decreases, indicating that the advantages of higher infusion temperature disappear earlier in the infusion process.

3.4. Process validation and simulation refinement

The cure reaction for epoxy is exothermic, and the heat generated during cure can increase the effective process temperature. The increased temperature can accelerate the cure reaction, producing a greater exotherm and further increasing the process temperature. The thermal runaway effect can become severe at higher infusion temperatures, as resin degree of cure and viscosity increase more rapidly, driving the resin to gelation more quickly. The nominal infusion process window estimated from the infusion process map does not account for the reaction exotherm, and thus is likely to be wider than the infusion window in practice. Thus, to validate and refine the process map and associated process parameters, the heated filling process was simulated using FEA software (PAM-RTM).

Simulation of a representative heated filling process yielded the result shown in Figure 7(a). The simulation assumed an infusion length of 530 mm, $\alpha_0 = 0.10$, and infusion temperature $(T_{infusion}) =$ 120 °C. Under these conditions, the infusion was completed in 33 min (fill time or t_{fill}), and the final degree of cure (α_{final}) and maximum temperature (T_{max}) at the outlet were ~ 0.2 and 128 °C, respectively. The simulation results for infusion lengths of 530 and 600 mm are summarized in Table 5. For both infusion lengths, higher infusion temperature resulted in shorter fill times, as expected. However, for 600 mm infusion length, both α_{final} and T_{max} increased more with increasing T_{infusion}, demonstrating that α (and thus η) rise much more rapidly at higher temperatures. A 670 mm infusion length was also analyzed. At 120 °C, the infusion process completed after 65 min, whereas at 130 and 140 °C, the resin gelled before the infusion completed, leaving unfilled dry regions near the outlet (Figure 7(b,c)). The unsaturated area was larger at 140 °C (vs. 130 °C), indicating that the degree of cure advanced more rapidly at higher temperature, leading to premature resin gelation.

For small parts of simple geometry, infusion is likely to be completed before the degree of cure and viscosity evolve significantly, favoring higher infusion temperatures (to reduce fill times). On the other hand, larger, more complex parts (i.e. parts



Figure 7. Representative simulation results of VI heated filling of aged resin ($\alpha_0 = 0.10$) for (a) infusion length of 530 mm and infusion temperature of 120 °C, expressed in terms of fill time gradient, and infusion length of 670 mm and infusion temperatures of (b) 130 and (c) 140 °C, expressed in terms of filling factor gradient.

Table 5. Heated filling simulation results for infusion lengths of 530 and 600 mm ($\alpha_0 = 0.10$).

| Infusion length | | 530 mm | | | 600 mm | | | |
|-----------------------|-------------------|--------------------|------------------|-------------------|--------------------|------------------|--|--|
| T _{infusion} | t _{fill} | α _{final} | T _{max} | t _{fill} | 𝕮 _{final} | T _{max} | | |
| 120 °C | 33 min | 0.188 | 128 °C | 44 min | 0.242 | 133 °C | | |
| 130 °C | 23 min | 0.197 | 139 °C | 30 min | 0.264 | 150°C | | |
| 140 °C | 16 min | 0.205 | 150 °C | 22 min | 0.294 | 159°C | | |



Figure 8. (a) Three-dimensional and (b) two-dimensional flow contour maps that show the maximum possible flow distance as a function of both resin age (α_0) and infusion temperature ($T_{infusion}$).

requiring greater fill time) can benefit from lower infusion temperature. Once the resin viscosity exceeds the η value at the cross-over points (determined from Figure 6), lower infusion temperature becomes advantageous, because η increases more slowly, providing a wider process window. Use of flow distribution media can mitigate the problem of long fill times (slow infusion) encountered in VI. However, as infusion length increases and part geometry becomes more complicated, the problem of premature resin gelation during high temperature infusion is increasingly likely.

A parametric infusion simulation study was conducted to construct 3D and 2D flow contour maps (Figure 8(a,b)) that show the maximum flow distance varying with resin age ($0 < \alpha_0 < 0.10$) and infusion temperature ($110 \,^{\circ}\text{C} < T_{infusion} < 150 \,^{\circ}\text{C}$). The flow surface maps were fit using a two-dimensional polynomial model to enable parametric analysis and process optimization for select temperatures and part geometries ($R^2 = 0.99$):

 Table 6. Two-dimensional polynomial fitting model parameters for the flow contour maps.

| Parameter | C ₀ | C1 | <i>C</i> ₂ | C3 | C4 | C5 |
|-----------|----------------|-------|-----------------------|------|---------------------|----------------------|
| Value | 2.55 | -22.1 | -9.13×10^{-3} | 57.7 | 3.81×10^{-6} | $6.78 	imes 10^{-2}$ |

$$D_{infusion} = C_0 + C_1 \alpha_0 + C_2 T_{infusion} + C_3 \alpha_0^2 + C_4 T_{infusion}^2 + C_5 \alpha_0 T_{infusion}$$
(9)

where $D_{infusion}$ is the maximum flow distance and C_i (i = 0 - 5) are the model fitting parameters. The values of the model parameters are summarized in Table 6.

Note that with increasing α_0 and $T_{infusion}$, the maximum flow distance decreases, yielding a narrower infusion process window and requiring more careful process design. The flow contour maps can be used to guide selection of process parameters (e.g. infusion temperature, as well as the number and locations of resin inlets) for parts of different sizes and geometry. For example, when infusing resin into a preform of 1.1 m in length, any parameter set falling left of the red dashed line in Figure 8(b) (maximum flow distance iso-contour of 1.1 m) would assure complete saturation. Aged resin with life that exceeds the x-intercept value of the 1.1 m iso-contour will require the use of multiple resin inlets to saturate the preform. When an infusion process requires multiple resin inlets, the same contour maps can be used to guide the placement and number of resin inlets. For SCRIMP, similar flow contour maps can be constructed using three-dimensional flow simulations that account for flow distribution media.

The methodology employed in this work can be used to guide effective VI process diagnostics and process adjustments and is depicted in Figure 9. First, coupling resin cure models to in situ dielectric analysis yields a resin cure map (shown earlier in Figure 3(b)). The cure map is used in conjunction with DCM to assess the physical state or age of resin, which provides the basis for process adjustments. Using material characterization results, an age-adjusted infusion process map is constructed (Figure 5) to define a nominal process window and process metrics. Then, the heated filling simulation (Figure 7) and flow contour maps (Figure 8) are used to validate and refine the process map, and guide selection of key process parameters for VI of aged resin, based on part size and geometry. Overall, deployment of these tools in conjunction (in situ process diagnostics, a resin cure map, an infusion process map, process simulation, and flow contour maps) provides a blueprint for more efficient use of aged resin and intelligent adjustment of process parameters for VI. The same



Figure 9. Methodology of material characterization and infusion process adjustment for the VI process.

Table 7. Design guidelines for VI heated filling process.

| | . : |
|----------------------|---|
| VI Design Guidelines | The competing effects of temperature on resin viscosity during heated infusion: As <i>T_{infusion}</i> increases, <i>η₀</i> decreases, expediting the infusion flow. Yet, higher <i>T_{infusion}</i> also accelerates increase in <i>η</i>, resulting in more rapid deceleration of resin infiltration. For an infusion process predicted to saturate before or shortly after reaching the <i>η</i> cross-over points, infusing at higher temperature would expedite infusion. Otherwise, infusing at lower temperature would help prevent premature resin gelation before infusion completion. |
| | Selection of infusion process parameters based on resin age and part geometry: For small parts of simple geometry, infusion is likely to be completed before η evolves significantly, favoring higher <i>T_{infusion}</i> to reduce fill times. Larger, more complex parts (requiring greater fill time) can benefit from lower <i>T_{infusion}</i> to decelerate η evolution and prevent premature resin gelation. With increasing α₀, the infusion process window narrows, requiring more careful process design. The flow contour maps can be used to guide selection of infusion process parameters (e.g. temperature and number/ placement of resin inlets), especially for an infusion process requiring multiple resin inlets. |

approach and blueprint can be implemented for other composites manufacturing processes, including RTM or prepreg-based processes. The design guidelines for VI heated filling are summarized in Table 7.

4. Conclusions

This study outlines material characterization and infusion guidelines for more efficient use of aged resin and corresponding process adjustments. The life of VI resin can be monitored dynamically and assessed using DCM and a resin cure map. DCM enables in situ measurement of resin ion viscosity, which can directly be converted into a measure of resin life (or cure advancement) using the cure map and ion viscosity model. The infusion process map provides a nominal infusion window and key process metrics adjusted for infusion of aged resin, while the filling simulation is used to validate and refine the process map and adjust process parameters accordingly. Furthermore, process simulations and the flow contour maps can be used to determine VI process parameters (e.g. temperature or resin inlet) for parts of different size and geometry.

Use of aged resin for VI requires careful selection of process parameters because of often lengthy infusion times. Thus far, DEA in composites manufacturing has been employed primarily for in situ process monitoring or validation of ex situ thermal analysis results, but less often for guiding process adjustments. In this work, in situ process diagnostics coupled with cure modeling yielded a tool for resin life assessment, as well as a process map that together accounted for resin age. Deployment of these tools enables more efficient use of aged resin and effective process adjustments for VI. For infusion of aged resin, small and simple parts can benefit from higher infusion temperatures, because infusion can be expected to complete before the resin viscosity approaches the critical threshold value. In contrast, parts requiring longer fill times can experience resin gelation before completing infusion due to the fast-evolving degree of cure at higher temperatures. Based on these principles, the filling process possibly can be adjusted either by reducing the process temperature after reaching the η cross-over point, or by imposing a temperature gradient (or at least multiple temperature zones) across the infusion length. However, lowering the

temperature can also cause resin viscosity to increase, and thus requires balancing the trade-off between increases in infusion window and viscosity.

In principle, the methodology described here can be extended to other composites manufacturing processes, including RTM or even conventional prepreg processing. Prepregs consist of B-staged resin pre-impregnated into fiber beds, and generally feature longer shelf-life and out-life compared to liquid molding resins. However, lay-up process often exposes prepregs to substantially longer out-time, causing advances in resin degree of cure [38, 39]. Using the approaches described here, resin cure maps and process maps can be developed for prepreg-based processes, which can be adjusted by modifying cure cycles based on process simulations or analysis of key process metrics (e.g. effective flow number [40]). In addition, use of aged resin (α_0 > 0.10 or even greater) may become viable for RTM, in which resin is injected more rapidly (compared to VI) under positive pressure.

Overall, this work describes a pathway to mitigate the problem of material waste in composites manufacturing. Material waste can be reduced by monitoring resin life, constructing a cure and process map, then employing filling simulations and flow contour maps to adjust key process parameters. However, the current infusion map assumes that the process temperature remains consistent throughout infusion, yielding a nominal process window that is wider than a practical or effective window. For more accurate prediction of the infusion window, a process map that accounts for the reaction exotherm must be developed. Moreover, the effects of η_0 and overall η profile on impregnation or part quality should also be assessed. This study demonstrates how to evaluate and modify process conditions primarily in terms of process (or fill) time, yet different η history during infusion can also affect dry spot or void formation. Further work is required to address other potential processing concerns, including cure exotherm-adjusted process map and effects of η history on part quality, and to refine the process guidelines described here.

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