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The Influence of Key Processing Parameters on Thermoset Laminate Curing

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Abstract

The many uncertainties in thermoset composite laminate processing can have undesirable consequences. It is impractical to address the uncertainties individually. A methodology is introduced that ranks parameters by an influence metric to give insights into how to reduce variability in cure time most effectively. The presented example considers a range of parameters from the material, geometry, and processing conditions within a thermochemical model of a representative aerospace laminate system. Due to the nonlinearities in the process, the influence metric must include representative parameter uncertainty. In the example, dwell temperature and diffusion terms in the cure kinetics model were most influential. This was a result of a long dwell period and a post-vitrification final degree of cure.

Keywords: Thermoset laminate, curing, sensitivity analysis, variability, processing

1. Introduction

The demand for composite materials within the aerospace industry has exploded in recent decades, with a trend of replacing metallic primary structures with high-performance thermosetting epoxy composites. In thermoset composite processing it is common for conditions to differ from those assumed/prescribed, this can occur in both the materials and the processing environment. This variability can cause higher scrappage, reducing efficiency and increasing costs. Potter [1] introduced a taxonomy of offending variability sources, listing more than sixty that are present during composite manufacturing. Given the high number of variables identified, it may not be practical to address them all and no method was given to determine which to prioritise.

Sensitivity analysis coupled with numerical simulation provides an effective tool for determining which parameters have the most influence on a given process. Loos et al [2] showed that a thermochemical model coupling heat transfer and cure kinetics was capable of modelling composite curing. Building on these concepts, sensitivity analysis has been used on a cure kinetics model to determine which parameters to consider in more detail [3], efficiency was improved by only selecting the most influential parameters. This approach can be extended to consider parameters of the whole process, by applying sensitivity analysis to a suitable thermochemical model.

In this study, a methodology is presented to identify which parameters to prioritise to increase the robustness of thermoset laminate processing. The parameters are ranked by an influence metric, similar to sensitivity, but accounts for real-world uncertainty. Values of the metric, based on the time to reach a degree of cure, are derived from a Finite Elements (FE) solution to coupled 1-Dimensional (1D) through thickness transient heat transfer and cure kinetics equations. Uniquely, the analysis considers the influence of key parameters, from the process, the material, and the geometry on composite curing. The numerical element of the approach is demonstrated by considering a flat plate, representative of epoxy laminate processed by vacuum bag moulding in an oven. Recommendations are provided based on the results.

2. Method

2.1 Predicting Parameter Influence

The metric of influence considered the rate of change of cure time with respect to the parameters listed in Table 1. Where, cure time was defined as the time for a degree of cure to be passed at every location through the thickness [2]. The parameters were classified as related to the process, geometry, or material, as well as cure kinetics, conductivity, and specific heat capacity fitting parameters. To accommodate the different units among the parameters, each gradient was multiplied by the standard deviation of the corresponding parameter, giving the influence metric the units of cure time.

Using the standard deviations as the step size for the gradients, the influence metric represented parameter variability in addition to the sensitivity of cure time. Given the standard deviations were not infinitesimally small, the influence metric approximates the gradient of the secant about the nominal cure time. This corresponds to the average rate of change over the interval. By combining sensitivity and variability, the influence metric indicates the likely cure time variability each parameter will cause.

Where possible the standard deviations were derived from data available in-house or in the literature. The dwell temperature, heat transfer coefficient and ramp rate from measurements in an industrial oven [4], fibre volume fraction from acid digestion of M21 composite panels, part thickness from measurements of IMA/M21 prepreg thickness [5] and the cure kinetics parameters from the fitting of Differential Scanning Calorimeter (DSC) data [3]. The two curves created by the conductivity model when the values of the fitting parameters were simultaneously shifted by 6%, up and down, bounded 68.2% of the laser flash analysis data points used to fit the model [3], corresponding ± 1 standard deviation from the mean. The same procedure was applied to the specific heat capacity fitting parameters, giving standard deviations equal to 5% of the parameter values. Manufacturer data suggested a 0.35 mm tolerance is typical for a 6mm thick metal sheet [6], assuming a normal distribution, the standard deviation for tool thickness was derived from a distribution with a 95% confidence interval of ± 0.35 mm from the mean.

An approach analogous to the central difference method, with step size equal to one standard deviation, was used to calculate the average rates of change. The matrix of influence metric values (unit corrected average rates of change) was written as,

$$\mathbf{S}^* = \mathbf{S}\boldsymbol{\sigma} \quad (1)$$

where \mathbf{S} is the matrix of average rates of change for a given degree of cure and $\boldsymbol{\sigma}$ is a diagonal matrix containing the standard deviations. Each element of \mathbf{S}^* took the form,

$$S_i^* = \sigma_i S_i = \sigma_i \left[\frac{t_c(\Phi_i + \sigma_i) - t_c(\Phi_i - \sigma_i)}{2\sigma_i} \right] = \frac{t_c(\Phi_i + \sigma_i) - t_c(\Phi_i - \sigma_i)}{2} \quad (2)$$

where t_c is the cure time, and Φ_i is the nominal parameter value. The values of Φ_i and σ_i for each parameter are shown in Table 1.

Table 1. Parameters with description, units, nominal values and standard deviations.

Parameter	Description	Units	Nominal Value Φ_i	Standard Deviation σ_i
A₁	Cure kinetics	s ⁻¹	420615	333
E₁	Cure kinetics	Jmol ⁻¹	78890	355
A₂	Cure kinetics	s ⁻¹	57440	33
E₂	Cure kinetics	Jmol ⁻¹	68978	1086
A_D	Cure kinetics		2.60E+20	2.80E+17
E_D	Cure kinetics	Jmol ⁻¹	87455.74	419
m	Cure kinetics		0.6	0.0032
n₁	Cure kinetics		0.8	0.026
n₂	Cure kinetics		3.2	0.031
b	Cure kinetics		1.98	0.014
w	Cure kinetics		1.65E-04	7.40E-07
g	Cure kinetics		0.058235	3.80E-04
Dwell temperature	Process	K	453.15	5
Ramp rate	Process	Kmin ⁻¹	2	0.16
Heat transfer coefficient	Process	Wm ⁻² K ⁻¹	50	4
Total heat of reaction	Material	Jkg ⁻¹	4.15E+05	11602
Fibre volume fraction	Material		0.6	0.008
Part thickness	Geometry	m	0.005	0.00023
Tool thickness	Geometry	m	0.006	0.00018
A	Heat capacity	Jkg ⁻¹ K ⁻¹	2.9	0.15
B	Heat capacity	Jkg ⁻¹ K ⁻¹	1840	92
C	Heat capacity	JK ⁻¹	0.15	0.0075
Δ	Heat capacity	Jkg ⁻¹ K ⁻¹	-260	-13
s	Heat capacity	°C	0.65	0.033
A_r	Conductivity	Wm ⁻¹ K ⁻²	-1.50E-03	-7.5E-05
B_r	Conductivity	Wm ⁻¹ K ⁻¹	0.392	0.020
C_r	Conductivity	Wm ⁻¹ K ⁻²	-1.00E-03	-5.00E-05
D_r	Conductivity	Wm ⁻¹ K ⁻¹	0.734	0.037

2.2 Numerical Implementation

Coupled cure kinetics and transient heat transfers equations were solved in 1D using FE in COMSOL Multiphysics. The cure kinetics for the M21/IMA prepreg with 13 fitting parameters was implemented as a distributed ordinary differential equation in COMSOL [3]. The cure kinetics model had both kinetic and diffusion terms (Equations (5) and (6)) because this specific material vitrifies, i.e., the glass transition temperature of the resin will exceed the process dwell temperature. The cure kinetics model is given in Equations (3) – (7). A non-zero value for initial degree of cure was required to escape the singular stationary point of the model; a convergence analysis showed negligible changes in cure time at values below 0.0001.

$$\frac{d\alpha}{dt} = k_1(1 - \alpha)^{n_1} + k_2\alpha^m(1 - \alpha)^{n_2} \quad (3)$$

$$\frac{1}{k_i} = \frac{1}{k_{iC}} + \frac{1}{k_D}, \quad i = 1,2 \quad (4)$$

$$k_{iC} = A_i e^{\left(\frac{-E_i}{RT}\right)}, \quad i = 1,2 \quad (5)$$

$$k_D = A_D e^{\left(\frac{-E_D}{RT}\right)} e^{\frac{-b}{f}} \quad (6)$$

$$f = w(T - T_g) + g \quad (7)$$

Heat transfer was modelled using the ‘Heat Transfer in Solids’ physics in COMSOL. The cure cycle is the recommended cycle for M21 [7], a 2°Cmin^{-1} ramp from 20°C to a dwell at 180°C which continued until 95% cure. The part and tool are assumed initially to be at 20°C . Figure 1 shows a schematic of a simplified curing arrangement, under the applied vacuum it was assumed that the combined thickness of the vacuum bag and breather was negligible [3]. This assumption enabled the same convective boundary condition to be applied at each end, with a heat transfer coefficient of $50 \text{ Wm}^{-2}\text{K}^{-1}$, representative of an industrial oven [4].

A 60% fibre volume fraction was assumed for the composite laminate. The thermal properties in the composite domain were representative of the through thickness direction. The density and specific heat capacity were homogenised using rule of mixtures according to fibre volume fraction and fibre weight fraction respectively [3]. The specific heat capacity model for the resin, with 5 fitting parameters, is shown in Equation (8). The thermal conductivity model (Equation (9)), has 4 fitting parameters [3]. All the fitting parameter values are given in Table 1.

$$c_{pr} = A_{rcp}T + B_{rcp} + \frac{\Delta_{rcp}}{1 + \exp(C_{rcp}(T - T_g - s))} \quad (8)$$

$$K_{33} = A_{kr}T\alpha + B_{kr}\alpha + C_{kr}T + D_{kr} \quad (9)$$

With the assumptions applied, the modelled geometry (Figure 1) consisted of a 5mm thick composite laminate and a 6mm thick invar tool in ideal contact. The described model conditions are typical of aerospace composite manufacturing. The results will give an indication of the parameters likely to be most influential.

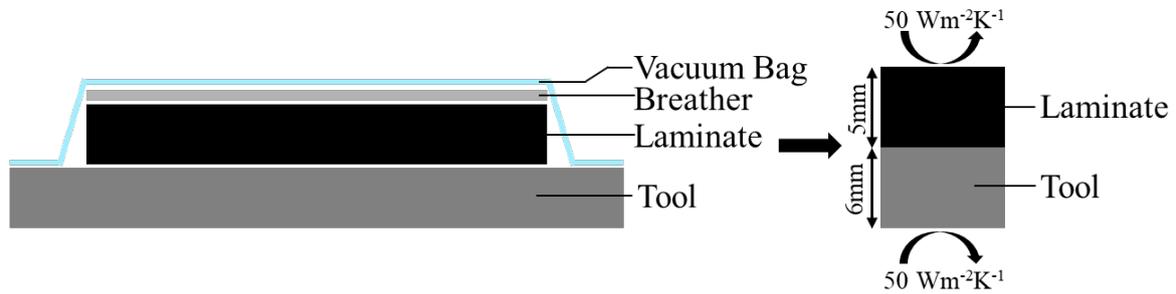


Figure 1. Layup schematic and simplified geometry and boundary conditions used in the Finite Elements model.

3. Results and Discussion

Figure 2 shows how the absolute value of the influence metric depends on the final targeted degree of cure. The parameters are ranked by the absolute value of the influence metric at 0.95 degree of cure, a typical end point when targeting full cure. For clarity, the results have been separated into subplots with similar values. Presenting the metric value versus targeted degree of cure is relevant for preliminary cure steps, such as those prior to co-curing and co-bonding where the level of partial cure effects the adhesion [8, 9].

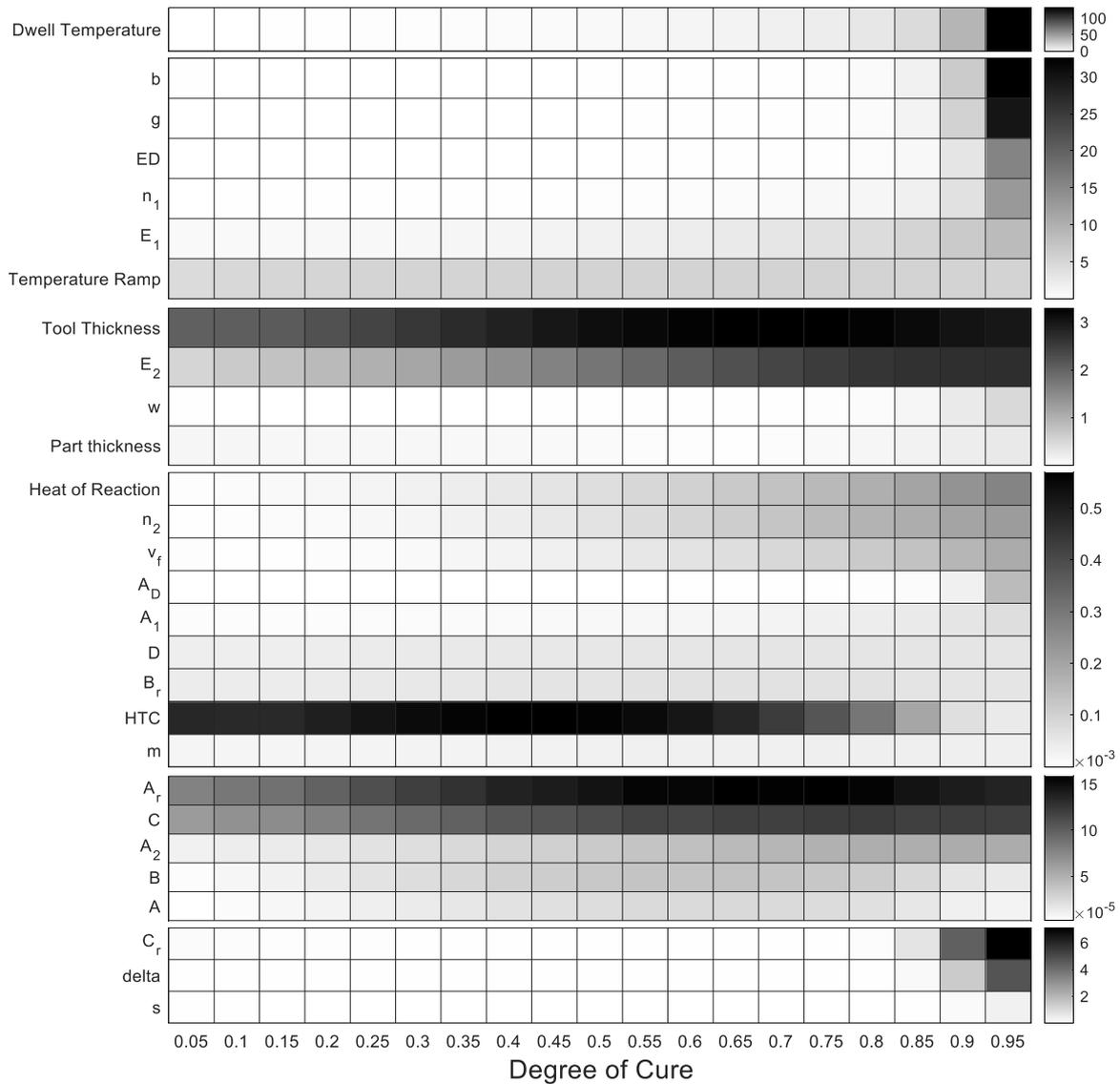


Figure 2. The absolute influence metric value for each parameter for degrees of cure up to 0.95. The parameters are ranked by the metric values at 0.95 cure.

Figure 3 focuses on the influence of dwell temperature, ramp rate and heat transfer coefficient. Dwell temperature has non-zero influence before the dwell is reached, because for a given temperature ramp rate, dwell temperature influences the duration of the ramp. The high 180°C dwell temperature and slow 2°Cmin⁻¹ ramp rate in this example resulted in an influence that grew slowly during the initial stages of the process, but increased rapidly at high degrees of cure, as the dwell became a more significant proportion of the cure cycle. As shown in Figure 3, beyond a degree of cure of 0.6, dwell temperature surpasses temperature ramp rate as the dominant influence on cure time. A similar trend is expected for other aerospace grade epoxies, among which 180°C dwell temperatures are common. For lower temperatures or higher ramp rates, the influence metric for dwell temperature would be more significant earlier in the process.

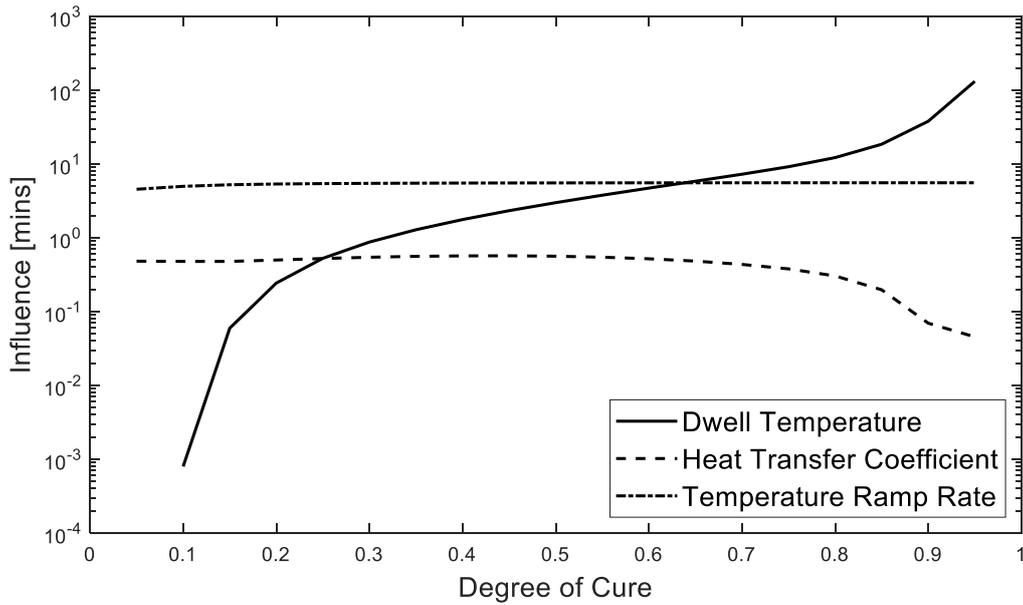


Figure 3. The absolute gradients values for the process parameters during the curing reaction.

Dwell temperature can be used to illustrate the need for case specific nominal values. Figure 4 shows that cure progresses as a sigmoid function of time, the rate starts to slow around gelation, the plateau coincides with vitrification [10], these occur at degrees of cure of approximately 0.7 and 0.9 respectively for M21 at 180°C [3]. At a higher dwell temperature vitrification occurs earlier in the plateau, so in terms of degree of cure, cure rate remains higher for longer, as demonstrated in Figure 4. Therefore, for cases such as this, where final glass transition temperature exceeds the dwell temperature, the influence of dwell temperature will be large and may not be representative of the reaction pre-vitrification.

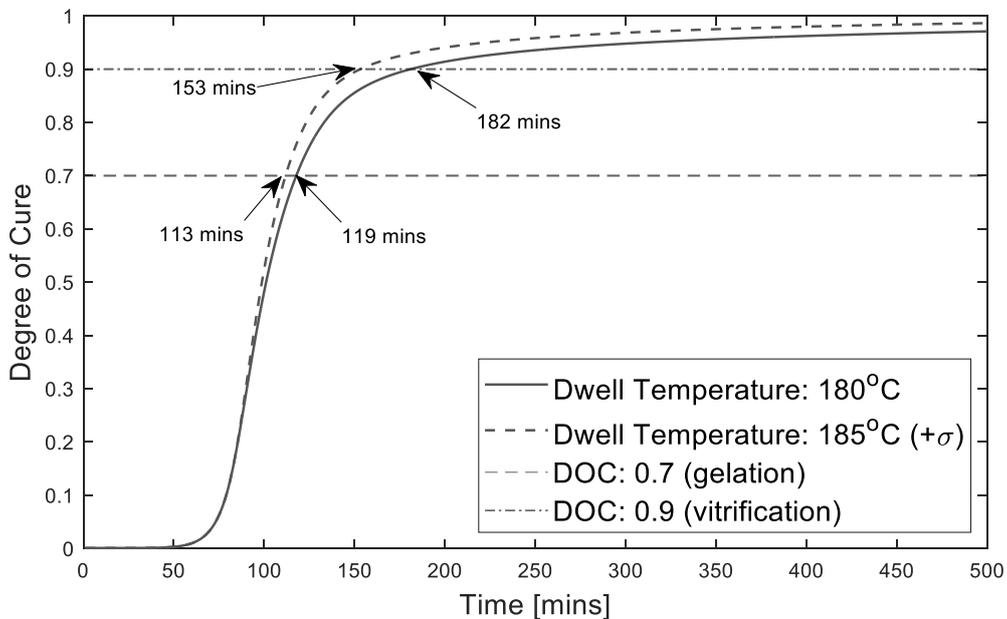


Figure 4. Degree of cure (DOC) with time for dwell temperatures of 180 and 185°C. Arrows mark gel time (0.7 DOC) and vitrification time (0.9 DOC) with the two dwell temperatures.

From Figure 2, the influence of the cure kinetics parameters was often highly weighted towards the end of the curing reaction; therefore, the high rankings of these parameters are not applicable to all processes. As shown in Figure 5, this is particularly true for the parameters representing post-

vitrification diffusion limiting effects (b , g , E_D). Away from 0.95 degree of cure, the influence of diffusion limiting effects drops more sharply than reaction effects. The results indicate that although accurately characterising DSC measurements is critical for process reliability at high degrees of cure, it becomes less important at lower degrees of cure.

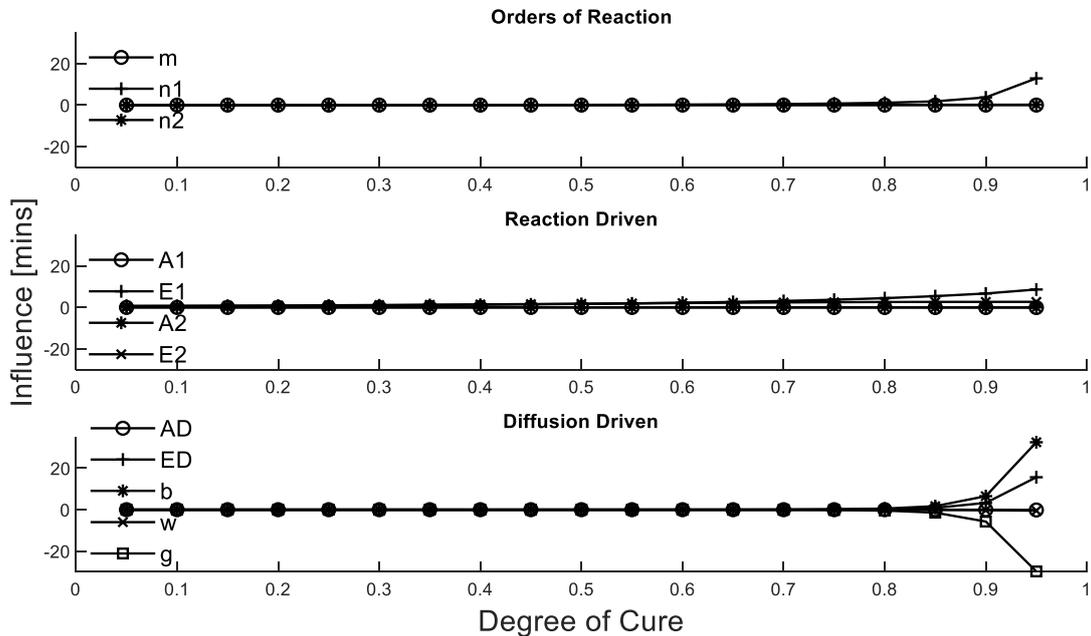


Figure 5. Influence metric of the cure kinetics parameters during the cure reaction.

In contrast to dwell temperature and the cure kinetics parameters, the influence of many process and geometry parameters is less concentrated towards higher degrees of cure. Hence, when only considering high degrees of cure the importance of these parameters can be overlooked. This is particularly true for heat transfer coefficient which as indicated by Figure 3, is only influential initially, when there is a temperature difference between the geometry and the imposed cure cycle, not applicable to the long dwell in this example. The contrasting distributions of parameter influence illustrates how the most effective parameters for reducing process variability can change with the targeted degree of cure.

4. Conclusion

A methodology that ranked parameters by an influence metric, based on cure time, to determine which parameters contribute most to variability in thermoset curing processes was presented. The ranking appeared to be dependent on the final degree of cure targeted.

Based on the methodology shown here, the results from the influence study can be used to optimise design and manufacturing processes for composite curing. For example, if material properties dominate, investment in better material characterisation instruments for deriving material models and verifying incoming batches would lead to more consistent parts. If the process equipment drives variability, an oven with more uniform temperature and convection heat-transfer coefficients might be a better investment. For geometry, metrology equipment or tighter tool tolerances might be the best approach. Based on our analysis, process equipment with temperature uniformity and repeatability is the best investment to minimise variability in curing.

Disclosure statement

The authors report there are no competing interests to declare.

Data access statement

The acid digestion data is available in the supplementary information.

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